

# Encyclopedia of INTERFACIAL CHEMISTRY

Surface Science and Electrochemistry

Klaus Wandelt

Editor in Chief

# ENCYCLOPEDIA OF INTERFACIAL CHEMISTRY

SURFACE SCIENCE AND ELECTROCHEMISTRY

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# SURFACE SCIENCE AND ELECTROCHEMISTRY

EDITOR IN CHIEF

Klaus Wandelt

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VOLUME 1

# 1.1 EXPERIMENTAL METHODS 1.2 SURFACE SCIENCE UNDER ENVIRONMENTAL CONDITIONS



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# PREFACE

The motivation for compiling and publishing this encyclopedia on Interfacial Chemistry was to promote the communication between chemists, electrochemists, physicochemists, as well as solid-state and surface physicists. The growing diversification and specialization of science and research makes mutual understanding more and more difficult, and therefore interdisciplinary communication imperative. Chemists take great advantage of heterogeneous catalysts often without knowing their properties and operation on the atomic scale. This knowledge, however, is necessary for a rational design and optimization of the catalysts' activity, selectivity, and stability. Electrochemists and surface physicists working on a similar problem such as film deposition and growth, just in different environment, may not share knowledge due to distinctly different "languages," such as "underpotential deposition" and "Franck-van-der-Merwe growth" for a similar phenomenon. And there are known differences between the more "practical" approach of chemists and the more "formal" approach of physicists, including the resultant communication "barriers". On the other hand, all modern experimental analytical tools are based on physicists. Interfacial chemistry, as an excellent example of interdisciplinary research, can only profit from an unbiased communication and mutual understanding between the different involved disciplines.

Interfaces are the divides between phases, e.g., solid/gas, solid/liquid, solid/solid, liquid/gas, liquid/liquid, and thus an inherent property of heterogeneous systems. "Heterogeneous" sounds, and actually is, more complex than "homogeneous" and therefore calls for a multidisciplinary approach. To investigate and understand "electrocatalysis," it is certainly helpful to take into account the experience and knowledge of electrochemists *and* solid-state and surface physicists, two communities that are not known for a close connection.

The difference in properties on either side of the divide has two important consequences: (1) interfaces are the locations of gradients that are a driving force for processes and (2) interactions across the interface will obviously also alter the properties in interface-near layers of the adjacent phases. If a solid iron surface is exposed to oxygen gas, the surface will oxidize; the resultant oxide layer differs from the pure iron underneath. If two different solids (or liquids) form a common phase boundary, interdiffusion will change the composition of the interface-near regions on both sides. If a platinum electrode in sulfuric acid solution is negatively polarized, protons (hydronium cations) are attracted with the consequence that the pH near the Pt/electrolyte interface is lower than in the bulk of the solution. And if a copper electrode in hydrochloric acid solution is positively polarized, chloride anions will be attracted, adsorb, and restructure the surface *before* surface atoms form soluble copper chloride species.

Interestingly, not only the presence of interactions across an interface causes alterations on either side, but also the sudden *absence* of interactions across an interface has a decisive influence: While an atom in the bulk of a solid in equilibrium is surrounded by and interacts with atoms on all sides, an atom at the very surface in vacuum has no neighbors to interact with on the vacuum side. This unbalance drives the system toward a new equilibrium and causes a repositioning of the surface atoms; most intuitively the surface atoms "relax" toward the bulk of the solid. But there are even cases where the surface atom layer as a whole assumes a two-dimensional lattice structure different from that of a parallel plane in the bulk, the surface "reconstructs."

Due to the missing neighbors, the "unsaturated bonds" of *surface* atoms (in contact with vacuum) add to the total energy of the solid. The surface "relaxation" and "reconstruction" are a response of the system to lower this "excess surface energy." The very same argument explains why in equilibrium also the *surface composition* of multicomponent materials, e.g., alloys, solutions, must be expected to be different from the bulk composition.

In equilibrium the surface will be enriched with those atoms whose unsaturated bonds add least to the excess surface energy.

Since it is the very surface of a solid (or liquid), which first interacts with the adjacent phase (gas, liquid, or solid), its chemical composition and structure must be known in detail, i.e., on the atomic scale, to understand and describe its involvement in chemical processes.

This information is nowadays available thanks to the development of a broad arsenal of incredibly sensitive high-resolution microscopic and spectroscopic techniques and the so-called "surface science approach." This approach starts with structurally and chemically well-defined surfaces, e.g., single-crystal surfaces, which under ultrahigh vacuum conditions are exposed to gases or vapors in a very controlled manner. In this way it is nowadays possible not only to characterize bare and adsorbate covered surfaces and monitor changes atom-byatom but also to modify surfaces by arbitrary manipulation of individual atoms. These achievements and abilities have occasionally misled "insiders" to statements such as "surface science has reached completion." Apart from the fact that claims like this in science have often been rash, there are at least two expectations on "surface science" still. The first is, due to the ubiquity and universal importance of interfaces, to disseminate the knowledge about their fundamental peculiarities more widely to "outsiders" in other disciplines—beyond materials sciences—and in particular to include it more regularly into curricula. The second is to transfer and apply the concepts and methods, largely resulting from the "surface science approach" under ultrahigh vacuum conditions, to more complex systems in realistic environment such as ambient gases and liquids, as they are dealt with by electro- and bioelectrochemists, materials scientists, and chemical engineers. This transfer, of course, requires to overcome the "barriers" indicated above and, sometimes, may also require the revision of "established views."

The present encyclopedia is an attempt to contribute to this transfer by including publications from rather different but inherently interface-related research fields under the common heading "Interfacial Chemistry." When I first proposed this project, I suggested 11 subjects: (1) model studies in heterogeneous catalysis, (2) surface science under environmental conditions, (3) ultrathin films, (4) clusters and nanoparticles at surfaces, (5) molecular self-assembly at surfaces, (6) surface-confined polymerization, (7) functionalization and grafting of surfaces and nanoparticles, (8) ultrafast surface dynamics, (9) general interfacial electrochemistry, (10) interfacial electrocatalysis, (11) model studies on corrosion, and left a 12th subject deliberately open for further suggestions. The reports of 19 (!) international reviewers of this proposal were unison positive and led to the suggestion of including (12) bioelectrochemistry as the 12th subject. All 12 topics are well covered in this encyclopedia thanks to the team of excellent subject editors whom I asked and who agreed to join this project. To accentuate "Interfacial Chemistry" as the common ground, all contributions are explicitly linked by cross-references between papers in the various sections, and—even though partly very different and subject specific—the most important experimental methods are grouped in one separate section "side-by-side."

In addition to the printed version of this encyclopedia, all articles appear within the section "Interfacial Chemistry" of the overarching and well-structured electronic-only Reference Module "*Chemistry*, *Molecular Sciences and Chemical Engineering*"<sup>1</sup>, which supports both an easy accessibility and, thereby, a wide dissemination among its readership.

The coming together of the relevant disciplines is a "steady" process. In 1995 I already edited jointly with S. Trasatti, Milano, a special issue "Surface Science and Electrochemistry" of the journal *Surface Science*<sup>2</sup>. Twenty years later in 2015 I repeated this initiative together with A. Gross, Ulm, in *Surface Science*<sup>3</sup>, and we came to the "disenchanting insight" that the progress in bringing solid state surface physicists and electrochemists together "was only moderate" and this even though the "interest in processes at electrochemical interfaces in the context of electrochemical energy conversion and storage plays an enormously important role for future energy technology."

As stated above, this encyclopedia is a further attempt to promote the mutual insight in the importance of a close collaboration between the involved disciplines, and the electronic version of this encyclopedia embedded in the section "Interfacial Chemistry" of the general Reference Module "*Chemistry, Molecular Sciences and Chemical Engineering*" even offers the possibility of a continuous updating.

I am deeply indebted to all those who have contributed to this work, primarily, of course, all authors of the articles, my fellow coeditors who identified and motivated the authors, and last but not least the Elsevier staff at the Oxford office, UK, who organized and handled the workflow.

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Figure 4 Ullmann Coupling of Porphyrins

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# A Review on In Situ Sum Frequency Generation Vibrational Spectroscopy Studies of Liquid–Solid Interfaces in Electrochemical Systems

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### Introduction: The Significance of Probing Electrified Interfaces for Renewable Energy Production and Storage

As an energy-driven society we are facing sustainability challenges<sup>1</sup> and therefore are constantly looking for better ways to design, manufacture, and use energy storage devices, including rechargeable batteries, fuel cells, and large-scale grid energy storage. Regard-less of the technology, the fundamental electrochemical process is most likely occurring on the nanoscale<sup>2</sup> at an interface of two phases (e.g., solid–liquid) under applied potentials. To improve our energy production and storage devices, we have to gain in situ, real-time information of the electrified interface on the nanoscale level, such as the solid surface geometric structure and the electronic properties of the solid–liquid interface. In addition, we need to obtain a clear understanding of the electrochemical mechanism by revealing the molecular structures of the reactants, intermediates, and products.<sup>3</sup> Over the years, different spectroscopy techniques have been adapted to probe electrochemical interfaces such as infrared reflection adsorption spectroscopy (IRRAS), Raman spectroscopy, and X-ray spectroscopy. While the IRRAS and Raman spectroscopies allow in situ probing, none of them is highly surface-specific. X-ray spectroscopy is surface-specific but cannot yet be applied to solid–liquid systems, though some considerable advances were reported.<sup>4</sup> Hence, our understanding of many aspects of interfaces in electrochemical systems is still lacking, and the need for a real-time analytical tool that can access solid–liquid interfaces is crucial.

The development of sum frequency generation vibrational spectroscopy (SFGVS) has enabled surface-specific studies of various surfaces and interfaces. SFGVS is a nondestructive, in situ nonlinear optical method that does not require any photoactive labeling or has any restrictions to the sample's preparation. SFGVS is a nonlinear optical method that yields vibrational spectra of molecules at buried interfaces with high-interface selectivity and sensitivity. Vibrational spectra are known to be the fingerprints of molecules. Consequently, SFGVS can be used to identify interfacial (adsorbed) species on a surface, probe their dynamics, and since it is a laser-based technique by polarizing the laser beams, it can provide the interfacial species orientation with respect to the surface plane.

In this article, we present recent applications of SFGVS in studies of research groups that took on the endeavor to understand interfacial processes on the molecular level of systems relevant to energy generation and storage like lithium ion batteries and fuel cells.

### **Basic Concepts of SFGVS for Studies of Electrified Solid–Liquid Interfaces**

Vibrational sum-frequency generation (VSFG) spectroscopy is a second-order nonlinear optical technique that is intrinsically sensitive to probing vibrational spectrum of molecules within a few molecular layers (Angstroms) of an interface. This section describes the general and basic theory of SFG, which provides guidelines for applying SFG for interfacial characterization.

Briefly, the SFG process from an interfacial system (any two mediums in contact) comprises two incident laser beams with frequencies of  $\omega_1$  and  $\omega_2$ , overlapping on the interface both spatially and temporary to induce a nonlinear polarization having the sum of the incoming laser frequencies  $\omega_s = \omega_1 + \omega_2$ . The outcome of a sum frequency radiation (beam) is in both the reflected and transmitted directions. Based on the electric-dipole approximation, SFG is forbidden in the bulk since it has an inversion symmetry but is allowed at the interface where the inversion symmetry is broken. If the higher order electric quadrupole response from a bulk is negligible, the SFG is dominated by the surface response and therefore intrinsically interface sensitive. Fig. 1A shows the SFG process in an interfacial system. The generated SFG beam is both in the reflected and the transmitted directions. In Fig. 1A, the two incident beams copropagate with respect to the plane normal to the surface incident on the interface at angles  $\theta_1$  and  $\theta_2$ , and the resulted SFG reflected and transmitted beams exit at angles  $\theta_{SR}$  and  $\theta_{ST}$ . We can calculate  $\theta_{SR}$  and  $\theta_{ST}$ , based on boundary



**Fig. 1** (A) A schematic of a SFG process at an interface. (B) Energy diagrams and description of resonant SFGVS with (1)  $\omega_2$  in resonance with a vibrational transition, (2)  $\omega_S$  in resonance with an electronic transition, and (3) both  $\omega_2$  and  $\omega_S$  are in resonances.

conditions and phase-matching requirements,  $k_{1||} + k_{2||} = k_{s||}$ . Eq. (1) describes the emitted SFG direction based on the wavelength of the input beams and the geometry of the setup:

$$\theta_S = \sin^{-1}(n_1\omega_1\sin\theta_1 + n_2\omega_2\sin\theta_2)/n_S\omega_S \tag{1}$$

where n is the refractive index of the medium in which the SFG is present.

Fig. 1B shows the energy levels for the excitations in a SFG process. In the SFGVS,  $\omega_1$  is typically in the visible spectral region and  $\omega_2$  is in the infrared (IR) spectral region. Whenever either  $\omega_1$  or  $\omega_2$  or/and  $\omega_8$  are in resonance with the electronic or vibrational mode at the interface, the SFG intensity increases several orders of magnitudes.<sup>5</sup> By scanning the IR frequency and monitoring the SFG intensity, we obtain the vibrational spectrum of surface molecules and the structural information from the molecules present at the interface. The output intensity of the reflected SFG is given by the square of the sum of the second-order nonlinear susceptibility and the intensities of the input beams, as shown in Eq. (2).

$$I_{SF} = \frac{8\pi^3 \omega^2 \sec^2 \theta_{SR}}{c^3 \sqrt{\varepsilon(\omega_S)\varepsilon(\omega_1)\varepsilon(\omega_2)}} \left| \hat{e}(\omega_S) \overleftrightarrow{\chi}_S^{(2)} : \hat{e}(\omega_1) \hat{e}(\omega_2) \right|^2 I(\omega_1) I(\omega_2) \propto \left| \overleftrightarrow{\chi}_{eff}^{(2)} \right|^2 I(\omega_1) I(\omega_2)$$
(2)

where  $\hat{e}(\omega_S)$ ,  $\hat{e}(\omega_1)$ , and  $\hat{e}(\omega_2)$  denote the Fresnel factors for the output and input beams. In SFGVS, in order to characterize the vibrational modes of adsorbates, one would use the expression in Eq. (3) to fit the observed spectrum.

$$\overleftrightarrow{\chi}_{eff}^{(2)}(\omega_{IR}) = \left(\widehat{e}_{S} \overleftrightarrow{L_{S}}\right) \left[ \chi_{NR}^{(2)} + \sum_{q} \frac{\overleftrightarrow{A_{q}}}{\omega_{IR} - \omega_{q} + i\Gamma_{q}} \right] \left(\widehat{e}_{vis} \cdot \overleftrightarrow{L_{vis}}\right) \left(\widehat{e}_{IR} \cdot \overleftrightarrow{L_{IR}}\right)$$
(3)

where  $\overrightarrow{A_q}$ ,  $\omega_q$ ,  $\Gamma_q$  are the amplitude, frequency, and damping coefficient of the *q*th vibration mode, respectively,  $\chi_{NR}^{(2)}$  is the secondorder nonlinear susceptibility from the nonresonant background.  $\overrightarrow{L_{\omega}}$  is the Fresnel factor at  $\omega$ , and these local field factors can be calculated based on the physical and geometrical properties of the SFG apparatus and experiment: the beam angles, the refractive index of the medium, etc. The SFG data has to be processed so that one can deduce the surface nonlinear susceptibility,  $\left|\overrightarrow{x}_{s}\right|$  from the SFG signal amplitude. Usually, this is carried out by removing the geometric factors and Fresnel coefficients and so we are left with the signal's amplitude that in turn gives  $\left|\overleftarrow{x}_{s}\right|$ . The nonlinear susceptibility holds the information of the adsorbate's molecular orientation and the adsorbate layer ordering degree,<sup>6</sup> of which we give examples later in this section.

When studying electrified interfaces, the effect from an electric field or so-called electric double layer (EDL) on the SFG signal needs to be considered due to the additional contribution from the second-order bulk nonlinear susceptibility inside the EDL. This potential-induced contribution originates from the electric-dipole-allowed third-order bulk nonlinear susceptibility and the field in the EDL.<sup>7–9</sup> The intensity of a potential-dependent reflected SFG beam in the presence of an EDL can be expressed as<sup>7</sup>:

$$I_{SFG}(\omega_{VIS} + \omega_{IR}, \phi) \propto I(\omega_{IR})I(\omega_{VIS}) \left[ \chi_{eff}^{(2)}(\omega_{IR}, \phi) + \int_0^\infty dz \chi^{(3)}(\omega_{IR}, z, \phi) E_{DC}(z) \right]^2$$
(4)

where  $\phi$  is potential and  $E_{DC}(z)$  is the static electric field from the electrode that is a decaying function of *z*. The third-order susceptibility,  $\chi^{(3)}(\omega_{IR}, z, \phi)$ , varies with the distance *z* from the electrode surface starting at *z*=0. If we assume that the field  $E_{DC}(z)$  is constant in the double layer and equals to zero in the bulk electrolyte, the equation can be expressed as follows:

$$I_{SFG}(\omega_{VIS} + \omega_{IR}, \phi) \propto I(\omega_{IR})I(\omega_{VIS}) \times \left\{ \left| \chi_{eff}^{(2)}(\omega_{IR}, \phi) \right|^2 + 2Re \left[ \chi_{eff}^{(2)}(\omega_{IR}, \phi) \chi_{DL}^{(3)}(\omega_{IR}, \phi) e^{i\delta} \right] + \left| \chi_{DL}^{(3)}(\omega_{IR}, \phi) \right|^{(2)} \phi^2 \right\}$$
(5)

where  $\chi_{DL}^{(3)}(\omega_{IR}, \phi)$  is the third-order potential-dependent susceptibility of the double layer. The third-order susceptibility in the double layer is the sum of the third-order hyperpolarizabilities of all the molecules in the double layer.<sup>10</sup>  $\delta$  is a phase factor that is

difficult to determine in the homodyne (i.e.,  $\left| \stackrel{\leftrightarrow}{\chi} \stackrel{(2)}{_{eff}} \right|^2$ ) detection scheme. This term also implies that SFGVS of metal interfaces can

suffer from an interference due to a strong background in the spectrum that comes from the metal or/and electrolyte and depends on the electrode's potential. In reality, the presence of a strong dispersive background that depends on the potential of the electrode needs to be considered in the SFG spectra analysis, as it may also cause the SFG spectra to be convoluted and reduce the accuracy of fitting.<sup>11</sup> By carefully evaluating the SFG spectrum dependence in the applied field, one can construct the molecular structure of the electrified interface.

One of SFGVS greatest advantages is the ability to carry out orientation analysis of the adsorbates. We can deduce the orientation of molecules at interfaces by analyzing sets of SFG spectra taken under different polarization combinations of the incident incoming lights and the resulting SFG light. For example, spectra acquired at SSP (where s-, s-, p- are the visible, IR, and SFG polarized fields, respectively) polarization is sensitive to dipole moments that are oriented perpendicular to the sample's surface plane for an isotropic surface. Generally, the molecular orientation of an adsorbate can be deduced from the ratio between symmetric and asymmetric stretching vibrations of a specific group (e.g., C=O or  $-CH_2-$ ) by specific polarization combinations. For example, in the case of a monolayer of C=O stretching mode on an azimuthally isotropic surface having a  $C_{\infty v}$  symmetry. We consider the Z axis to be along the surface normal and the X and Y axis, to lie in parallel to the surface. For a SFG measurement with the SSP and SPS polarization combinations,  $x_{ijk}^{(2)}$  can be reduced to nonzero component  $x_{ijy2}^{(2)} = x_{xxz}^{(2)}$  and  $x_{jxy}^{(2)} = x_{xzx}^{(2)}$  respectively, where  $x_{ijk}^{(2)} = N_s \sum_{abc} \langle \left( \hat{i} \cdot \hat{a} \right) \left( \hat{j} \cdot \hat{b} \right) \left( \hat{k} \cdot \hat{c} \right) \rangle \alpha_{abc}^{(2)}$ . *a*, *b*, and *c* represent the molecular coordinates as described in Fig. 2A,  $\alpha_{abc}^{(2)}$  is the molecular of a specific plane for a first plane for a specific plane for a monolayer of C=O stretching mode on an azimuthally isotropic surface having a  $C_{\infty v}$  symmetry. We consider the Z axis to be along the surface normal and the X and Y axis, to lie in parallel to the surface. For a SFG measurement with the SSP and SPS polarization combinations,  $x_{ijk}^{(2)}$  can be reduced to nonzero component  $x_{ijk}^{(2)} = x_{xxz}^{(2)}$  and  $x_{ijx}^{(2)} = x_{adc}^{(2)}$  is the molecular coordinates as described in Fig. 2A,  $\alpha_{abc}^$ 

hyperpolarizability and is related to the IR dipole and Raman polarizability of a vibrational mode. For the stretching mode of C=O:

$$x_{\gamma\gamma z}^{(2)} = \frac{1}{2} N_s \alpha_{ccc} \left[ \langle \cos\theta \rangle (1+R) - \langle \cos^3\theta \rangle (1-R) \right]$$
(6)

$$x_{yzy}^{(2)} = -\frac{1}{2} N_s \, \alpha_{ccc} \left[ \langle \cos\theta \rangle - \langle \cos^3\theta \rangle \right] (1 - R) \tag{7}$$

with  $\theta$  denoting the tilt angle of C=O with respect to the *z*-axis. *R* is hyperpolarizability ratio of  $\alpha_{acc}$  and  $\alpha_{ccc}$ . The angle brackets represent the ensemble average over  $f(\theta)$ , with a polar orientation distribution of the C=O bonds in the tilt angle  $\theta$ , at the range of  $0 \le \theta \le \pi/2$  from the surface normal. Fig. 2B shows a simulation for the ratio of  $x_{PZP}^{(2)}$  to  $x_{PZP}^{(2)}$  and the orientation angle for different angle distribution of 0 and 10 degrees. We can calculate the average  $\theta$  from the normalized intensity ratio of the SSP and SPS spectra. Another orientation analysis example is the CH<sub>2</sub> stretching intensities of an azimuthally isotropic sample. The SSP measurements of the CH<sub>2</sub> stretches yield that  $x_{xxz}^{(2)} = x_{PTZ}^{(2)}$ . The explicit expression for the symmetric stretching mode of CH<sub>2</sub> is:

$$x_{xxz}^{(2)} = \frac{1}{2} N_s \left[ \alpha_{aac} + \alpha_{ccc} \right] \langle \cos \theta \rangle + \frac{1}{2} N_s \left[ \alpha_{aac} - \alpha_{ccc} \right] \langle \cos^3 \theta \rangle$$
(8)

and for the asymmetric stretching:

$$x_{xxz}^{(2)} = -\frac{1}{2} N_s \,\alpha_{aaa} \langle \cos\theta - \cos^3\theta \rangle \tag{9}$$

with  $\theta$  denoting the polar angle of the symmetry axis *c* with respect to the *z*-axis. From the ratio deduced from the s-CH<sub>2</sub> and as-CH<sub>2</sub> spectra, the average  $\theta$  can be determined.

In practice, when applied to metallic interfaces, the determination of the molecular orientation is challenging as the s-polarized component of the reflected light from metal surfaces is usually weak. SFG with all polarization combinations containing an



**Fig. 2** (A) The molecular coordinates of a carbonyl (C=0) group and a methylene (CH<sub>2</sub>) group. (B) The ratio of  $x_{yzy}^{(2)}$  to  $x_{yyz}^{(2)}$  in regard to average angle  $\theta$  of a carbonyl group. *Black* and *red* lines are for the ratio of  $x_{yzy}^{(2)}$  to  $x_{yyz}^{(2)}$  which is calculated with the Gaussian distribution function and angle distribution of 0 and 10 degrees, respectively.

s-component (except for PPP) has shown low signal-to-noise ratio. Hence, most SFGVS studies on metal electrochemical interfaces apply the PPP polarization combination. The PPP combination in turn also limits the accuracy of orientation determination since it has contributions from all possible polarizations.

### **Probing Solid–Liquid Interfaces Under Reaction Condition**

### **Li-Ion Batteries**

Since the birth of the commercial lithium ion battery in the 1990s when Sony Inc. engineers clamped together a carbonations anode with a discharged oxide cathode, as envisioned by Goodenough, <sup>12,13</sup> significant technological advances had occurred in the field of energy storage, specifically in the lithium (Li) ion battery. Generally, the Li-ion battery is composed of two electrodes, a separator membrane designed to ensure electrical insulation of the two electrodes and a medium that allows the Li-ions to diffuse through it between the two electrodes. Many aspects of the Li-ion battery have been designed to achieve the maximal efficiency without compromising safety, capacity, and power demands.<sup>14,15</sup> The lithium ion battery is a dynamic system even at open circuit potential (OCP) when no external potential is applied. The difference of the Gibb's free energy between the organic molecules to the electrode energy levels is enough to initiate redox reactions upon mere contact of the electrolyte/electrode<sup>16</sup>; thus, in situ methodologies should be employed for their study. Moreover, it was suggested that the overall behavior of the Li-ion battery is defined at the electrode-electrolyte interface.<sup>17</sup> SFGVS is the best option as it can be used to probe the lithium ion battery components (mainly electrode surface, the effect of surface termination, and the electrode-electrolyte interface) under "as prepared" and reaction conditions. For example, by applying SFG one can deduce the surface concentration and orientation of the various electrolyte molecules on a cathode material.<sup>18</sup> Yu et al. have demonstrated that at OCP, there is a preferential adsorption of cyclic carbonates, mainly ethylene carbonate (EC) over linear carbonates such as diethyl carbonate (DEC) and dimethyl carbonate (DMC).<sup>19</sup> EC was found to be the dominating adsorbate on the LiCoO<sub>2</sub> (cathode material) regardless of its molecular proportion in the solution bulk. Refer to Fig. 3.

The interpretation of SFG spectra of solid–liquid interfaces is challenging and at times ambiguous; therefore, computational modeling can greatly improve our understanding and decipher the resulting nonlinear vibrational spectra. As a general case, we can examine the differences between probing the  $[\chi^2]^2$  (absolute square) versus probing the imaginary part  $Im[\chi^2]$ . As we have noted in our explanation for Eq. (3),  $\chi^2$  holds the chemical and physical information of the adsorbates that we probe by SFGVS. Eq. (3) can be rearranged so that:

$$I_{SFG} \propto \left| \sum_{v} \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q} e^{-i\phi_q} + \chi_{NR}^2 \right|^2$$



**Fig. 3** The SPS polarized SFG spectra of LiCoO<sub>2</sub> in contact with EC:DMC (1:1 in volume) at open circuit potential. Top panels: SFG spectra where the nonresonant background is removed. Middle panels: SFG spectra (*circle*) and their fitting results (*solid traces*). Bottom panels: deconvoluted bands for the SFG spectra. The upward and downward peaks represent modes with reversed phases. All the spectra (except for the middle panels) are offset for clarity. Adapted with permission from Yu, L.; Liu, H.; Wang, Y.; et al. Preferential Adsorption of Solvents on the Cathode Surface of Lithium Ion Batteries. *Angew. Chem. Int. Ed. Engl.* **2013**, *52*, 5753–5756.

where  $\phi_q$  is a phase angle with respect to the nonresonant signal  $\chi^{2}_{NR}$ . While obtaining  $[\chi^2]^2$  is well established and is based on a straightforward design of the SFG apparatus, there is a fundamental shortcoming of this technique, whereby all information on the complex nature of  $\chi^2$  is lost. For example, for a given vibration associated with a specific bond, we can deduce the angle distribution of the dipole moment by calculating the intensity ratio between SSP and SPS. However, just from the  $|\chi^2|_{sps}^2/|\chi^2|_{sps}^2$ 

ratio, we cannot predict if the dipole moment is pointing away from the surface or pointing to the surface. Probing the complex representation of  $\chi^2$ , specifically its imaginary component,  $Im[\chi^2]$  readily reveals the dipole orientation. Nevertheless, it requires either a phase-modulation or a heterodyne SFG set up together with solid mathematical modeling.

In order to simplify the interpretation of phase-sensitive SFGVS, that is,  $Im[\chi^2]$ , Morita and Hynes, begun by modeling the SFG spectra according to the energy representation of the nonlinear susceptibility,  $\chi^2$ , in molecular dynamics (MD) calculations.<sup>20</sup> They have pioneered the computational analysis of SFG spectroscopy in general and suggested an alternative MD model based on the time correlation function.<sup>21</sup> Recently, Morita et al. have incorporated the charge response kernel (CRK) model in their work bringing the computational model to better interpret the experimental SFG spectra.<sup>22,23</sup> The CRK was successfully implemented in investigating the vapor–liquid interface structure of DMC and propylene carbonate (PC), both common solvents in Li-ion electrolyte solutions.<sup>22</sup> The study probed the C=O stretch and its orientation at the liquid–gas interface. In Fig. 4, we can see that the simulated MD SFG (A, C) and experimental SFG (B, D) spectra of PC and DMC at the solid–gas interface correspond well. However, the importance of the MD simulation was demonstrated by revealing that the reason for the C=O bipolar bands lies with DMC having an almost isotropic orientation while PC has an ordered structure due to PC dimers as discussed in Ref. [23].

The advantages of SFG vibrational spectroscopy as a surface specific spectroscopy are demonstrated in the study of the solid (electrode)–liquid (electrolyte) interface and even more so in examining the solid electrolyte interphase (SEI).<sup>24</sup> The SEI<sup>25,26</sup> is a term and concept that has been widely accepted for the reduction products formed on an anode of the liquid hydrocarbon electrolyte molecules interacting with Li-ions during the charging process. The SEI serves as a physical barrier and a chemically inert coating that hinders further electrolyte reduction on the surface of the anode. Meanwhile, it allows lithium ions diffusion, at a reasonable rate, through it to the lithium ion host (anode) upon charging and back to the electrolyte solution once the discharge of the Li-ion battery takes place.

One of the key steps for a major improvement of the Li-ion battery is understanding the SEI's structure-related diffusion in energy storage materials. The SEI formation is a crucial step as charge and discharge rates of Li-ion batteries are diffusion-limited. The fundamental understanding of the ion transport and diffusion mechanism will ultimately lead to faster charging, longer lasting, and safer Li-ion batteries. Several groups have set to explore the composition, structure, and formation/degradation mechanisms of the solid electrolyte interface on the surfaces of electrodes at OCP and during charge/discharge cycles by applying advanced in situ SFG vibrational spectroscopy.

The SEI's behavior was also investigated under applied potentials. Dlott et al. carefully chose an electrochemical system to produce a single SEI product.<sup>24</sup> They cycled lithium perchlorate (LiClO<sub>4</sub>) salt dissolved in an EC diluted with tetrahydrofuran (THF) in contact with either gold or copper anodes between 2.0 and 0.2 V (vs. Li/Li<sup>+</sup>). The single reduction product was lithium ethylene dicarbonate with a trace amount of ethylene having two C=O distinct vibrational frequencies at 1782 and 1800 cm<sup>-1</sup>, refer to Fig. 5. They had reported two main findings. The first is that the SEI "breaths" as a function of applied potential only when reduced on a copper electrode. This increase and decrease of the SEI width is not apparent when a gold electrode is used even though the same electrolyte and the same electrochemical conditions as in the Cu case are maintained. The second, presented in Fig. 6, was that the applied external potential affects the SFG profile<sup>27</sup> and so one should carefully examine the SFG profile obtained under potentiodynamic conditions.



**Fig. 4** The simulated MD SFG (A, C) and experimental SFG (B, D) spectra of propylene carbonate (PC) and dimethyl carbonate (DMC) solid–gas interface. Left—The SSP-polarized SFG spectra are shown in *red* and SPS spectra in *blue*. Right—The SSP polarized imaginary component,  $Im[\chi^2]$ , calculated SFG spectra of PC (up) and DMC (bottom) solid–gas interface. The MD simulations show that the SFG bipolar band originates from different molecular interactions, dimerization for PC (up) and random for DMC (bottom). Reprinted with permission from Wang, L.; Peng, Q. L.; Ye, S.; Morita, A. Surface Structure of Organic Carbonate Liquids Investigated by Molecular Dynamics Simulation and Sum Frequency Generation Spectroscopy. *J. Phys. Chem.* **C 2016**, *120*, 15185–15197; Ishiyama, T.; Morita, A. Computational Analysis of Vibrational Sum Frequency Generation Spectroscopy. *Annu. Rev. Phys. Chem.* **2017**, *68*, 355–377. Copyright (2017) American Chemical Society.



**Fig. 5** The breathing effect of the solid electrolyte as depict by SFG measurements. Left—copper electrode. The overall SFG peak areas at two typical SEI frequencies (ethylene carbonate, carbonyl group, Fermi doublet) 1782 and 1807 cm<sup>-1</sup> as a function of scanned potential 2.0 V  $\Rightarrow$  0.2 V at 2 mV/s. Right—gold electrode. The overall SFG peak areas at two typical SEI frequencies (EC Fermi doublet) 1795 and 1831 cm<sup>-1</sup> as a function of scanned potential 2.0 V  $\Rightarrow$  0.2 V at 2 mV/s. Right—gold electrode. The overall SFG peak areas at two typical SEI frequencies (EC Fermi doublet) 1795 and 1831 cm<sup>-1</sup> as a function of scanned potential 2.0 V  $\Rightarrow$  0.2 V at 5 mV/s. Adapted with permission from Mukherjee, P.; Lagutchev, A.; Dlott, D. D. In Situ Probing of Solid-Electrolyte Interfaces With NonlinearCoherent Vibrational Spectroscopy. *J. Electrochem. Soc.* **2012**, *159*, A244–A252. Copyright 2012, The Electrochemical Society.



**Fig. 6** The SFG intensity of the ethylene carbonate carbonyl stretch as a function of applied potential. The SEI region (*blue*) is around 1400 cm<sup>-1</sup>, and the carbonyl stretch is around 1800 cm<sup>-1</sup>. Inset—the cyclic voltammograms of LiClO<sub>4</sub> in tetrahydrofuran (THF). Adapted with permission from Nicolau, B. G.; García-Rey, N.; Dryzhakov, B.; Dlott, D. D. Interfacial Processes of a Model Lithium Ion Battery Anode Observed, In Situ, With Vibrational Sum-Frequency Generation Spectroscopy. *J. Phys. Chem. C* **2015**, *119*, 10227–10233. Copyright (2017) American Chemical Society.

Somorjai et al. successfully performed in situ potentiodynamic SFG analysis (Fig. 7) of a common electrolyte, 1.0 M of lithium hexafluorophosphate (LiPF<sub>6</sub>) dissolved in EC and DEC, diluted with THF in contact with crystalline silicon (Si) electrodes in a lithium half-cell system under reaction conditions.<sup>28</sup> They found that with a Si(100)-hydrogen-terminated wafer, a Si-ethoxy (Si-OC<sub>2</sub>H<sub>5</sub>) surface intermediate forms due to DEC decomposition at 1.0 V versus Li/Li<sup>+</sup> to an ethoxy radical. This radical is generated only when DEC is present in the solution. Furthermore, they have shown that the SEI surface composition varies depending on the termination of Si surface, that is, the acidity of the Si surface. Moreover, their finding supports an electrochemical electrolyte reduction mechanism in which the reduction of the DEC molecule occurs before the reduction of the EC molecule. The formation of the Si-ethoxy termination allows the growth of a protective solid electrolyte interface that sticks to the silicon surface and inhibits its structural deterioration. This finding can lead to a novel electrolyte design that upon reduction will better adhere to and protect the silicon surface.

In a recent study, the Somorjai group employed the ability of SFGVS to detect the adsorption angles (and tilt) of the electrolyte molecules at the surface of an anode to study the effect of fluorine on the electrolyte–electrode interface (Fig. 8).<sup>29</sup> The motivation to explore the fluorine's effect on the SEI arises from the beneficial effect of fluorine-based additives on the performance of lithium-ion batteries,<sup>30–32</sup> yet the origin of this phenomenon is unclear.<sup>33–35</sup> They have studied an anode specific model system, the reduction of 1,2-diethoxy ethane with lithium bis(trifluoromethane)sulfonimide, (LiTFSI) as the lithium salt on an amorphous silicon anode, and compared the electrochemical response and SEI formation from the hydrocarbon ether to its fluorinated version, bis(2,2,2-trifluoroethoxy) ethane (BTFEOE). They have found that fluorinated electrolyte has tighter, upright packing on the silicon anode



**Fig. 7** The SFG of Si(100)-O<sub>x</sub> anode after cycling between 3.0 V  $\Rightarrow$  -0.05 V vs. Li/Li<sup>+</sup> (lithiation). In order to emphasize the evolution of the Siethoxy peaks, we divided the SFG spectra by their former potentials. Adapted with permission from Horowitz, Y.; Han, H. L.; Ross, P. N.; Somorjai, G. A. In Situ Potentiodynamic Analysis of the Electrolyte/Silicon Electrodes Interface Reactions – A Sum Frequency Generation Vibrational Spectroscopy Study. J. Am. Chem. Soc. **2016**, 138, 726–729. Copyright (2017) American Chemical Society.



**Fig. 8** Left—the SFG profiles of 0.1 M LiTFSI: 1,2-DEE (*black*) and 0.1 M LiTFSI: BTFEOE (*red*) in contact with amorphous Si anode at OCP. We note the frequencies corresponding to  $\alpha$ -OCH<sub>2</sub> (backbone) and  $\beta$ -OCH<sub>2</sub> (adjacent to -CX<sub>3</sub> end groups) methylene groups. Right—an illustration of structures of the ethers adsorbed on a-Si at OCP. Adapted with permission from Horowitz, Y.; Han, H.-L.; Ralston, W. T.; et al. Fluorinated End-Groups in Electrolytes Induce Ordered Electrolyte/Anode Interface Even at Open-Circuit Potential as Revealed by Sum Frequency Generation Vibrational Spectroscopy. *Adv. Energy Mater.* **2017**, 1602060.

surface leading to higher lithium ion diffusion rates in the silicon anode bulk in comparison to its regular hydrocarbon electrolyte version.

In future Li-ion batteries research, one can extend SFGVS to study cathode (sulfur, air, or polyanionic compounds) or anode materials under reaction condition to understand the fundamental aspects of surface redox reactions, like surface species and reaction dynamics, leading to the formation of a stable SEI.

#### **Fuel Cells**

In its most broad definition, a fuel cell generates electricity from the chemical reaction of a hydrogen-containing fuel with oxygen. The fuel cell's operation requires a constant feed of hydrogen-containing fuel (e.g., molecular hydrogen, alcohols, etc.) and oxygen. The end products of its operation are water and electricity. Hence, fuel cells are considered as sustainable energy devices. As any electrochemical system, the fuel cell has a metallic electrode that is in contact with an electrolyte, usually an aqueous salt solution. Once the fuel cell is operating a voltage develops and so to simulate a working fuel cell, we apply an external potential on the metal surface. Tadjeddine et al.<sup>11,36,37</sup> and others<sup>38–42</sup> have demonstrated that the use of SFGVS in fuel cell studies is effective in probing electrodes under working conditions since it provided fundamental information on the bonding geometry of adsorbed molecules, identified reaction intermediates, and revealed oxidation/reduction mechanisms while under working conditions. Ethanol is known as a feed for fuel cells, also named ethanol fuel cell. Liquid ethanol has the potential to become an alternative energy resource since upon its complete oxidation to  $CO_2$  it yields 12 electrons per one ethanol molecule.<sup>43</sup> Also, ethanol can be either reformed to produce hydrogen which can operate the proton exchange membrane fuel cells or directly used in the fuel cell. The oxidation of ethanol on polycrystalline Pt electrodes was studied by conventional IR spectroscopy, and the main conclusion of

that study was that acetaldehyde and acetyl are the predominant intermediates on the Pt electrode surface.<sup>44</sup> Recently, in a combined SFGVS and density functional theory study, Gomes et al. observed new adsorbed intermediates by using isotope-labeled ethanol as the reactant.<sup>45</sup> Their SFGVS study revealed many new intermediates on top of the previously reported ones. Their findings showed that the Pt surface is much more reactive than previously considered as multiple ethanol oxidation intermiedates were identified. **Fig. 9** shows the proposed intermediates of ethanol oxidation on a platinum electrode in an acidic medium under oxidation conditions. Gomes et al., observed that during the catalytic oxidation of ethanol, acetaldehyde and acetyl are the dominant intermediates. These in turn, can subsequently decompose to form CO which at lower potentials poisons the surface.<sup>44,45</sup> CO poisoning is a limiting factor for the performance of fuel cells. However, the CO poisoning mechanism is still under debate as conventional IR spectroscopic methods lack the necessary surface sensitivity that SFGVS has.<sup>46</sup> Humbert et al. reported a strategy to study the



Fig. 9 Proposed intermediates of ethanol oxidation on platinum electrode in acidic medium. The geometry of the adsorbed intermediates is not considered in this scheme. Adapted with permission from Gomes, J. F.; Bergamaski, K.; Pinto, M. F. S.; Miranda, P. B. Reaction Intermediates of Ethanol Electro-oxidation on Platinum Investigated by SFG Spectroscopy. *J. Catal.* **2013**, *302*, 67–82.

CO poisoning mechanism of Pt by combining sum-frequency generation spectroscopy with applied potential.<sup>47</sup> They correlated between Stark shifts in the spectra of C==O vibrations to different surface coverage that in turn changes as a function of the applied potential. In the potential range of hydrogen evolution and CO oxidation, -800 to -450 mV and +600 to +1000 mV, the Stark shift is not significant. However, in the potential range of -450 to -50 mV and -50 to +600 mV, two Stark shifts of 31 and 15 cm<sup>-1</sup> are observed, respectively. Humbert et al. claimed that this observation was due to the dipole–dipole coupling inside the CO layer: a more densely packed layer gives rise to stronger coupling and therefore induces a shift of the resonance frequency to higher values. In other words, the tilt angle (orientation) of CO on Pt(110) manifested in the strong frequency shift plays a major role since the straighter the molecules, the bigger the coupling. They concluded that in the potential range from -50 to +600 mV, the CO adlayer is so densely packed that it prevents ions from accessing the electrode surface. The small additional peak (gray arrow in Fig. 10) at 1955 cm<sup>-1</sup> around -200 mV was attributed to the Pt–H stretch. The weak Pt–H signal shows the amount of adsorbed hydrogen is low and the quenching of hydrogen evolution as a consequence of the dense CO coverage. A potential of zero-charge of +650 mV is measured by a careful analysis of the SFG spectra, confirming that this potential corresponds to the onset of oxidation processes at the surface.

While SFGVS has excellent surface sensitivity, it suffers from absorption of the IR radiation when passing through the liquid electrolyte medium. Therefore, most of the above experiments were conducted in an electrochemical cell with a window separated about 1–50 µm away from the metal electrode in order to reduce the IR attenuation due to electrolyte absorption.<sup>38</sup> Some concerns may arise from this type of configuration; for instance, the ion diffusion rate may be different from a bulk solution and may affect the electrochemical reaction during a potential scan, and the sum frequency generated from the window and solution may interfere with the sum frequency generated from the metal electrode during the frequency scan.



**Fig. 10** SFG spectra of the CO layer deposited from CO (C/10) solution on Pt(110) for applied potentials ranging from -800 to -50 mV (A) and -50 mV to 1 V (B) (vs. Ag/AgCl/KCI (3 M)). Lines are fitted to the data. The same SFG intensity scale is for all spectra. Reprinted with permission from Humbert, C.; Busson, B.; Tadjeddine, A. Enhanced Stability of a Carbon Monoxide Monolayer Adsorbed on Platinum Under Electrochemical Control Probed by Sum-Frequency Generation Spectroscopy. *J. Phys. Chem. C* **2016**, *120*, 16211–16220. Copyright (2017) American Chemical Society.



**Fig. 11** Surface plasmon-SFGVS setup and spectra from gold–water(air) interfaces. (A) Schematic of experimental arrangement. (Inset) Reflection of IR input at 3300 cm<sup>-1</sup> from the prism–gold–air interface as a function of incident angle. The dip in the insect indicates surface plasmon excitation. *Dots* are measured data, and the *solid curve* is from the calculation. (B) In situ SP-SFGVS of electrochemical desorption and re-adsorption of a thiol-SAM on a gold electrode. SFG spectrum of interface taken at three different potentials during a scan: at +1.2 V (*blue*) before the occurrence of oxidative desorption of thiols, at +1.7 V (*green*) after near-completion of oxidative thiol desorption, and back at +1.2 V (*violet*) with no indication of thiol re-adsorption. Taken with permission from Liu, W. T.; Shen, Y. R. In Situ Sum-Frequency Vibrational Spectroscopy of Electrochemical Interfaces With Surface Plasmon Resonance. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 1293–1297.

To overcome this, Liu and Shen<sup>48</sup> employed a surface plasmon-enhanced SFG vibrational spectroscopy. Their model system was a gold thin film deposited on a prism in contact with the liquid medium. The incoming visible and IR beams propagated through the 20 nm thin film, and the SFG was reflected to the detector thus enabling the researchers to probe the electrode–electrolyte interface directly without any diffusion or interference related concerns. **Fig. 11A** presents the schematic electrochemical cell and beam geometry. **Fig. 11B** shows the SFG spectra taken at three different potentials with an alkanethiol self-assembled monolayer on Au film immersed in a 10 mM KOH solution. They showed that the oxidation state of the desorbed thiols affects their diffusion. Reduced thiols stay near the gold surface as an ordered layer in the electrolyte, whereas the oxidized desorbed thiols diffuse away from the gold electrode. This approach helps us to better understand electrochemical reactions at the molecular level. However, we should take into account that when applying SFGVS at wider IR spectrum ranges (e.g., OH stretching) we face plasmon resonance contributions that convolute with the SFG spectra.

SFG spectroscopy can also probe the correlation between the adsorption/desorption, and oxidation/reduction of surface species with the surface electronic structure.<sup>49–52</sup> According to theoretical frameworks established by Föhlisch et al.,<sup>53,54</sup> Bennich et al.,<sup>55</sup> and Smotkin et al.,<sup>56</sup> the interfacial electronic structure is significantly modified by the hybridization of the metal's electronic states with the molecular orbitals of chemisorbed molecule. As a result, new energy states are formed at the interface. Recently, Uosaki et al. studied the substrate's effect on the electronic structure of CO adsorbed on Pt electrodes in a H<sub>2</sub>SO<sub>4</sub> solution by applying an IR/visible double resonance SFG spectroscopy and showed a direct in situ result supporting those theoretical models.<sup>51,52</sup> Fig. 12A shows the normalized SFG amplitude of CO adsorbed on (1) polycrystalline Pt and (2) Pt(111) as a function of the



**Fig. 12** (A) The contour maps of the normalized SFG amplitude of CO adsorbed on (1) polycrystalline Pt and (2) Pt(111) as functions of the potential and energy of visible light obtained using visible light at wavelengths of 635 nm (1.95 eV), 620 nm (2.0 eV), 605 nm (2.05 eV), 590 nm (2.10 eV), 575 nm (2.15 eV), 560 nm (2.21 eV), 550 nm (2.25 eV), and 527 nm (2.35 eV). (B) A model of the  $5\sigma_a$  anti-bonding state of CO adsorbed on polycrystalline Pt and Pt(111) electrodes at a given potential, showing that the energy distribution of the  $5\sigma_a$  state of CO adsorbed on a polycrystalline Pt is broader than that on a Pt (111). Adapted with permission from Yang, S.; Noguchi, H.; Uosaki, K. Broader Energy Distribution of CO Adsorbed at Polycrystalline Pt Electrode in Comparison With That at Pt(111) Electrode in H<sub>2</sub>SO<sub>4</sub> Solution Confirmed by Potential Dependent IR/Visible Double Resonance Sum Frequency Generation Spectroscopy. *Electrochim. Acta* **2017**, *235*, 280–286.

potential and energy of the visible light. The SFG results suggest that the energy distribution of the  $5\sigma_a$  state of CO on polycrystalline Pt surface is broader than that on Pt(111) due to the complex surface structure of the polycrystalline Pt electrode, as shown in **Fig. 12B**. The electronic transition from  $E_f$  to  $5\sigma_a$  can also be explained by the resonance with the visible light. In an electrochemical cell, the Fermi level is modulated by applying the potential with respect to the reference electrode. The researchers found that the energy difference between  $E_f$  and  $5\sigma_a$  varied as a function of potential. Thus, the origin of the potential-dependent SFG enhancement at the CO/Pt(111) electrode is the resonance of the visible/SFG light with the electronic transition from the  $E_f$  of Pt, which is varied linearly with the electrode potential, to the  $5\sigma_a$  state of the adsorbed CO. For example, as the potential becomes more negative, the energy difference between  $E_f$  and  $5\sigma_a$  decreases, and so it is probed with lower photon energy. To conclude, the IR/visible double resonance SFG spectroscopy was demonstrated as an efficient in situ method to probe both molecular and electronic structures at electrochemical interfaces.

### **Conclusions and Remarks**

In this article, we have presented current SFGVS work associated with renewable energy studies on lithium ion batteries and fuel cells. This article shows that SFG vibrational spectroscopy, owing to its surface specificity with sub monolayer sensitivity and nondetrimental nature, is widely applicable to probe a variety of complex solid–liquid interfaces under reaction conditions. SFGVS has proven as a powerful tool in our attempt to understand electrochemical reactions taking place at various electrode–electrolyte interfaces on a molecular-level that will eventually lead to technological breakthroughs. Combining SFG experiments with computational models has proven to be most beneficial as MD allow us to interpret an otherwise ambiguous experimental SFG spectra. We hope that this article leads to further investigations of electrified interfaces, ultimately probing the electrical double layer at any given interface under applied potential.

Finally, we discuss the challenge of probing a metal surface under an applied potential. We wish to point out that phase-sensitive SFGVS, which has not yet been applied to metal interfaces, could be implemented to study electrified interfaces of metal or semiconductor electrodes. Recent advances in SFG instrumentation and data processing have led to heterodyne two-dimensional VSFG (HD 2D-SFGVS) as well as time-resolved heterodyne-detected SFGVS that have higher sensitivity and selectivity when compared to traditional SFGVS.<sup>57</sup> Unfortunately, there are no relatively straightforward heterodyne SFG instruments available to probe the orientation of interfacial molecules. Such a development together with advanced computational methods would further advance our fundamental understanding and better control of electrochemical reactions in the field of energy storage.

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## **Ambient Pressure X-Ray Photoelectron Spectroscopy**

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#### Introduction

The surface sensitivity of X-ray photoelectron spectroscopy (XPS) is exquisitely suited to study the elemental composition and chemical nature of a wide range of surfaces, ranging from single crystals and model systems to device materials. Most XPS investigations are performed under vacuum conditions, for both control of the sample cleanliness and reduction of electron scattering by gas molecules. The first XPS studies at conditions above high vacuum were performed by Kai Siegbahn's group in the 1970s,<sup>1,2</sup> and recent developments and instrument commercialization have prompted a strong increase in the number of ambient pressure X-ray photoelectron spectroscopy (APXPS) instruments and studies performed by them. (Other names for the technique are high-pressure XPS, near ambient pressure XPS, and *in situ* XPS.) APXPS instruments are now available commercially with laboratory-based sources (monochromatized X-ray anodes) or at synchrotron radiation facilities around the world, affording opportunities for researchers in various disciplines to conduct XPS studies at pressures of up to tens of mbar.

Over the recent decades, surface science has expanded from the study of well-defined single crystals under ultra-high vacuum (UHV) conditions to more complex surfaces, including liquids, under elevated pressures. Many different *operando* techniques have been developed by now, including infrared spectroscopy (IR)<sup>3,4</sup> and vibrational sum frequency generation<sup>5,6</sup>; X-ray emission spectroscopy<sup>7</sup>; surface X-ray diffraction<sup>8</sup>; scanning probe techniques, such as scanning force microscopy in both contact<sup>9</sup> and noncontact<sup>10</sup> modes; scanning tunneling microscopy<sup>11</sup>; transmission electron microscopy<sup>12</sup>; and scanning electron microscopy.<sup>13</sup> APXPS is an important part of this range of tools, as it is surface-sensitive, has element and chemical specificity, and allows the correlation of the surface chemical composition with local changes in the work function or electrical potentials under *operando* conditions. In the following, we will first briefly discuss the fundamentals of XPS and APXPS before demonstrating the application of APXPS to a variety of systems, including model electrochemical cells and liquid–vapor interfaces.

### X-Ray Photoelectron Spectroscopy

When photons with an energy greater than the binding energy of electrons impinge on an atom, electrons are emitted in the process known as the photoelectric effect. Any energy from the incoming photon that is not used in the ionization event is transferred as kinetic energy to the electron. An electron spectrometer can measure this kinetic energy, and by knowing the photon energy, the ionization energy can be calculated from

$$h\nu = KE + BE + \Phi \tag{1}$$

where hv is the photon energy, KE is the kinetic energy of the electron, BE is the binding energy, and  $\Phi$  is the work function of the spectrometer. Binding energies measured by XPS are used to identify the elements contained in a sample. The chemical environment of elements can be deduced from chemical shifts in the binding energies, offering insight into, for example, an atom's functional group or oxidation state. The surface sensitivity of XPS stems from the strong interaction of electrons with matter. For example, the

inelastic mean free path (IMFP) of an electron in a solid at kinetic energies relevant to soft X-ray sources (100–1000 eV) varies between subnanometer and several nanometers. The strong scattering of electrons by matter poses a fundamental problem for measurements at elevated pressures, since electrons will undergo elastic and inelastic scattering events with gas molecules. In most electron spectrometers, the emitted photoelectrons are collected by an electrostatic lens and travel tens of centimeters before entering the electron energy analyzer, usually a concentric hemispherical analyzer. At a pressure of 1 mbar, a gas is about 10<sup>6</sup> times less dense than solids, giving electrons an IMFP of the order of millimeters, which prevents a significant amount of photoelectrons from reaching the electrostatic lens and electron energy analyzer — one major reason why XPS has traditionally been conducted under high vacuum conditions. Another technical reason for performing XPS under vacuum conditions is the potentially high voltage differences between electrostatic lens elements (or the detector) and ground, which can lead to arcing at elevated pressures. These obstacles were addressed first by the Siegbahn group (Uppsala) in their original APXPS designs from the early 1970s; their principle approach and the subsequent adaptations are described in the following.

#### Ambient Pressure X-Ray Photoelectron Spectroscopy

The key to reducing the effect of scattering of the photoelectrons on the signal collected from the sample is the development of a differential pumping scheme between the elevated pressures in the analysis chamber and the electron energy analyzer, which needs to be kept in vacuum. The sample is located inside an *in situ* cell at the desired gas pressure *p* (see Fig. 1). X-rays enter this cell through either an X-ray transparent window (eg, 100 nm thick  $SiN_x$ ) or a set of differentially pumped apertures in order to maintain the necessary vacuum environment in the X-ray source (X-ray anode or synchrotron). Electrons and gas molecules escape the analysis chamber into the electron energy analyzer through a small, differentially pumped aperture (typical diameters are 0.1-1 mm). The distance between this aperture and the sample (*z* in Fig. 1) is greater than 2 aperture diameters to reduce effects of the pressure drop in front of the aperture on the sample chemistry. This design minimizes the distance that a photoelectron travels through the gas phase.

Two main factors influence the pressure limit in an APXPS system: the attenuation of the signal by scattering in the gas phase and the threshold pressure in the sample compartment at which the vacuum pumps in the differential pumping system start to stall. This threshold pressure depends on the size of the entrance aperture, the conductance of the pumping system, and the capacity of the pumps. For very small entrance apertures ( $<\sim$ 10 µm diameter), only one differential pumping stage (ie, the front aperture) might be sufficient, even at pressures in the tens of torr range. Virtually all current APXPS instruments use larger entrance aperture sizes that match the size of the illuminated sample area for high detection efficiency, which requires entrance apertures with diameters of typically larger than 100 µm. In these cases, several differential pumping stages are necessary to maintain a pressure of well below  $10^{-6}$  mbar in the hemispherical analyzer, as required for the safe operation of the electron detector (eg, channeltrons and multichannel plates). The principal layout of early differential pumping stages is shown in Fig. 2A, where there is a trade-off between pumping efficiency (smaller apertures) and detection efficiency (larger apertures). This drawback was overcome in later designs (Fig. 2B) by incorporating electrostatic lenses between the differentially pumped apertures, which preserve the solid angle of electron detection of a conventional electrostatic lens. The addition of these lenses increases the signal and in turn the pressure limit with respect to the design in Fig. 2A by more than an order of magnitude.<sup>14</sup>

The fundamental pressure limit in an APXPS experiment is given by the scattering of electrons by gas molecules, mostly in inelastic scattering events for electrons with more than 100 eV KE. The IMFP of electrons through a gas is dependent on the type of gas, the pressure, and the kinetic energy of the electron, as demonstrated in Fig. 3. While typical pressures in APXPS experiments are in the torr range, Pt 4f spectra have been collected under a 100 torr of  $O_2$ , with an accumulation time of 90 min.<sup>15</sup> There are several parameters that determine the scattering of electrons in an APXPS experiment, among them, the gas pressure (*p*) and the



**Fig. 1** Layout of the sample environment in an APXPS experiment, including the incoming photon beam, sample surface, and the differentially pumped conical entrance aperture to the electrostatic lens system and energy analyzer. Reprinted from Starr, D. E.; Bluhm, H.; Liu, Z.; Knop-Gericke, A.; Hävecker, M. Application of Ambient-Pressure X-ray Photoelectron Spectroscopy for the *In-situ* Investigation of Heterogeneous Catalytic Reactions. In *In-situ Characterization of Heterogeneous Catalysts*; Rodriguesz, J. A., Hanson, J. C., Chupas, P. J., Ed.; Wiley: Hoboken, NJ, 2013, Chapter 12, pp 315–343, with permission from Wiley.



**Fig. 2** (A) The transmission of photoelectrons through the differential pumping system can result in a large loss of spectral intensity due to the limited solid angle that is subtended by the apertures. (B) Using electrostatic lenses to focus the electron beam at each stage of the differential pumping results in a substantial retention of the photoelectron signal. Reprinted from Starr, D. E.; Bluhm, H.; Liu, Z.; Knop-Gericke, A.; Hävecker, M. Application of Ambient-Pressure X-ray Photoelectron Spectroscopy for the *In-situ* Investigation of Heterogeneous Catalytic Reactions. In *In-situ Characterization of Heterogeneous Catalysts*; Rodriguesz, J. A., Hanson, J. C., Chupas, P. J., Ed.; Wiley: Hoboken, NJ, 2013, Chapter 12, pp 315–343, with permission from Wiley.

distance between the sample and the entrance aperture (z in Fig. 1). The effect of these parameters on the signal intensity, I, at a specific pressure, p, compared with the same signal in UHV conditions,  $I_{vac}$  is given by the Beer–Lambert law:

$$\frac{I}{I_{\text{vac}}} = e^{\frac{z\sigma(E)p}{kT}}$$
(2)

where  $\sigma(E)$  is the electron-scattering cross section of a gas at a specific kinetic energy.<sup>14</sup> The distance between the sample and aperture requires extra consideration. Because gas escapes through the aperture into the differential pumping system, a local pressure differential is created directly in front of the aperture. If the sample is too close, the local pressure of the sample being irradiated will be significantly lower than the measured pressure in the analysis chamber. Molecular flow calculations have found that the distance between the sample and the aperture should be at least twice the diameter of the aperture to avoid changes in the local sample pressure (ie,  $z \approx 2d$  in Fig. 1).<sup>16,17</sup>

According to Eq. (2), photoelectrons with a kinetic energy of 100 eV that travel a distance of 1 mm in 1 mbar of  $N_2$  at room temperature are attenuated by 90% compared with the same signal under vacuum conditions. Fig. 3 shows that the attenuation depends critically on the type of gas, with greatly reduced scattering for  $H_2$  at the same pressure and increased scattering for  $CH_3Cl$  compared with  $N_2$ .

The photon flux on the sample is another factor that determines the photoelectron signal. The gas phase in the analysis chamber absorbs incoming X-rays and reduces the number of photons that impinge on the sample. By minimizing the path length of the X-rays within the measurement cell, this effect can be reduced. A photon source with a high flux and a small photon beam size matching that of the entrance aperture to the electrostatic lens system are optimum. Synchrotron sources fit these requirements and have a tunable photon energy. Spectrometers outside of synchrotron facilities are also available where, ideally, a focused, monochromatic X-ray anode source is used. It cannot be overly stressed, however, that the use of strongly focused and intense X-rays also bears the danger of beam-induced changes to the sample surface, known as beam damage. These effects can be



**Fig. 3** Inelastic mean free path of electrons in H<sub>2</sub>, N<sub>2</sub>, and CH<sub>3</sub>Cl under 1 mbar of pressure at 300 K calculated from total electron-scattering cross sections in the literature. Adapted from Hoffman, K. R.; Dababneh, M. S.; Hsieh, Y.-F.; Kauppila, W. E.; Pol, V.; Smart, J. H.; Stein, T. S. *Phys. Rev. A* **1982**, *25*, 1393–1403; Karwasz, G. P.; Brusa, R. S.; Piazza, A.; Zecca, A. *Phys. Rev. A* **1999**, *59*, 1341–1347.
exacerbated in APXPS measurements through the additional channel for beam damage resulting from the ionization of the gas phase in the vicinity of the sample surface. It is therefore of great importance to check for beam-induced changes in each APXPS investigation.

The gas-phase adsorption of the incoming photons and subsequent photoemission can also be advantageous. In addition to the ionization signal from the sample surface, a gas-phase signal, detectable at pressures above  $10^{-2}$  mbar, can offer simultaneous chemical information about gas-phase reactants and products. (Combining mass spectrometry with APXPS can yield further details about gaseous species.) Also, electrons generated in the gas phase can help to reduce sample charging to some degree in the case of insulating samples. The efficiency of this process depends critically on the type of gas and incident photon energy.<sup>16</sup>

In addition to providing information about the chemical nature of the surface, XPS in general<sup>18-20</sup> and APXPS in particular under operando conditions can be used to simultaneously determine changes in the electrical potentials or work function. Measurement of these values is an important advantage of the method specifically in electrochemical reactions.<sup>2,21</sup> The principle is illustrated in Fig. 4 for the case of a metal, where the Fermi level of the sample ( $E_{\rm F}$ ) is aligned with that of the entrance aperture of the differentially pumped lens system and the spectrometer. In general, the vacuum levels ( $E_{vac}$ ) of these components are different. Therefore, the Evac of the gas phase varies spatially between the sample and aperture, as shown in Fig. 4A. When molecules absorb onto a surface, the  $E_{\rm vac}$  of the sample can shift (a decrease in Fig. 4B) and change the sample work function ( $\Phi^{\rm sam}$ ). Since the  $E_{\rm F}$  has not moved, there is no shift in the BE of the surface peaks. Due to the spatial variation of  $E_{\rm vac}$  of the gas phase, the binding energy shift of the gas-phase peaks is smaller than the actual change in  $E_{vac}$  at the sample surface. By applying a bias to the sample, a change in the electrical potential of a surface shifts both  $E_{\rm vac}$  and  $E_{\rm F}$  of the sample, resulting in a binding energy shift of both the gas-phase and the surface peaks, shown in Fig. 4C. Again, the shift in the gas-phase peaks is less than that of the change in the Evac of the sample. In these examples, it is assumed that the aperture work function ( $\Phi^{ap}$ ) does not change. These shifts can be utilized to measure work functions of materials under different conditions<sup>2,22</sup> or changes in electrical potentials in electrochemical applications.<sup>23</sup> It should be noted that the apparent binding energy shifts caused by work function or potential changes can readily be distinguished from shifts due to changes in the surface chemistry, since shifts due to work function or potential changes affect all core and valence levels in exactly the same way, while chemical shifts show specific changes for a core or valence level of a given element.

APXPS can be coupled with other techniques to yield additional information. As previously mentioned, the gas in the analysis chamber can be sampled by mass spectrometry to identify of gas-phase species and relative concentrations of products and reactants.<sup>24</sup> Electrochemical experiments can be simultaneously performed while collecting APXPS data on surface species at different applied potentials.<sup>25,26</sup> Though it cannot be conducted simultaneously with APXPS, near-edge X-ray absorption fine structure spectroscopy studies can be conducted in close temporal proximity to the APXPS measurements with synchrotron sources at high pressures to yield information on unoccupied states, which are sensitive to, for example, molecular orientation on surfaces<sup>27</sup> and oxidation states.<sup>28</sup> IR also probes electronic structure and complements XPS data well.<sup>29</sup> Some functional groups have similar binding energies, making the concrete identification of these surface functional groups difficult based only on chemical shifts; a vibrational probe would offer a powerful method to further study reaction mechanisms and will also help with the identification of beam-induced changes in APXPS experiments. While no current spectrometer has the capability for simultaneous APXPS and IR spectroscopy measurements, this development is likely to occur in the near future.

#### **Examples of APXPS Applications**

Vacuum XPS investigations are limited to studying surfaces of materials with low vapor pressure at typical background pressures well below  $10^{-6}$  mbar. These types of studies provide an understanding of fundamental chemical and physical processes in the most ideal case of a chemical system since impurities and contamination can be controlled. APXPS opens opportunities to investigate the chemical changes at surfaces under more complex conditions that are closer to those found in real systems, specifically solid–vapor, liquid–vapor, and solid–liquid interfaces. In the following, we will discuss representative examples of APXPS investigations for each of these interfaces.

#### Solid–Vapor Interface

The study of the interaction between gas molecules and a surface has much relevance to real-world systems, such as automotive three-way catalysts. In terms of technical challenges, the solid–vapor interface is one of the easiest to study as the preparation of this interface is straightforward and the dilute gas phase the overall scattering of photoelectrons from the interface on their way to the detector. The adsorption of gases, most importantly water vapor, to surfaces is relevant in corrosion studies, geochemistry, materials science, and atmospheric chemistry. Beyond simple adsorption studies, chemical reactions of gas molecules with surfaces (eg, of catalysts) can also be monitored. Depending on the speed of the reaction and the features of the instrument, kinetic



**Fig. 4** Measurement of work function and electrical potential changes at the sample surface in APXPS experiments. The upper right corner shows the orientation of the sample, aperture, and photon beam that irradiates both the surface and gas phases. (A) The position of surface and gas-phase peaks with the energy scheme depicted on the right. (B) The gas-phase peak shifts, while the surface peak remains constant when the vacuum level ( $E_{vac}$ ) changes as the Fermi level ( $E_{F}$ ) remains constant, resulting in a change in the sample work function ( $\Phi^{sam}$ ). (C) A change in the chemical potential of the surface shifts both  $E_{vac}$  and  $\Phi^{sam}$ , resulting in shifts of both the gas and surface peaks. In this example, it is assumed that the work function of the aperture ( $\Phi^{ap}$ ) is constant. Reprinted from Shavorskiy, A.; Bluhm, H. Ambient Pressure Photoelectron Spectroscopy. In *Heterogeneous Catalysts for Clean Technology: Spectroscopy, Design, and Monitoring*, Wilson, K., Lee, A. F., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2014; Chapter 14, pp 437–468, with permission from Wiley.

information can be obtained in addition to monitoring surface chemistry. The ability to detect the transformation of gaseous reactants, changes in surface oxidation states, and shifts in surface potential makes this technique ideal to monitor catalytic reactions and electrochemical processes.

#### Catalytic methanol steam reforming

The advantages of the combination of APXPS and mass spectrometry are illustrated in a study of the catalytic conversion of methanol to hydrogen via steam reformation over a  $Pt/In_2O_3$  catalyst on an  $Al_2O_3$  support.<sup>24</sup> Three reactions are known to occur during this process: methanol decomposition (Eq. (3)), steam reforming (Eq. (4)), and water gas shift (Eq. (5)):

$$CH_3OH \rightarrow CO + 2H_2$$
 (3)

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \tag{4}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{5}$$

The selectivity of the catalyst toward the reactions is thought to be influenced by the catalyst pretreatment in either a reducing or an oxidizing environment, which determines its initial oxidation state and surface composition. The effect of both pretreatments on the catalytic selectivity and surface chemistry was investigated in simultaneous APXPS and mass spectrometry studies.

The Pt/In<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalytic material was deposited into a microreactor that simulates the gas flow and temperature of industrial processes but still allows for APXPS measurements. The depth distribution of the elements can be probed by increasing the IMFP of the photoelectrons by increasing the photon energy and thus the photoelectron kinetic energy for a given core level. **Fig.** 5 compares the results of the element depth profiling during heating under the two pretreatment conditions: the reducing condition in 0.2 mbar of H<sub>2</sub> and the oxidizing condition in 0.2 mbar of O<sub>2</sub>. Overall, the trends in the depth distribution of the elements are the same for In, Al, and Pt in both the reducing and oxidizing environments. There is a slight enhancement of In on the surface under oxidizing conditions and Pt under reducing conditions. The oxidation state of In also varies, becoming partially metallic under reducing conditions.

The conversion of reactants and the yield of products are plotted in **Fig. 6**. The oxidizing treatment has higher selectivity for the CO, though less methanol and water are consumed in the steady-state regime. This behavior indicates a preference for methanol decomposition or suppression of the water gas shift reaction. Despite the reaction preference of the different pretreatments, the core-level spectra and atomic concentrations are similar under steady-state conditions as illustrated in **Fig. 7**. Compared with initial surface concentrations in **Fig. 5**, the concentration of Pt and Al on the surface has increased, while there is less In. These data show that the surface of the catalyst dynamically changes until the active phase is obtained, regardless of the pretreatment. Additionally, the oxidation states in the active phase are independent of the pretreatments. These results illustrate how detailed information can be obtained under reaction conditions that cannot be studied using *ex situ*, postmortem techniques.



**Fig. 5** Comparison of the atomic concentrations of the surface components of Pt/In<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst under 0.2 mbar of H<sub>2</sub> and O<sub>2</sub> gas environments at different analysis depths. The abundance of the different components as a function of depth was obtained from the XPS spectra of Pt 4f, Al 2p, and In 3d using different photon energies. On the upper *x*-axis, the estimated information depth is given. Error bars represent the estimated systematic error in the atomic concentration based on the uncertainties of the atomic photoionization cross section and of the model used in the calculations. Lines serve as guides to the eye. Reprinted with permission from Barbosa, R. L.; Papaefthimiou, V.; Law, Y. T.; Teschner, D.; Hävecker, M.; Knop-Gericke, A.; Zapf, R.; Kolb, G.; Schlögl, R.; Zafeiratos, S. *J. Phys. Chem. C* **2013**, *117*, 6143–6150. Copyright © 2013 American Chemical Society.



**Fig. 6** Mass spectrometry data recorded during methanol steam reforming (0.2 mbar,  $CH_3OH:H_2O = 1:2$ ) of  $Pt/ln_2O_3/Al_2O_3$  catalyst pretreated in  $H_2$  (solid line) and  $O_2$  (scatter line). The temperature profile is shown at the right axis. The dashed region represents the time period of acquisition of APXPS spectra. Reprinted with permission from Barbosa, R. L.; Papaefthimiou, V.; Law, Y. T.; Teschner, D.; Hävecker, M.; Knop-Gericke, A.; Zapf, R.; Kolb, G.; Schlögl, R.; Zafeiratos, S. *J. Phys. Chem. C* **2013**, *117*, 6143–6150. Copyright © 2013 American Chemical Society.



**Fig. 7** Deconvoluted (A) Pt 4f and Al 2p and (B) In 3d core-level spectra of Pt/ln<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> under 0.2 mbar of methanol and water ( $CH_3OH:H_2O = 1:2$ ) obtained at 250°C using photon energy of 655 eV for Pt and Al and 1025 eV for In. (C) Comparison of the atomic concentrations of the surface components of Pt/ln<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst at different depths for samples pretreated in H<sub>2</sub> and O<sub>2</sub>. The calculation of the atomic components was obtained from the XPS spectra of Pt 3d, Al 2p, and In 3d using different photon energies. Error bars represent the estimated systematic error in the atomic concentration based on the uncertainties of the atomic photoionization cross section and of the model used in the calculations. Reprinted with permission from Barbosa, R. L.; Papaefthimiou, V.; Law, Y. T.; Teschner, D.; Hävecker, M.; Knop-Gericke, A.; Zapf, R.; Kolb, G.; Schlögl, R.; Zafeiratos, S. *J. Phys. Chem. C* **2013**, *117*, 6143–6150. Copyright © 2013 American Chemical Society.

#### Mapping the surface potential of a working electrochemical cell

As illustrated in Fig. 4, shifts in core-level binding energies can yield information about surface potential changes. This concept has been applied to investigate the local potential changes in a working solid oxide electrochemical cell (SOC).<sup>23</sup> Fig. 8A shows the layout of the SOC with a Pt counter electrode, a ceria working electrode, and Au current collectors on a polycrystalline yttria-stabilized zirconia (YSZ) cell. When a positive bias is applied to the Pt counter electrode in the presence of H<sub>2</sub> and H<sub>2</sub>O vapor, water-splitting electrolysis (Eq. (6)) occurs at the ceria electrode, while hydrogen electrooxidation (Eq. (7)) occurs at the Pt electrode. The locations of the reactions are reversed upon application of a negative bias to Pt. These reactions and the current flow through the cell are schematically illustrated in Fig. 8B:

$$H_2O + 2e^- \rightarrow O^{2-} + H_2$$
 (6)

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$
 (7)

When applying a bias voltage to the sample, all surface core ionization energies should shift by the amount of the voltage. However, local potential changes on the sample arise as a result of the electrochemical processes occurring on the SOC, as well as the resistance to electronic and ionic currents. By comparing the shift in the core ionization energy of surface species with the applied bias, the local potential can be calculated. **Fig. 9** shows how the local potential across the SOC varies with a positive and negative 1.2 V bias as measured by Pt, Zr, Ce, and Si core levels. Si was present on the entire SOC surface as an impurity and was used as an additional probe of the local potential. Spectra were collected every 20 µm along a cross section of the SOC, and the core-level shift was plotted over a lateral section of the SOC. Since the bias is applied to the Pt counter electrode while the Au electrode is held at ground potential, the Pt 4f core level shifts by 1.2 V in the expected direction. At the interface of the Pt and YSZ, hydrogen electrooxidation occurs for a positive bias, and water-splitting electrolysis occurs at a negative bias, inducing the sharp change in the local potential in **Fig. 9**. Around 150–200 µm from the Au current collector, the local potential begins to dramatically change, indicating the area of electrochemical activity of the complementing half reaction at the ceria electrode. This study is an example of how changes in surface potentials of an electrochemical device can be directly investigated with spatial resolution under working conditions.

#### Vapor-Liquid Interface

The interface between liquids and gases is important in understanding chemical reactions in environmental, aerosol, and colloid chemistry. The composition of the interface can vary significantly from that of the bulk, which changes heterogeneous chemical reactions at these interfaces. Creative techniques to generate stable vapor–liquid interfaces in analysis chambers of APXPS instruments have emerged. A simple way of generating a thin film of solution is to deliquesce, or rehydrate, *ex situ* deposited salts by increasing the relative humidity in the analysis chamber until a signal from liquid water is seen.<sup>30</sup> Liquid



Fig. 8 (A) Schematic illustration of the SOC with the Pt electrode (blue), the ceria working electrodes (green), the Au current collectors (gold), and the YSZ support (light blue). 30 nm of alumina (black) prevents ionic transport from YSZ to Au. (B) Schematic illustration of SOC cross section showing the chemical reactions and current flow under positive and negative biases. Neither are drawn to scale. Reprinted with permission from Zhang, C.; Grass, M. E.; Yu, Y.; Gaskell, K. J.; DeCaluwe, S. C.; Change, R.; Jackson, G. S.; Hussain, Z.; Bluhm, H.; Eichhorn, B. W.; Liu, Z. ACS *Catal.* 2012, *2*, 2297–2304. Copyright © 2012 American Chemical Society.



**Fig. 9** Plots of the local potentials ( $V_L$ ) calculated from the shifts in photoelectron kinetic energies away from open-circuit voltage condition. The data shown were collected at +1.2 V (-600  $\mu$ A) and -1.2 V (+130  $\mu$ A) applied bias ( $\sim$ 720°C with 0.5 torr 1:1 H<sub>2</sub>/H<sub>2</sub>O mixtures). The  $V_L$  values of Pt <sup>0</sup>, Zr<sup>4+</sup>, and Ce<sup>4+</sup> are represented by dark blue, light blue, and green dots, respectively. The red dots show the  $V_L$  values of Si <sup>4+</sup> across the entire cell. Reprinted with permission from Zhang, C.; Grass, M. E.; Yu, Y.; Gaskell, K. J.; DeCaluwe, S. C.; Change, R.; Jackson, G. S.; Hussain, Z.; Bluhm, H.; Eichhorn, B. W.; Liu, Z. *ACS Catal.* **2012**, *2*, 2297–2304. Copyright © 2012 American Chemical Society.

jets with a waist on the order of 200 µm or less can be directed past the entrance aperture of the electron analyzer.<sup>31–33</sup> Similarly, a train of liquid droplets for aerosol studies can be generated using a vibrating orifice aerosol generator.<sup>34</sup> Another method is to dip a solid sample into a beaker of solution and slowly remove it until a thin liquid layer is formed. Since the thin film is in contact with the bulk solution, there is constant ion exchange with the bulk. This sample preparation is called the meniscus method or the "dip and pull" method.<sup>25</sup> Another method to utilize a liquid reservoir in the analysis chamber involves a partially submerged rotating disk; a constantly refreshed liquid film is present at the top of the disk.<sup>35</sup> Analogously, a metal wire continuously pulled through a vial of liquid has also been used.<sup>35</sup> Two examples are presented in the following that show how ions and molecular distributions at the liquid-vapor interface can be probed. These studies are important for comparison with molecular dynamics (MD) simulations and lay the experimental foundation for future investigations of interfacial reactions with environmentally relevant gases.

#### Ion distribution at the vapor-liquid water interface

To demonstrate the application of APXPS to liquid–vapor interfaces, an example of a model system for environmental chemistry is presented. Deliquesced KBr and KI salts were studied to directly probe the ion distribution at the liquid–vapor interface and as a way to validate previous MD simulations.<sup>30</sup> The relative depth distribution of the ions was probed by changing the IMFP by variation of the incident photon energy. **Fig. 10** shows that the anion-to-cation ratio is increased at the interface and approached the expected bulk value of 1 farther away from the interface, qualitatively matching predictions of MD simulations. It was found that the segregation effect depends on the size of the anion, with larger anions showing a higher propensity for the interface than smaller ones, agreeing qualitatively with MD simulations.<sup>36,37</sup>



Fig. 10 Measured anion/cation atomic ratio of a KI solution (black squares) and KBr solution (gray circles) as a function of the photoelectron kinetic energy. The solutions were formed by deliquescing crystalline KI and KBr. From Ghosal, S.; Hemminger, J. C.; Bluhm, H.; Mun, B. S.; Hebenstreit, E. L. D.; Ketteler, G.; Ogletree, D. F.; Requejo, F. G.; Salmeron, M. *Science* 2005, *307*, 563–566. Reprinted with permission from AAAS.

#### Methanol distribution at the vapor-liquid interface of aerosol particles

The same depth probing technique has been applied to a second model system, namely, a train of 110 µm droplets of a 37.5 vol.% methanol aqueous solution, which was studied with different photon energies to probe the depth distribution of methanol close to the droplet–vapor interface.<sup>34</sup> The graph in Fig. 11 plots the ratio of methanol to water (as determined from C 1s and O 1s spectra) versus the calculated IMFP and the photoelectron kinetic energy, showing that methanol is more prominent at the surface of the droplets. Again, the results were found to quantitatively agree with previous MD simulations.<sup>38</sup> Both of the presented studies on vapor–liquid interfaces lay the foundation for future studies where environmentally relevant gases could be introduced to probe interfacial chemical reactions on liquid aerosol particles.

#### Solid-Liquid Interface

Despite the importance across many disciplines, such as biophysics, corrosion science, catalysis, electrochemistry, and environmental chemistry, there is still a large gap in our knowledge about the molecular-scale processes occurring at liquid-solid interfaces, including charge and mass transport across the interface. This gap is largely due to the lack of methods to investigate directly the changes occurring on a surface in a spatially thin layer.<sup>39</sup> The challenging aspect is to enhance the signal from the thin (~nm) interface region over that from the adjacent bulk liquid and solid phases. Due to the small IMFP of electrons from the commonly used photon energies (100–1000 eV), XPS is inherently a surface-sensitive technique. To access solid–liquid interfaces, the electrons need to pass in general through at least a few nanometers of solution. We show another example where depth profiling is achieved by increasing the photon energy to the extent that the IMFP of the photoelectron is on the order of the thickness of the solution. A more complex but precise method of depth probing that utilizes the standing wave approach is presented in the final example.

#### Pt electrode species in KF solution

Simulations show that in order to probe interfaces through 10-30 nm of an aqueous solution, photons in the range of 2-7 keV, called the tender X-ray region, offer the best signal-to-noise ratio.<sup>25</sup> Combining higher energy photons with APXPS instrumentation has allowed for the characterization of a Pt working electrode in 6 M KF solution<sup>25</sup> With the attenuation of the Pt signal and a derivation of Eq. (2), the thickness of the electrolyte film under working conditions can be calculated:

$$d = -\lambda \ln\left(\frac{I_{\rm E}}{I_{\rm V} \cdot \cos\theta}\right) \tag{8}$$

where *d* is the electrolyte thickness,  $\lambda$  is the IMFP through water, *I*<sub>E</sub> is the Pt signal intensity after exposure to the electrolyte, *I*<sub>V</sub> is the Pt intensity after exposure to only water vapor, and  $\theta$  is the emission angle. At a +0.8 V potential, the electrolyte film, which was prepared by the meniscus method, was found to be about 13 nm thick.



**Fig. 11** Methanol–water ratio as a function of photoelectron kinetic energy in 110  $\mu$ m droplets of 37.5 vol.% methanol aqueous solution. At the highest kinetic energies, the expected bulk methanol–water ratio for a  $\chi_{liquid} = 0.21$  solution is recovered. However, for low kinetic energies, the ratio is enhanced in favor of methanol, indicating segregation of methanol to the vapor–liquid interface. Reproduced from Starr, D. E.; Wong, E. K.; Worsnop, D. R.; Wilson, K. R.; Bluhm, H. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3093–3098, with permission of the PCCP Owner Societies. https://doi.org/10.1039/B800717A.



**Fig. 12** (A) Pt 4f, (B) 0 1s, and (C) K 2p of Pt foil covered by a thin film of 6 M KF after cyclic voltammetry between -0.8 V and 0.8 V are applied, followed by holding the potential at -0.8 V and -0.4 V and (D) Pt 4f with potential holding at 0 V and 1.2 V during the XPS measurement. All of the potentials are reported with respect to Ag/AgCl reference electrode. Reproduced from Axnanda, S.; Crumlin, E. J.; Mao, B.; Rani, S.; Chang, R.; Karlsson, P. G.; Edwards, M. 0. M.; Lundqvist, M.; Moberg, R.; Ross, P.; Hussain, Z.; Liu, Z. *Sci. Rep.* **2015**, *5*, 09788.

Using the principles outlined in Fig. 4, core-level shifts of the signal from the working electrode and the electrolyte solution were monitored during applied potentials to ensure that the thin film and bulk solution are at the same potential. Since the working electrode is connected to ground, there is no shift in the Pt 4f core level at -0.8 V or -0.4 V (Fig. 12A). The applied potential affects the liquid film and bulk solution, causing a 0.4 eV shift between O 1s and K 2p spectra taken at -0.8 V and -0.4 V, respectively. This shift confirms that the film is in electrical contact with the bulk electrolyte and that indeed a film of electrolyte, as opposed to droplets, coats the working electrode. This study demonstrates how electrole surfaces can be characterized using APXPS and the meniscus method. The interface between the Pt electrode and the electrolyte film was probed under conditions for Pt oxidation, here at +1.2 V potential. Fig. 12D shows how the Pt 4f spectrum changes upon application of the potential. Two new oxidation states are formed, consistent in binding energy to Pt<sup>2+</sup> and Pt<sup>4+</sup>, offering further confirmation that the thin electrolyte layer is sufficient to study the species on solid electrode surfaces under real electrochemistry conditions.





**Fig. 14** Depth distributions of the chemical species in a CsOH and NaOH solution on a hematite sample as derived by fitting experimental rocking curves from an SWAPPS experiment to theory. The concentration distributions of all species are shown overplotted as curves, with the horizontal scale in normalized atomic concentrations that are unity at the maximum for each species. Reproduced from Nemšák, S.; Shavorskiy, A.; Karslioğlu, O.; Zegkinoglou, I.; Rattanachata, A.; Conlon, C. S.; Keqi, A.; Greene, P. K.; Burks, E. C.; Salmassi, F.; Gullikson, E. M.; Yang, S.-H.; Liu, K.; Bluhm, H.; Fadley, C. S. *Nat. Commun.* **2014**, *5*, 1–7, with permission from The Royal Society of Chemistry. https://doi.org/10.1039/C5FD00003C.

#### Ion distribution at the hematite-liquid water interface

While changing the photon energy offers depth resolution, the information gained in that manner is limited since the photoelectron signal is always integrated over the whole probing depth, weighted by the exponential decay of the signal with depth. To improve the precision of depth measurements, a method to probe liquid–solid interfaces with sub-nm accuracy using APXPS has been adapted from previous investigations of solid–solid interfaces.<sup>40–43</sup> The technique is based on tailoring the incident X-rays into a standing wave field that can be moved through the region of interest by half of its period by changing the angle (or the photon energy) around the Bragg condition. This results in rocking curves that show the relative intensity of the photoelectrons of interest as a function of incident angle (or photon energy), which are then compared with calculated rocking curves for different models of the chemical speciation at the interface as a function of depth. The advantage of this technique is that it uses a built-in ruler (the period of the standing wave), which can ultimately result in depth resolution on the sub-nm scale.

In a proof-of-concept experiment, the interface between a hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) surface and a solution of CsOH and NaOH was probed using standing wave ambient pressure photoemission spectroscopy (SWAPPS).<sup>44</sup> A standing wave is generated by using a substrate composed of a multilayer mirror, in this case 80 layers of 15 Å of Si and 19 Å of Mo. The material of interest, Fe<sub>2</sub>O<sub>3</sub>, is deposited on top of the mirror; the sample is schematically shown in Fig. 13A. In this study, a drop of 0.1 M CsOH/0.1 M NaOH solution was placed on the sample and dried. In the analysis chamber of the instrument, a thin solution layer was established by increasing the relative humidity to 8%. The meniscus method can also be used to generate the thin liquid layer.<sup>25,43</sup>

Core-level spectra are collected with the photon beam incidence equal to the first-order Bragg angle (about 11.5 degrees for 910 eV photons and the multilayer period of 3.4 nm). Fig. 13B shows that the O 1s spectrum contains four components: gasphase water, liquid-phase water, OH<sup>-</sup> groups, and oxide from the hematite. As the sample angle is incrementally scanned through the Bragg angle, the phase and amplitude of the standing wave are changed. Correspondingly, the intensity of the spectral components changes as a function of angle. By plotting the area of each component versus the incidence angle, a so-called rocking curve is generated; the rocking curve for each oxygen component is plotted in Fig. 13C. Similar plots are shown in Fig. 13D–H for Cs 4d, Na 2p, and C 1s (carbon is present as an impurity). Detailed analysis of the rocking curves yields the spatial distribution of each species, summarized in Fig. 14. It is found that Na<sup>+</sup> is preferentially at the hematite surface, and Cs<sup>+</sup> is closer to the vapor–liquid interface. Combining APXPS with standing wave photoemission spectroscopy generates a powerful technique to measure quantitatively the depth of chemical species at the liquid–solid interface.

**Fig. 13** (A) The sample configuration with some relevant dimensions noted of an SWAPPS experiment on a CsOH and NaOH solution on hematite. (B) An O 1s spectrum, resolved into four components by peak fitting. The component labeled OH may also contain contributions from carboxyl and bicarbonate species. (C) The rocking curves derived from the four components of (B). (D) A Cs 4d spectrum, including peak fitting. (E) Analogous overlapping Na 2p and O 2s spectra, with peak fitting. (F) The rocking curves for Cs 4d and Na 2p derived from spectra such as those in (D) and (E). (G) A typical C 1s spectrum, showing the two components, one at low binding energy (LBE) and one at higher binding energy (HBE). (H) The rocking curves for the two C 1s components. Reproduced from Nemšák, S.; Shavorskiy, A.; Karslioğlu, O.; Zegkinoglou, I.; Rattanachata, A.; Conlon, C. S.; Keqi, A.; Greene, P. K.; Burks, E. C.; Salmassi, F.; Gullikson, E. M.; Yang, S.-H.; Liu, K.; Bluhm, H.; Fadley, C. S. *Nat. Comm.* **2014**, *5*, 1–7, with permission of The Royal Society of Chemistry. https://doi.org/10.1039/C5FD00003C.

#### Summary

XPS experiments at mbar pressures and above are becoming more commonplace through the development of differentially pumped electrostatic lens systems that separate the analysis chamber and electron energy analyzer, thereby maximizing the solid angle for collection of photoelectrons and at the same time minimizing the scattering of photoelectrons by gas-phase molecules. While current pressure limits are several orders of magnitude lower than in some applications such as industrial catalysis, these experiments are a significant step toward closing the pressure gap between UHV surface science experiments and measurements under real-world conditions. Combined with other techniques, opportunities to apply APXPS to various disciplines for new chemical and electronic structure information are plentiful, as demonstrated by the examples presented.

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# Angle-Resolved Photoelectron Spectroscopy at Surfaces With High-Order Harmonic Generation

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## Glossary

**High-order harmonic generation (HHG)** Production of high multiples of incident photon energy of a driving laser field, usually in the vacuum-ultraviolet range of the electromagnetic wave spectrum.

Photoelectron spectroscopy (PES) Spectroscopy of electrons ejected from a material due to an incident photon.

#### Introduction

Photoelectron spectroscopy (PES) has provided fundamental information on physical and chemical properties at surfaces and interfaces.<sup>1,2</sup> Among the immense varieties of PES experiments, PES using high-order harmonic generation (HHG) as a light source allows spectroscopy in a laboratory with a widely tunable photon energy, variable polarization of light, and attosecond to femtosecond time resolution. Therefore, HHG-based PES has been developed over more than two decades to study dynamical processes at surfaces and interfaces.<sup>3–5</sup> In this article we provide an overview of HHG-based PES experiments on surfaces and interfaces. In Section "**Experimental Development**" we outline the key ingredients of HHG-based PES setups, and in Section "**Theory for Time-Dependent Photoemission Processes**" a short reminder of theoretical concepts with emphasis on electron dynamics is given. In Section "**Surfaces Investigated by HHG-Based PES**" we summarize and discuss state-of-the-art HHG-based PES experiments. In order to keep this article compact and straightforward to understand, we are restricted to present limited amounts of aspects in the literature. For a possible incompleteness of our perspectives we apologize to the readers and would like to refer to materials in "Further Reading" for extended reading.

#### **Experimental Development**

#### **Overview**

High-order harmonic generation (HHG) is a process to convert a number of low-energy photons to one high-energy photon in a strong laser electric field. It is not only most well known for experiments with gas media<sup>6-8</sup> but has also been extensively studied in solids<sup>9,10</sup> as well as at surfaces.<sup>11</sup> In a classical model of HHG in atoms, as illustrated in Fig. 1, a bound valence electron is ionized under the influence of a strong laser field from the distorted atomic potential by a tunneling process. This electron is then accelerated



Fig. 1 Three-step model for high-order harmonic generation (HHG) from atoms. Reprinted figure with permission from Winterfeldt, C.; Spielmann, C.; Gerber, G. Colloquium: optimal control of high-harmonic generation. *Rev. Mod. Phys.* **2008**, *80*, 117. Copyright (2017) by the American Physical Society.

in the laser electric field and recollides with its parent ion with a high kinetic energy  $(W_{kin})$ .<sup>12,13</sup> The recollision can lead to emission of light with a photon energy  $(h\nu)$  comparable to the sum of  $W_{kin}$  and the ionization potential (I<sub>P</sub>). Because  $W_{kin}$  can be high due to the ponderomotive acceleration in the laser field,  $h\nu$  can extend into the few keV regime.<sup>14–16</sup> The light generated from the single atom process in Fig. 1 adds up during its propagation in the medium<sup>17–20</sup> and is collected in far field with the corresponding vacuum-ultraviolet (VUV) optics for PES experiments.

A typical HHG setup consists of a generation chamber and a monochromator. For generation, setups with a free jet<sup>21,22</sup> or a fiber wave guide<sup>23,24</sup> are commonly employed. As a monochromator either a diffraction grating or band pass mirrors can be used, and they will be discussed in Sections "Photon Energy Range" and "Energy and Time Resolution." In addition to laboratory setups, there are also large HHG user facilities available such as the existing Artemis<sup>25</sup> and the Extreme Light Infrastructure (ELI) in the future.<sup>26</sup>

#### **Photon Energy Range**

HHG can provide photon energies beyond 1 keV.<sup>14–16</sup> For HHG-based PES experiments at surfaces as summarized in Fig. 2, lower photon energies from 10 to 100 eV have been used. The output photon energies from HHG depend on (1) the driven laser peak intensity, (2) the generation medium, as well as (3) the phase-matching conditions for the coherent sum of light emitted from single atoms. These dependencies have been thoroughly reviewed in the literature.<sup>7,8,11,27</sup> In addition, in HHG setups a metallic filter is usually used to block the driving laser field but allows the harmonics to transmit. An Al filter, for example, allows harmonics below 70 eV to pass through, whereas a Zr filter for harmonics above 70 eV.<sup>28,29</sup> These metallic filters limit the available photon energies in the PES experiments.

Moreover, in HHG-based PES experiments, a monochromator is often required for a reasonable energy resolution. Exceptions are time-resolved PES experiments using the reconstruction of attosecond beating by interference of two-photon transitions (RAB-BITT<sup>30–32</sup>), where an interference between photoexcitation by neighboring harmonics is required via an additional infrared excitation. Otherwise a monochromator, either consisting of gratings or dichroic mirrors, is used in HHG-based PES experiments. For a monochromator based on dichroic mirrors, only a fixed photon energy range can be selected.<sup>33–36</sup> In contrast, a grating monochromator allows experiments over a wide photon energy range and studies of a photon energy-dependent cross section of electronic states.<sup>37,38</sup>

#### **Energy and Time Resolution**

Conventional electron spectrometers can have a high energy resolution better than few meV<sup>39-42</sup>; therefore the energy resolution in HHG-based PES experiments is mostly limited by the bandwidth of a single harmonic. In the very earlier experiments, Mathais et al. demonstrated an energy resolution of around 0.8 eV.<sup>43</sup> Nowadays the energy resolution has become better than 150 meV.<sup>44-46</sup> As an example, photoelectron spectra from the Shockley surface state on Cu(111) are compared in Fig. 3. With a HHG-based PES setup



Fig. 2 HHG-based PES experiments at surfaces sorted according to the applied photon energy. The numbers in References are indicated.



**Fig. 3** Photoelectron spectra from the Shockley surface state on Cu(111) at  $\overline{\Gamma}$ . *Blue* circles show spectrum from Trützschler et al. measured at a repetition rate of 0.7 MHz using a time-of-flight electron spectrometer.<sup>47</sup> The *red* curve shows a Lorentzian fit with a full-width-at-half-maximum (FWHM) of 86 meV. Provided that an intrinsic FWHM of 56 meV at 300 K is taken into account,<sup>48</sup> an upper bound of light band width of 65 meV is estimated. *Gray* triangles display the spectrum from Frietsch et al. measured at 100 K using HHG at 10 kHz and a hemispherical energy analyzer.<sup>45</sup> Due to the temperature dependence of the binding energy of the surface state,<sup>49</sup> their spectrum is shifted by +50 meV for comparison.

using a time-of-flight electron spectrometer, Trützschler et al. measured a linewidth of 86 meV. Taking the intrinsic linewidth at 300 K into account,<sup>48</sup> an upper bound of the light bandwidth of 65 meV can be estimated. The improvement in bandwidth can be clearly seen in comparison to an earlier work by Frietsch et al., where a 90-meV bandwidth of light at a higher photon energy was used.<sup>45</sup>

The temporal resolution in pump-probe HHG-based PES depends on several factors: (1) transform-limited bandwidth of the harmonics, (2) pulse stretching due to the monochromator, and (3) temporal broadening in focusing the harmonics onto the sample. A temporal width determined by factor (1) is about 18 fs for an energy bandwidth  $\Delta E$  of 100 meV for a single harmonic, and it scales reciprocally with  $\Delta E$ . Factor (2) is important for grating-based monochromators and has been intensively discussed in the literature.<sup>4,50–53</sup> This temporal broadening due to diffraction is proportional to the line density of the grating, but it can be compensated by a pair of identical gratings.<sup>54</sup>

Since the harmonics are usually focused by mirrors onto the sample in PES experiments, factor (3) can only have a significant influence for spherical mirrors due to the spherical aberration. For instance, a temporal broadening for a 3-mm beam diameter and a 25-mm focal length (f) is 0.1 fs.<sup>55</sup> Because of its scaling with  $f^{-3}$ , this contribution should be negligible in practical HHG-based PES experiments with a long focal length of focusing mirrors. In addition to the temporal duration of the harmonics on the sample, the overall time resolution in the time-resolved pump-probe PES experiments includes the temporal overlap with the pump excitation (cross-correlation).

#### **Photon Flux and Repetition Rate**

The photon flux as a function of the repetition rate of existing HHG light sources has been nicely reviewed in the literature.<sup>56–58</sup> In all optical experiments, the repetition rate of HHG can go beyond 100 MHz.<sup>59</sup> However, until now, repetition rates only up to 4 MHz have been used in static HHG-based PES experiments at surfaces.<sup>60</sup> Moreover, due to the requirement of a short, intense pump laser pulse in the pump–probe experiments, only a few hundred kilohertz repetition rates were demonstrated in time-resolved PES experiment.<sup>61</sup> Since the maximum number of photoelectrons generated from each HHG light pulse is limited by space charge effects,<sup>62,63</sup> there is still potential to increase the efficiency of HHG-based, time-resolved PES experiments by increasing the repetition rate into MHz range.<sup>64,65</sup> An overview for HHG-based PES at different repetition rates can be found in a previous publication.<sup>66</sup>

#### **Band Mapping**

Due to the moderate bandwidth of harmonics, HHG-based PES has a lower energy and momentum resolution than conventional PES with discharge lamps or synchrotron radiation. Therefore, static band mapping using HHG-based PES is usually used only as a reference for time-resolved PES experiments where the momentum-resolved electron dynamics can be probed.

However, due to the widely tunable photon energy range, laboratory HHG-based PES allows to probe the crystal momentum perpendicular to the surface using photoexcitation transitions at different photon energies, which otherwise require synchrotron radiation. This has been utilized to distinguish a surface resonance on Pt(111) from bulk transitions.<sup>67</sup> Moreover, by selecting a specific photon energy, electronic states at a specific point in the three-dimensional (3D) Brillouin zone can be probed. This momentum selection is important for cases where the dynamics of excited electrons depends strongly on the 3D band dispersion of the final states.<sup>31</sup>

#### **Theory for Time-Dependent Photoemission Processes**

The photoemission process has been formulated using diverse theoretical approaches in the literature. In view of several existing reviews,  $^{68-71}$  only selected key ingredients will be discussed in the following. The photoemission intensity can be described in a simplified form<sup>69</sup>:

$$I(p_{surf}, s, E_f) \propto \left| \langle \Psi_f | \Delta | \Psi_i \rangle \right|^2 \delta \left( E_f^{total} - E_i^{total} - h\nu \right)$$
(1)

Here the quantum mechanical operator  $\Delta$  describes the interaction between the vector potential of the incident electromagnetic wave and the electron in solid via the single particle canonical momentum operator.  $p_{surf}$  is the momentum component of the photoelectron parallel to the surface, and *s* is its spin.  $\Psi_f$  and  $\Psi_i$  are the final and initial state wave functions of the whole system at energies  $E_f^{total}$  and  $E_i^{total}$ .  $\Psi_f$  includes the photoelectron in vacuum and the solid left behind with one photo-hole, whereas  $\Psi_i$  represents the system in the ground state before the photoexcitation.

If the lifetime of the photo-hole is neglected and the electrons in the solid are assumed to be independent from each other, Eq. (1) can be further simplified to a summation over all initial states of occupied single electron wave function and one electron final states that include the transport of the photoelectron away from the system.<sup>72</sup> For a realistic consideration on the transport, scattering processes have to be taken into account.<sup>73</sup> If the photoelectron and the rest of the system with a photo-hole is considered separately in the so-called sudden approximation,<sup>71,74,75</sup> the photoemission intensity can be rewritten as:

$$I(p_{surf}, s, E_f) \propto \sum_{i} \left| \left\langle \psi_f | \Delta | \psi_i \right\rangle \right|^2 A(E_i = E_f - h\nu)$$
<sup>(2)</sup>

Here  $A(E_i = E_f - h\nu)$  is the spectral function of the system with one photo-hole at the energy  $E_i$ . It describes the probability to create one photo-hole by the projection of the initial ground state of the whole system  $\Psi_i$  to the final state with one photo-hole. The summation i runs through all the occupied one-electron initial states  $\psi_i$ , and  $\psi_f$  is the one-electron final state at the energy  $E_f$ . By analyzing the photoelectron with the energy  $E_f$ , information regarding the system with one photo-hole as represented by  $A(E_i = E_f - h\nu)$  can be obtained.

In reality, the interaction between electrons in solids needs to be taken into account.<sup>76,77</sup> Furthermore, the time-dependent interaction between the photoelectron and the photo-hole as well as the lifetime of the photo-hole can have significant effects on the line shape of photoelectron spectra.<sup>78–80</sup> A more direct measurement of these dynamical processes is the time-resolved pump-probe PES experiments using high-order harmonics, whose theoretical description includes: (i) the macroscopic optical response of surfaces with the light field at the femtosecond time scale; (ii) the dynamics in the creation of the photoelectron; (iii) the microscopic time evolution of the system on the time scale of the photo-hole lifetime, within which the photoelectron can interact with the hole strongly; and (iv) the time-dependent propagation of the photoelectron away from the system. These aspects are summarized in **Table 1**, and a more thorough discussion can be found in the review by Pazourek et al.<sup>101</sup>

#### Surfaces Investigated by HHG-Based PES

In the following sections, we summarize HHG-based PES experiments at surfaces in the literature and categorize them according to the systems investigated.

Table 1	Overview of the	eoretical calculat	ions for time-	resolved PES
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Theoretical description	Reference
Optical response at surfaces	81–85
Dynamics in the creation of photoelectrons	85–90
Photoelectron interacting with photo-hole/other electrons	88,90–95
Propagation of photoelectron	83-85,93,96-100

Table 2         Summary of HHG-based PES on adsorbate and molecular la	ayers
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Adsorbate system	Electronic state	Time scale (fs)	Reference
 CO/Pt(111)	1π, 4σ, 5σ		37,102–104
l <sub>2</sub> /Cu	4d <sub>3/2</sub> 4d <sub>5/2</sub>		105
lodo-phenylphenol/Si(100)	$  4d_{3/2}   4d_{5/2}$	$0.5{\sim}5{\times}10^4$	106
Iodobenzoyloxy-functionalized resorc[4]arenes/Au/Ti/Si	$  4d_{3/2}   4d_{5/2}$		107
In <sub>2l6</sub> /Ag/Si	4d <sub>3/2</sub> 4d <sub>5/2</sub>		108
0 <sub>2</sub> /Pt(111)	$1\pi_a^*$	$550 \pm 140 {\sim} 5 {\times} 10^3$	109–111
0/Ni(111)	0 <i>2p</i>		103
W(CO) <sub>6</sub> /Śi	4σ, 4π, 5σ		105
Xe/Pt(111)	Xe 4d	7.1±1.1	112
Xe/Re(0001)	Xe 4d, Xe 5p		113

#### **Adsorbates**

There are only a few adsorbate systems that have been studied by HHG-based PES (Table 2). Due to the high photon energies from HHG, photoelectrons in core levels of atoms and molecules can be excited. Therefore, photoelectrons from the adsorbates can be clearly identified apart from the substrate signals. Moreover, the energy of core levels depends sensitively on the environment, and the resultant chemical shifts provide information regarding the local structure at the surface. With pump–probe HHG-based PES, this information can be used to characterize optically excited relaxation pathways of surface chemistry on the femtosecond to picosecond time scales.<sup>106,109</sup>

## **Two-Dimensional and Layered Materials**

The high photon energies from HHG also allow access to electronic states in the full Brillouin zone, in contrast to purely laser-based PES. Since the K points in the Brillouin zone of graphene are beyond the momentum range probed by PES using conventional ultraviolet laser sources, HHG-based time-resolved PES (tr-PES) gives a unique opportunity to study electron dynamics in graphene.<sup>114–120</sup> These studies are summarized in Table 3. Very similarly, HHG-based tr-PES allows to study electron dynamics at  $\Gamma$ , M, and K points in the Brillouin zone of other two-dimensional (2D) materials such as 1 T-TiSe<sub>2</sub> and 1 T-TaS<sub>2</sub>. These valuable investigations essentially elucidate different mechanisms behind the electronically driven metal-to-insulator phase transitions.<sup>127–129</sup> In Table 4 we summarize the HHG-based tr-PES experiments on these 2D materials.

#### Metals

With HHG-based tr-PES, even intriguing electron dynamics can be found in conventional metals. In **Table 5** HHG-based PES studies on metals are summarized. By using the high photon energies of HHG, the attosecond time delays between photoemission processes from core and valence electrons in bulk Cu, Ni, and  $W^{30,31,159}$  as well as in Mg/W(110) films<sup>151–153</sup> have been identified. The high photon energy makes it also possible to study spin dynamics of shallow core levels in rare earth ferromagnets Gd(0001) and Tb(0001). In these materials, it was discovered that the exchange splitting between electronic states can evolve transiently depending on their spatial localization and orbital angular momentum.<sup>149,150,158</sup>

Table 3	Summary of HHG-based tr-PES on graphene		
Graphene	Electronic state (hv <sub>pump</sub> )	Time scale (fs)	Reference
<i>p</i> -doped	$E_{ m F}$ near K (0.1 $\sim$ 0.3 eV)	135±35	118
	$E_{ m F}$ near K (0.30 $\sim$ 0.95 eV)	$13\pm4{\sim}860\pm50$	117
	$E_{\rm F}$ near K ( $\sim$ 0.95 eV)	$150 {\sim} 3 {\times} 10^3$	116,120,121
	$E_{\rm F}$ near K ( $\sim$ 1.6 eV)	$25\!\sim\!2.8\! imes\!10^3$	114,115,119,122
<i>n</i> -doped	$E_{\rm F}$ near K (0.1 $\sim$ 0.4 eV)	160~280	123
	E <sub>F</sub> near K (1.6 eV)	$87\!\sim\!490$	114
	<i>E</i> <sub>F</sub> near K (3.1 eV)	≈ 400	124
Bilayer	$E_{\rm F}$ near K (0.1 $\sim$ 0.3 eV)	$150\pm\!20\!\sim\!2.8\pm\!0.6\!\times\!10^3$	118
	<i>E</i> <sub>F</sub> near K (0.8 eV)	$220\pm 50{\sim}1.8\pm 0.3{\times}10^3$	116
	E <sub>F</sub> near K (1.6 eV)	$650{\sim}10^4$	125
On Ni(111)	$\sigma, \pi$ bands		38
	$E_{ m F}+0.4{\sim}2$ eV		126

 $h\nu_{pump}$ , excitation photon energy in an optical pump, HHG-probe experiment;  $E_{F_7}$  Fermi level.

System	Electronic state	Time scale (fs)	Reference
1 T-TiSe <sub>2</sub>	Se 3d <sub>3/2</sub> , Se 3d <sub>5/2</sub>	$100 \sim 1.2 \times 10^{3}$	130
-	Se 4p band	$51\pm15$	44
	Se 4p band at M	20~110	127-129,131
	Ti <i>3d</i> band	$31\pm3$	44
	Ti <i>3d</i> band near M	<200	127
	Ti <i>3d</i> band along ΓK	$11\pm10$	132
	Ti 3d band along $\Gamma M$	$81\pm 6$	132
	VBM and CBM near M	$70\!\sim\!7\! imes\!10^3$	133
1 T-TaS <sub>2</sub>	Ta 4f <sub>7/2</sub>	$460\pm50{\sim}3{\times}10^3$	134
-	Ta <i>5d</i> bands near $\Gamma$	$30\pm 300$	135,136
	Ta 5d band at $\Gamma$ (Mott gap)	<20	128
	Ta <i>5d</i> band near M (Peierls gap)	$226 \pm 38$	128
Graphite	<i>E</i> <sub>F</sub> near H	$100 {\sim} 10^4$	137
1 T-TaSe <sub>2</sub>	Ta <i>5d</i> bands	$<\!40\!\sim\!280$	136
n-Doped Bi <sub>2</sub> Se <sub>3</sub>	Near CBM at $\Gamma$	160	138
MoS <sub>2</sub>	VBM, CBM along $\Sigma K$	$\sim$ 30	61
MoS <sub>2</sub> /Au(111)	VBM, CBM at K	$50\pm20$	139
MoS <sub>2</sub> /graphene	VBM, CBM at K	$40{\sim}5{\times}10^4$	140
2H-MoS <sub>2</sub>	VBM, CBM	$1 \sim 3 \times 10^{3}$	141
WS <sub>2</sub> /Ag(111)	VBM, CBM near K	$100\pm50$	142
2H-WSe <sub>2</sub>	VBM, CBM	$0.1{\sim}1{\times}10^4$	141,143

Table 4	Summary of	HHG-based	tr-PES	on two	-dimensional	(2D)	materials	besides	graphene

VBM, valence band maximum; CBM, conduction band minimum; E<sub>F</sub>, Fermi level.

#### Semiconductors

Electron dynamics in semiconductors has been studied since the 1980s using conventional tr-PES experiments with low photon energies. Nevertheless, these earlier experiments could only focus on the electronic states in the proximity of the band gap. With HHG-based PES, as one can clearly see in **Table 6**, shallow core levels at larger binding energies, such as the Ga and As *3d* states, can be investigated, and it paves the way toward an element-specific identification of electron dynamics in compound semiconductors.<sup>164,168</sup>

Table 5	Summary of HHG-based PES on metals

Metal	Electronic state	Time scale (fs)	Reference
Ag(001)	4d, 5sp bands		66,144
Ag(111)	4d PE delay	$-0.2\!\sim\!0.2$	145
Au(111)	<i>5d</i> PE delay	0~0.2	145
Au/Si(001)	Valence band	$\sim$ 0.07	146
Bi(001)	5d <sub>3/2</sub> , 5d <sub>5/2</sub>		147
Co/Cu(001)	Spin-resolved 3d		148
Cu(001)	3d space charge	$1{\sim}2{\times}10^6$	148
Cu(111)	Shockley surface state		45,60
	3d, 4sp bands		43
	<i>3d</i> PE delay	$-0.3\!\sim\!0.2$	30
Gd/W(110)	Exchange-split Gd 5d	$800\pm100$	149,150
	Magnetic dichroism at Gd 4f	$14\pm3\times10^3$	150
Mg/W(110)	Mg 2p versus conduction band PE delay	$0\!\sim\!0.06$	151,152
	Mg 2p versus W 4f PE delay	0.08~0.22	151
	Mg 2p versus plasmon satellite PE delay	$0.06 \pm 0.01$	153
Ni(111)	3d bands		103
· · ·	3d $\Lambda_1$ versus $\Lambda_3$ PE delay	0~0.25	31
Pb	5d <sub>3/2</sub> , 5d <sub>5/2</sub>		108
Pt(110)	Near $E_{\rm F}$	<100	154
Pt(111)	5d bands		37,67,102,103,112
( )	LAPE of PE from valence bands		155–157
	Near <i>E</i> ⊧	$260\pm80$	156
Tb/W(110)	Exchange-split Tb 5d	$300{\sim}500$	158
W(110)	$4f_{3/2}, 4f_{5/2}$		105
. ,	4f versus conduction band PE delay	$0.11\pm0.07$	159

PE, photoemission; LAPE, laser-assisted photoemission.

Semiconductor	Electronic state	Time scale (fs)	Reference	
10 nm Alg film	LUMO	$\sim 4 \times 10^5$	160	
As-terminated Ge(111)	Unoccupied surface resonance at $\overline{M}$	$400 \sim 2 \times 10^{3}$	161	
	As-derived surface state at $\overline{\Gamma}$	$1.5  imes 10^3 \! \sim \! 2 \!  imes 10^5$	162,163	
$Ga(2 \times 2)/Si(001)$	Ga <i>3d</i>	$< 1 \times 10^{5}$	164	
GaAs(001)	Ga <i>3d</i> , As <i>3d</i>		105	
aAs(UUT)	Valence band		165	
	Ga <i>3d</i>	$> 1.5 \times 10^4, < 10^6$	166,167	
<i>p</i> -doped GaAs(001)	Ga <i>3d</i>	$500 \sim 1.5 \times 10^4$	168	
GaAs(110)	Ga <i>3d</i>		108	
Ge(110)	Valence band	$21\pm2\times10^3$	165	
PCPDTBT polymer	$E_{\rm F}{-}0.2$ to $E_{\rm F}{+}2.3$ eV	$45{\sim}1.1\pm0.1{\times}10^3$	169	

Table 6	Electron c	ivnamics i	in	semiconductors	studied	bv	HHG-based PE	S
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Alg, tris (8-hydroxy quinoline) aluminum; LUMO, lowest unoccupied molecular orbital.

lable 7	Summary for	HHG-based	tr-PES	on surfaces	of oxide	s and	strongly	correlated	materials
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Oxide	Electronic state	Time scale (fs)	Reference	
BaFe2As2	Near E <sub>F</sub>	$60 \sim 1 \times 10^{3}$	170	
$Bi_2Sr_2CaCu_2O_{8+\delta}$	Nodal region	640	171	
	Off-nodal region	150	171	
	Antinodal region	$300 \sim 1.85 \times 10^{3}$	171	
K <sub>0.3</sub> MO <sub>3</sub>	Near E <sub>F</sub>	$0.6 \sim 1.3 \times 10^3$	172	
HfO <sub>2</sub> /Si(001)	Near E <sub>F</sub>	$> 2 \times 10^{5}$	173	
$\alpha$ -SiO <sub>2</sub> (Quartz)	30 eV above CBM	$\sim - 4 \times 10^4$	174,175	
U0 <sub>2</sub>	U <i>5f</i> upper Hubbard band	$5 \sim 8 \times 10^{3}$	176	
URu <sub>2</sub> Si <sub>2</sub>	Near E <sub>F</sub>	$20 \sim 301$	177	
VO <sub>2</sub> film	V 3p	$\sim$ 500	178	
15 nm VO <sub>2</sub> /TiO <sub>2</sub> (001)	Near <i>E</i> <sub>F</sub>	$3 \times 10^3$	179	
20 nm WO <sub>3</sub> /Si(001)	Valence band	0.1	146	

E<sub>F</sub>, Fermi level; CBM, conduction band minimum.

#### **Oxides and Strongly Correlated Materials**

In strong contrast to the well-established studies on 2D materials, metals, and semiconductors, only few HHG-based tr-PES experiments have been realized on oxides as listed in Table 7. The superconducting electronic states in a high-T<sub>C</sub> superconductor  $Bi_2Sr_2CaCu_2O_{8+\delta}$  have been characterized in the time domain.<sup>171</sup> In addition, the strongly correlated oxide UO<sub>2</sub> was investigated, and the dynamics of correlated electrons in the Hubbard bands was revealed.<sup>176</sup>

## Summary

In this article we summarize the literature reporting photoelectron spectroscopy (PES) at surfaces using light sources that are based on high-order harmonic generation (HHG). These HHG-based PES experiments have established studies of surfaces dynamics and provide valuable information regarding relevant physical and chemical properties on the picosecond to femtosecond time scales. On the surfaces with adsorbates, or that of the two-dimensional materials, metals, semiconductors, and oxides, HHG-based PES reveals pathways of electronic excitation as well as relaxation, which can depend sensitively on the electron momentum coordinates. This information enables fundamental understanding of surfaces in the time domain, which in the future may pave a way toward ultrafast manipulation of the properties of solids at surfaces and interfaces.

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## Atomic Scale STM Imaging of Alloy Surfaces With Chemical Resolution

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## Nomenclature

## **Symbols and Units**

- *A* Pre-exponential factor taking into account the LDOS of the tip and surface
- *d* Distance between tip and sample
- *I*<sub>T</sub> Tunneling current
- $\phi$  Tunneling barrier height
- *U*<sub>T</sub> Tunneling voltage

#### **Abbreviations and Acronyms**

- CCI Constant current imaging
- CHI Constant height imaging
- **DFT** Density functional theory
- ECI Effective cluster interactions
- EPI Effective pair interactions
- FIM Field ion microscopy
- ISS Ion scattering spectroscopy
- LDOS Local density of states
- LEED Low-energy electron diffraction
- LEISS Low-energy ion scattering spectroscopy
- LRO Long-range order
- ML Monolayer
- SRO Short-range order
- STM Scanning tunneling microscopy
- UHV Ultrahigh vacuum
- **XPS** X-ray photoemission spectroscopy
- XRD X-ray diffraction

#### Introduction

Real space imaging of surface structures on an atomic scale level and the differentiation between different types of atoms is of fundamental interest to understand material properties, such as structure formation, electronic, magnetic, and chemical properties, as well as the interaction of the surface with adsorbed atoms or molecules in relation to, e.g., electro- or heterogeneous catalysis. Historically, most surface science techniques employed, such as low-energy electron diffraction (LEED),<sup>1</sup> gracing incidence X-ray diffraction (XRD),<sup>2</sup> X-ray photoemission spectroscopy (XPS),<sup>3</sup> low-energy ion spectroscopy (LEIS),<sup>4</sup> or ion scattering spectroscopy (ISS<sup>4</sup>), allowed for investigating the composition as well as the structural properties of extended surfaces. Specific surface order on an atomic scale level was and is, however, only accessible if well-ordered structures are present on large areas, and thus the atomic structure of local disorder or completely disorder surfaces are not accessible. The first real space technique for imaging individual atoms and differentiate between different atoms on a surface was achieved by field ion microscopy (FIM).<sup>5–8</sup> The application of this technique is, however, limited to a small number of materials and can only be applied to very sharp tips with a few nanometers in diameter. Real space imaging of large areas of extended surfaces was finally achieved by scanning tunneling microscopy (STM), which was invented by G. Binnig and H. Rohrer in 1981.<sup>9</sup> They were awarded the Physics Nobel Prize in 1986,<sup>10</sup> since it presents until today one of the most important techniques for the characterization of nanostructured surfaces, adsorbate structures, and surface dynamics both on the macroscopic scale and, especially, on an atomic scale. Furthermore, the technique can be operated in any environment, e.g., high pressures, (ultrahigh) vacuum (UHV), and liquids, which allows for comparison of the results with more complex systems investigated under realistic conditions.<sup>10-14</sup>

In this work first the fundamental concept of the STM is introduced, including experimental aspects and theoretical concepts. Next, the prerequisites for atomic scale imaging and the underlying processes that allow for discrimination between different types of atoms via chemical resolution or chemical contrast are discussed based on experimental and theoretical findings. The relevance of STM imaging with chemical resolution is highlighted on some historical and recent studies with respect to structure formation and (electro-)catalysis on alloy surfaces. Last we discuss some experimental limitations for certain systems where care has to be taken in the interpretation of STM images in order to prevent erroneous conclusions.

#### **Experimental and Theoretical Background**

For STM imaging an atomically sharp conducting tip, e.g., W or Pt–Ir, is approached in the vicinity of a conducting surface, typically in the range of 0.3–1 nm, until their quantum mechanical wave functions overlap, which is illustrated in Fig. 1A and B for a retracted and an approached tip, respectively.<sup>15</sup> When a positive bias is applied on the sample the electrons can tunnel from the tip to the sample, and vice versa, as shown in Fig. 1C and D, respectively.<sup>15</sup> The tunneling current (I<sub>T</sub>) is in general in the range of a few nanoamperes and depends exponentially on the distance (*d*) between the tip and surface, which can be expressed in a simple approximation by  $I_T = A \cdot \exp(\sqrt{\phi} \cdot d)$ , where *A* is a pre-exponential factor taking into account the density of states of the tip and the surface and  $\phi$  being the average tunneling barrier height, which is related to the work functions of the involved metals. In order to obtain a map of the topography of the surface, the tip is scanned in *x* and *y* direction on the surface. The motion is performed by piezoelectric elements attached either to the tip or the sample (stage), depending on the actual design of the STM. The topography of the surface can be obtained by two different modes of operation, namely, constant height imaging (CHI) and constant current imaging (CCI). In CHI, the height of the tip above the surface is kept constant and the change in current is recorded, which is used to generate



Fig. 1 Energy level diagrams for sample and tip. (A) Independent sample and tip. (B) Sample and tip, separated by a small vacuum gap. (C) Positive sample bias: electrons tunnel from tip to sample. (D) Negative sample bias: electrons tunnel from sample into tip. Reprinted with permission from Hamers, R. Atomic-Resolution Surface Spectroscopy With the Scanning Tunneling Microscope. *Ann. Rev. Phys. Chem.* **1989**, *40*, 531–559. Copyright 1989, Annual Reviews Inc.



Fig. 2 Schematic illustration of the topography (line scan in one dimension) of a surface imaged with (A) an ideal atomically sharp tip, (B) a broad tip, and (C) a multitip.

a map of the topography of the surface. The most common approach is the CCI mode, where the current between tip and the surface is kept constant by applying a fixed voltage between tip and surface, and thus the change in height in the sub-Ångström range between tip and sample is measured from the elongation or retraction of the *z*-piezoelectric element. A resulting line scan in one dimension is schematically illustrated in Fig. 2A. The recorded map of the topography of the surface is finally a result of the electronic density of states at the Fermi level of the elements, i.e., the local density of states (LDOS), present on the surface as well as the geometric structures resulting from the variation in size of the different elements present on the surface or the actual height differences resulting from atomic steps or particles.

The resulting STM images can to some extent be modeled by computational approaches. The simple approximation introduced earlier,  $I_T = A \cdot \exp(\sqrt{\phi} \cdot d)$ , can be derived from a simple one-dimensional quantum mechanical model, by solving the Schrödinger equation for an electron tunneling through a finite energy barrier, defined by the work function of the tip and the surface as well as the distance between both.<sup>16</sup> A more realistic approach allowing for a more quantitative analysis of STM images is described by the Tersoff–Hamann model.<sup>17,18</sup> In this model more realistic three-dimensional wave functions are taken into account, with the assumptions that the tip has a spherical apex which is approximated by a *s*-wave function and interactions between the tip and the surface are neglected. Further below we will show that with these simplifications, in some cases the STM images of surfaces obtained with chemical resolution cannot be rationalized and described by the Tersoff–Hamann theory. Nevertheless, this model is nowadays the standard model, serving as a basis for further refined models, including additional effects resulting from different tip states and tip surface interactions.<sup>19</sup>

#### **STM Imaging With Atomic and Chemical Resolution**

The breakthrough of the STM was finally marked by the capability of the technique to image surfaces on an atomic scale level, which lead to the award of the Nobel Prize in 1986 to Binnig and Rohrer.<sup>10</sup> A few years later in 1989 Hamers reported for the first time on STM imaging with chemical resolution on Si(111) surfaces modified by submonolayers of Al<sup>20</sup> and the pioneer study for bimetallic surfaces has been presented by Schmid, Stadler, and Varga in 1993 for bulk  $Pt_{25}Ni_{75}(111)$  alloy surfaces,<sup>21</sup> shown in Fig. 3A and B, respectively. Imaging surfaces on atomic scale level with STM is in principle possible in almost any environment (vacuum, liquids, gases, etc.).<sup>10–14</sup> A prerequisite is, however, that a planar and perfectly clean surface is available. Therefore most studies on STM imaging with the intention of imaging the surface with chemical resolution are performed under UHV conditions and only few reports exist that show chemical resolution in other environments, such as in electrolyte.<sup>22</sup> In addition, it has been reported in the literature that the image resolution strongly depends on the shape and the state of the STM tip, which shall be elaborated on in more detail in the following paragraphs.

#### Macroscopic Tip Effects

Considering that an almost planar surface is mapped in CHI mode, it was shown further above in Fig. 2A how an ideal atomically sharp tip images a surface in one dimension. The recorded image (or line scan) is a perfect representation of the atomic structures on the surface, elucidating the location of individual atoms and other structural properties, such as atomic steps and holes. In the case where the apex of the tip is broad, i.e., consists of more than one atom, the recorded image is a superposition of the surface topography as well as the shape of the tip which is illustrated in Fig. 2B. This will consequently lead to a broadening of the structures



**Fig. 3** STM images of 1/6 ML Al/Si(111) at (A) positive (+2 V) and (B) negative (-2 V) sample bias. The images cover exactly the same region of the surface.<sup>20</sup> (C) STM constant current topograph of the (111) face of a Pt<sub>25</sub>Ni<sub>75</sub> single crystal. Tunneling and sample treatment: 5 mV/16 nA, less cleaning. 125 Å × 100 Å. Image has been high-pass filtered and distorted to correct for drift and creep of the STM. (A) reprinted with permission from Hamers, R. Characterization of Localized Atomic Surface Defects by Tunneling Microscopy and Spectroscopy. *J. Vac. Sci. Technol. B* **1988**, *6*, 1462–1467. Copyright 1988, American Vacuum Society. (B) Reprinted with permission from Schmid, M.; Stadler, H.; Varga, P. Direct Observation of Surface Chemical Order by Scanning Tunneling Microscopy. *Phys. Rev. Lett.* **1993**, *70*, 1441–1444. Copyright 1993, American Physical Society.

present on the surface in the STM image. Evaluating such STM images would, for example, lead to an overestimation of the size of the imaged structures. This phenomenon is commonly known as tip broadening or tip convolution.<sup>23,24</sup> More complex to interpret STM images are obtained when the apex of the tip is not smooth, but consists of multiple tip apexes of different elongation and separation, as demonstrated in Fig. 2C.

In large-scale STM images broad and multitips can be discriminated from the shape of the structures observed in the STM image. These STM images can to some extend still be evaluated, and the respective effects can be accounted for in posttreatment of the STM images. In atomic scale STM imaging, however, these effects cannot be accounted for and thus recording of reasonable atomic resolution STM images becomes basically impossible if the tip is not atomically sharp.

#### Local Tip Effects

In principle three reasons have been proposed in the literature to rationalize the chemical resolution obtained and observed by STM imaging on atomic scale level, namely, (i) a topographic effect, (ii) an electronic effect, or (ii) tip surface interactions. A topographic effect is observed when the atoms in the alloy surface show a significant difference in size, as in the case of Pb in Cu(111), where Pb is 37% larger compared to the Cu atoms.<sup>25</sup> The resulting height difference between the atoms can easily be imaged with the STM on an atomic scale level which leads to the chemical contrast observed on these surfaces. This explanation fails, however, for most transition metal alloys, where the atomic radii are very similar. In that case, the resulting chemical resolution is attributed to an electronic effect, where the LDOS near the Fermi edge of the individual atoms differ significantly, as shown, for example, for bulk AgPd(111),<sup>26</sup> AgPd(100),<sup>26</sup> and Au<sub>3</sub>Pd(100)<sup>27</sup> surfaces. In order to rationalize that the electronic effect is actually responsible for the observed chemical resolution in the STM image, ab initio calculations of the LDOS with density functional theory (DFT)<sup>28,29</sup> in frame of the Tersoff-Hamann theory have to be performed. There exist, however, also a number of systems where this explanation is not sufficient. Thus when both topographic and electronic effects are not the source of the observed chemical contrast,<sup>21,30,31</sup> tip surface interactions have to be considered which are not covered by the Tersoff–Hamann theory. These interactions depend on the investigated system and especially on the actual state of the tip apex, i.e., the tip material, guest metals, or adsorbates located at the tip apex, which can furthermore cause deformation of the tip apex or formation of tip-induced states.<sup>32–34</sup> Experimentally there exists no general recipe, describing unambiguously how to obtain a sharp tip required for atomic and chemical resolution in STM imaging. The outcome is rather based on the investigated system, experimental expertise, and to large extends on patience.

#### **Alloyed Surfaces**

In the following paragraphs we discuss the relevance of STM imaging with chemical resolution on alloyed surfaces with respect to structural and (electro-)chemical properties. Alloyed surfaces can be separated in three categories: (i) alloy surfaces, which refer to the topmost layer of a bulk alloy; (ii) surface alloys, which refer to a single alloy layer supported on a monometallic substrate; and (iii) near-surface alloys, in which an alloy structure is situated below the surface, which in turn is supported on a monometallic bulk. The latter will not be discussed, since other techniques than STM are required to elucidate the alloy structure in the near-surface region of the crystal. Alloy surfaces are prepared from a bulk alloy with specific composition and structure which are sputtered (removal of surface atoms by Ions) and subsequently annealed at specific temperatures and varying time which leads to smoothing of the surface as well as alloy surface formation. Surface alloys consist of a composition AB and BC atoms supported on a monometallic substrate metal A. In general AB alloys on a support metal A are prepared by deposition of a metal B on a substrate metal A with subsequent annealing to elevated temperatures, schematically illustrated in the top row of Fig. 4. For BC alloy formation on A,



Fig. 4 Schematic illustration for the preparation of AB and BC surface alloys on a substrate metal A.

a metal C is deposited on the previously described metal B modified metal A substrate, followed by an annealing step, schematically illustrated in the bottom row of Fig. 4.

#### Structural Properties of Alloyed Surfaces

Investigation of alloy surfaces with STM with chemical resolution is of fundamental interest to determine the actual order of surface atoms and evaluate the interaction between the atoms on the surface. This is relevant since it has been shown that surface structures can be significantly different than those observed in the bulk of the material.<sup>35</sup> The main reason is that the atoms on the surface have lower coordination number than those in the bulk, which is energetically unfavorable. This can be compensated for by accumulation or incorporation of atoms with lower surface free energy on the surface or by incorporation of larger atoms in the surface to reduce surface strain. The structures and composition in the alloy surfaces finally depend strongly on the annealing temperature and time, which determine the segregation of the metals from the bulk to the surface or vice versa, which in turn depend on the bulk composition and structure of the alloy material. For example, for the  $Pt_{25}Ni_{75}(111)$  bulk alloy shown in Fig. 3B, 5 min annealing at 780 K leads to an accumulation of Pt on the surface, resulting in a final surface composition of 50:50 (Pt:Ni), caused by the preferential segregation of Pt to the surface.<sup>21</sup>

Structure formation in surface alloys depends on the same energetic reasons as mentioned earlier for bulk alloys. In this case, however, it is much simpler to tune the composition of the surface by the amount of guest metals initially deposited on the substrate metal. The exact amount of deposited material can be determined from large-scale STM images. During the annealing procedure, required to form the surface alloy, the composition of the surface remains constant, unless the temperature is too high which could cause bulk segregation or desorption of the guest metals from the surface. With this approach it is even possible to form surface alloys which would not be miscible in the bulk. The surface atomic order depends primarily on the interaction of the metals in the surface alloy. **Fig. 5** shows a set of STM images of surface alloys with different order of the atoms in the topmost layer of the crystal. By visual inspection of the STM images it is evident that  $Au_{44}Pt_{56}/Pt(111)$  surface alloys in **Fig. 5A** phase separate, <sup>36</sup> Pt<sub>53</sub>Ru<sub>47</sub>/Ru(0001) surface alloys in **Fig. 5B** show random distribution of the atoms, <sup>37</sup> and Cu<sub>48</sub>Pd<sub>52</sub>/Ru(0001) surface alloys in **Fig. 5C** show a tendency for ordering, also referred to disperse distribution of the atoms. <sup>38</sup>

Even though no long-range order (LRO) of the atoms is observed in the atomically resolved STM images with chemical resolution, both on the alloy surfaces and surface alloys presented in **Fig. 3B** and **Fig. 5**, respectively, local short-range order (SRO) can be determined from Warren–Cowley SRO parameters,<sup>39–41</sup> historically used to determine the order of bulk alloys. These SRO parameters can be used as input parameters for further kinetic Monte-Carlo simulations to determine the effective pair or cluster interactions (EPI or ECI) of the atoms involved, which allow to derive the surface mixing energy and finally allows for the construction of surface phase diagrams. The mixing and segregation energies can also be derived from DFT calculations.<sup>42</sup> These allow for the prediction of surface order in surface alloys. The predicted tendencies from DFT are in very good agreement with the order of the atoms observed experimentally with STM in the surface alloy systems presented in **Fig. 5**. Nevertheless there exist also a few examples where DFT calculations fail to predict the surface structures, and thus proof by STM imaging is always mandatory in order



**Fig. 5** Atomically resolved STM images of surface alloys showing (A) phase separation for  $Au_{44}Pt_{56}/Pt(111)^{36}$  (10 nm × 10 nm), (B) random distribution in  $Pt_{53}Ru_{47}/Ru(0001)^{37}$  (7 nm x 7 nm), and (C) disperse distribution in  $Cu_{48}Pd_{52}/Ru(0001)^{38}$  (10 nm × 10 nm).

not to draw any erroneous conclusions.<sup>43</sup> This is especially important, when a link between the observed structures and the chemical properties of a surface is anticipated, as discussed in the following paragraphs.

#### **Chemical Properties of Alloyed Surfaces**

Over the last decades, atomic scale STM imaging played a crucial role in the field of (electro-)catalysis. The reason is that the activity of a complex three-dimensional catalyst depends on the structure and composition of their surface and their bulk, where the catalytic reaction takes place on the catalyst surface. In these complex systems the actual surface structure, especially on an atomic scale level is, however, not accessible. Thus fundamental studies on appropriate planar model systems with STM play a crucial role in elucidating the effect of specific surface structures on the processes occurring on the surface. The results can finally be used to rationalize the processes occurring at the surface of the complex systems. Before the invention of the STM in 1981<sup>10</sup> and the first STM images with chemical resolution were obtained on bimetallic surfaces in 1993,<sup>21</sup> many fundamental concepts that explain the catalytic activity of bimetallic surfaces have been elucidated from numerous surface science techniques. The most notable effects are the atomic ligand<sup>22,44-46</sup> and ensemble effect,<sup>22,47</sup> which can be directly observed in the STM images with chemical resolution.

The ligand effect is referred to the change in the LDOS of a guest metal atom in the surface which is surrounded by a certain number of host metal atoms or vice versa, which changes the binding energy of adsorbates on the respective sites. The ligand effect is schematically illustrated in **Fig. 6A**. Such a change in the LDOS of individual atoms can be imaged with STM with chemical resolution, <sup>22,44,45</sup> which is illustrated in **Fig. 7** on a Ni(111) surface with 2% of a monolayer of Au atoms.<sup>44</sup> The change in the LDOS of the Ni atoms surrounding the Au (back dots) is apparent by its brighter appearance compared to the rest of the surface. This study revealed that Au alloying in Ni significantly increases the stability of the catalyst, or, in other words, almost suppresses the deactivation of the catalyst, relevant for the steam reforming process.<sup>44</sup> The ligand effect can, furthermore, also be imaged by monitoring with STM with chemical resolution the actual adsorption site that an adsorbate occupies on the surface, which has been demonstrated for the first time for CO adsorption on PtCo(111) alloy surfaces.<sup>45</sup>

The ensemble effect refers to an adsorption site, which consists of a specific mono- or bimetallic ensemble of atoms, that an adsorbate requires to adsorb on the surface, as demonstrated schematically in Fig. 6B for 2- and 3-fold ensembles. For the surface



Fig. 6 Schematic illustration of the ligand and ensemble effect, where the adsorption of a probe molecule/adsorbate (*red circle*) is located (A) on an atom surrounded by an increasing number of guest atoms and on (B) pure and mixed 2- and 3-fold ensembles, respectively.



**Fig. 7** STM image of a Ni(111) surface with 2% of a monolayer Au. The Au atoms appear black in the images. The Ni atoms next to the Au atoms appear brighter because of a charge in geometry and electronic structure, indicating that the chemical activity of the Ni atoms may be modified by nearest-neighbor Au atoms. Reprinted with permission from Besenbacher, F.; Chorkendorff, I.; Clausen, BS.; Hammer, B.; Molenbroek, A. M.; Nørskov, J. K.; Stensgaard, I. Design of a Surface Alloy Catalyst for Steam Reforming. *Science* **1998**, *279*, 1913–1915. Copyright 1998, Science.

alloy systems shown in Fig. 5A-C and others, the exact distribution of different ensembles has been statistically evaluated from a systematic study of the surfaces alloys with different composition. This is shown exemplary in Fig. 8A for the Au<sub>x</sub>Pt<sub>1-x</sub>/ Pt(111) surface alloy, showing a phase separation of the atoms in the surface (see Fig. 5A).<sup>40</sup> The symbols represent the experimental data points, and the dashed lines represent the trimer ensemble distribution for surface alloys with a random distribution of the atoms in the surface, such as for PtRu/Ru(0001) surface alloys shown in Fig. 5B. The ensemble effect is illustrated on a combined UHV-STM electrochemistry study on the Au<sub>x</sub>Pt<sub>1-x</sub>/Pt(111) surface alloy.<sup>36,48</sup> Fig. 8B shows the positive scans of cyclic voltammograms (recording faraday currents by applying a potential) of Pt(111) and  $Au_xPt_{1-x}/Pt(111)$  surface alloys with increasing Au content, recorded in 0.5 M HClO<sub>4</sub> supporting electrolyte at a scan rate of 50 mV s<sup>-1</sup>. The region between 0.05 and 0.40 V (0.60 and 0.90 V) shows the hydrogen desorption (OH adsorption) current densities. The evaluated charges in these potential ranges are plotted in the inset of Fig. 8B with blue dots for the hydrogen desorption and with red dots for adsorbed OH. From the results in the inset, it is clear that the charge does not decrease linearly with increasing Au content (straight line) but decreases with a third-order polynomial. From the ensemble distribution plotted for  $Au_xPt_{1-x}/Pt(111)$  surface alloys in Fig. 8A, we observed that the distribution of the Pt trimer ensembles also follows a third-order polynomial, which is hence plotted with the dotted line in the inset of Fig. 8B. Therefore, it can be concluded that H (and OH) require a 3-fold Pt hollow adsorption site on the surface. This result clearly indicates that the ensemble effect is not linearly related to the composition of the alloy, but strongly depends on the order of the atoms in the surface alloy, e.g., phase separation, random distribution, or disperses distribution of the atoms, which has been demonstrated for several other surface alloy systems investigated in a combined UHV electrochemistry set-up.49,50

## **Technical and Experimental Limitations**

Even though it has been demonstrated that with atomic scale STM imaging it is possible to elucidate the exact position of different types of atoms, care has to be taken in the interpretation of the STM data in order not to derive any erroneous conclusions, which was referred to as "tunnel vision" by Demuth and coworkers.<sup>24</sup> This is especially important when the local structures observed in STM are related to catalytic processes, which record the activity of the entire surface. In the following we will briefly summarize some key technical and experimental limitations in STM imaging.

#### **Tip Effects**

Several imaging problems arising from tips which are not atomically sharp have been elucidated already further above (macroscopic tip effect). It was proposed that tip surface interactions allow for imaging surfaces with chemical contrast. However, in some cases it is not possible to image the surface on an atomic scale level, since the large tunneling currents required to image the surface lead to an irreversible restructuring or even destruction of the investigated surfaces. For example, an attempt to image low concentrations of Pt in a  $Pt_xCu_{1-x}/Ru(0001)$  surface alloy was not feasible, since the high tunneling currents lead to the formation of small metal clusters on the bimetallic surface, which was probably due to strong tip sample interactions.<sup>51</sup>



**Fig. 8** (A) Trimer ensemble distribution of  $Au_xPt_{1-x}/Pt(111)$  surface alloys. Symbols represent experimental data points evaluated from STM images with chemical resolution, and the dashed lines represent the statistical distribution of trimer ensembles in surface alloys with a random distribution of the atoms in the surface. (B) Base cyclic voltammograms in 0.5 M HClO<sub>4</sub> at 50 mV s<sup>-1</sup> (anodic part only) for  $\circ$  Pt(111),  $\triangle Au_{03}Pt_{97}/Pt(111)$ ,  $\triangle Au_{24}Pt_{76}/Pt(111)$ ,  $\triangle Au_{21}Pt_{49}/Pt(111)$ ,  $\bigcirc Au_{72}Pt_{28}/Pt(111)$ . Inset shows the charge displaced for hydrogen desorption (*blue dots*) and for hydroxyl adsorption (*red dots*) as function of the Au surface content. Copyright 2013, Elsevier. (B) reprinted with permission from Brimaud, S.; Engstfeld, A. K.; Alves, O. B.; Behm, R. J. Structure–reactivity Correlation in the Oxygen Reduction Reaction: Activity of Structurally Well Defined  $Au_xPt_{1-x}/Pt$  (111) Monolayer Surface Alloys. *J. Electroanal. Chem.* **2014**, *716*, 71–79.

#### **Tunneling Conditions**

When imaging surfaces with STM, the whole parameter space of current and voltage combinations needs to be explored, since certain structures only become visible when the correct potential or current is applied.<sup>51</sup> STM images with chemical resolution can only be obtained in a small voltage–current window. In other cases variations in potential and current can lead to a contrast inversion of the depicted atoms, as shown in **Fig. 3A**. The latter example shows that the assignment of different elements on the surface is experimentally challenging.

#### Homogeneity

As mentioned earlier, STM is a local probe and thus one could easily make the mistake to assume that the order of the atoms imaged in a series of atomically resolved STM images reflects the structure of the entire surface. This is, however, not always the case. For example, on  $Pt_xCu_{1-x}/Ru(0001)$  surface alloys it could be shown that on extended terraces the atoms tend to form structures with a specific SRO, while in the vicinity of the steps a phase separation of the atoms is observed. This indicates that different alloy formation mechanisms have to be considered in different regions of the surface.<sup>51</sup> This effect would have to be accounted for in the interpretation of further (electro-)catalytic studies where the contribution of all the sites present on the surface have to be considered.

#### **Bulk Contribution**

STM remains a surface probe technique, mapping geometric and electronic effects of the surface. In the process of alloy formation at elevated temperatures it is, however, possible that guest metals dissolve into the bulk. These subsurface atoms might change the LDOS of surface atoms via a vertical ligand effect, which are eventually not observed in STM imaging with chemical contrast but could influence the (electro-)chemical properties of the surface. Establishing an unambiguous structure–activity relationship becomes rather challenging and further theoretical studies are required, as demonstrated in a combined experimental and theoretical study on the CO adsorption on  $Ag_xPd_{1-x}/Pd(111)$  surface alloys.<sup>52</sup>

#### **Concluding Remark**

In this work the fundamental experimental aspects and theoretical concepts of STM imaging have been introduced, and, furthermore, the concepts and limitations of atomic scale STM imaging with chemical resolution to differentiate between different types of atoms have been elucidated. Besides the presented relevance of these studies on alloy surfaces over the last decades with respect to structure formation and the structure-activity relationship in (electro-)catalysis, the presented fundamental principle can be extended to other systems such as semiconductor surfaces or the investigation of adsorbate and molecular structures on planar substrates.

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#### **Relevant Website**

Gallery of STM images with chemical resolution-http://www.iap.tuwien.ac.at/www/surface/STM\_Gallery/index.

## **Cyclic Voltammetry**

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Introduction         Processes Controlled by the Rate of Mass Transport         Complex Mechanims         Cyclic Voltammetry in the Presence of Adsorption Processes         Coadsorption Phenomena         Cyclic Voltammetry of Platinum Single Crystal Electrodes. Voltammetry as a Surface Sensitive Characterization Technique         Fit of Voltammetric Peaks to Adsorption Peaks         Ideally Polarizable Electrodes         Kinetic Effects in the Adsorption Pseudocapacity         Oxidation of Small Organic Molecules         Concluding Remarks	<b>48</b> 50 55 63 64 67 68 69 72 <b>73</b>
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#### Introduction

The use of electrochemical measurements for the study and characterization of chemical systems and materials has undergone an extraordinary expansion in the last decades thanks to the existence of cheaper and more accessible electronics. Today, there is a large range of electrochemical instruments from many different companies capable of performing a large variety of electrochemical experiments and measurements. The large majority of these experiments involve the imposition and / or measurement of electrode potentials and current and the study of their relationship.

The electrode potential is the most important parameter governing the rate of an electrodic process. Any electrochemical reaction is characterised by a thermodynamic equilibrium potential that defines a zero current situation. At this potential, anodic and cathodic currents are equal. If the electrode potential is lower than the equilibrium potential the reaction is normally shifted towards the cathodic process while, in the opposite case, the net anodic reaction is obtained. Studying the electrochemical kinetic behaviour of a given electrode in the presence of one or several electroactive species is therefore a matter of scanning the electrode potential to investigate the sign and magnitude of the current that circulates through the electrochemical techniques that has been described in classical textbooks. Already in 1975 the IUPAC gave a classification of electrochemical techniques involving the variation of the electrode potential that included more than 20 different techniques. In most of them, the system in equilibrium is perturbed by applying a potential and the relaxation to the perturbation of the electroactive species is recorded in the form of electrical current.

Obviously, the easiest potential perturbation would be to maintain a constant potential value. This leads to the family of chronoamperommetric techniques, where the current is measured as a function of time while the potential is kept at a constant value. In this simplest case the system in equilibrium is perturbed and current reflects the relaxation of the system to the new conditions. The next logical step towards a more complex potential program is to scan it with a constant velocity, recording the current as a function of the applied potential at each instant. This constitutes the linear scan voltammetry technique. A step further would be to repeat the scanning back and forth leading to the cyclic chronoamperommetric or voltammetric experiment. These are by far the most common operational modes, but the possibilities do not end here. Another approach that has become popular is the staircase voltammetry. In this approach, the potential is swept between two potential limits but using a sequence of steps instead of using a linear ramp. Such potential program is inevitably obtained when a digital (in opposition to analog) instrument is used. In this case, the resolution of the applied potential is limited by the bit resolution of the digital to analog converter and the potential program becomes quantized. Other approaches that use stepped programs of potential are the differential pulse voltammetry and the square wave voltammetry. Finally, a combination of a linear ramp with a sine modulation of the potential leads to the AC voltammetry technique. Figure 1 summarises the relationship between some of the most common potential programs mentioned above and the name of the electrochemical technique. This chapter will focus mainly on linear and cyclic voltammetry in quiescent solutions (mass transport controlled by diffusion). Special consideration will be given to characteristic voltammetric results for electrosorption processes or for purely capacitive responses, since these cases have received comparatively less attention in the literature. Applications described here will focus on macroelectrodes and no mention will be given to the special mass transport conditions that operate when the electrode belongs to the micrometre size scale. Extensive bibliography exists discussing these and more sophisticated techniques.

In a cyclic voltammetry experiment the potential is scanned back and forth between two potential limits while the current that circulates through the circuit is recorded. In quiescent solutions and using a suitable supporting electrolyte, the graph of the current





as a function of potential is called a cyclic voltammogram. This is normally characterised by the appearance of several peaks corresponding to the different electrochemical processes that can take place at different potentials. The identification of the peaks in the voltammogram already provides very valuable information about the processes taking place, since different electrochemical processes generate different characteristic peaks. Relevant parameters obtained from the voltammogram are potential, current (height) and width of the peak. Peak potential provides qualitative information about the nature of the process when compared to thermodynamic equilibrium potential values. The shape of the peak (for instance, whether is symmetric or not) also gives information about the nature of the process taking place. Dependence of these measurements with various parameters such as scan rate, concentration, pH, temperature ... allows a very detailed and quantitative characterization of the electrochemical reaction under study. For example, observation of the currents in the positive and negative going scan provides information about the reversibility of the process.

The quantitative interpretation of the voltammogram is usually rather complex although the mathematical framework has been developed through various decades. One circumstance that complicates significantly the analysis of voltammetric data is the effect of mass transport. This is an inevitable consequence of the fact that an electrochemical reaction is always a heterogeneous process taking place at the interphase between the electrode and the solution. Therefore, mass transport process is, in general, coupled with the electron transfer to account for the supply of reactants to the surface of the electrode and products back to the bulk of the solution. In this regards, two broad families of voltammetric responses must be distinguished. Those in which the mass transport is relevant or even limiting the current and those processes confined to the surface of the electrode where either mass transport is not necessary or is not affecting the overall rate of reaction.

The chapter is organised as follows: First, we describe briefly the properties of the voltammogram when the electrochemical process is controlled by mass transport. Because this part has been more extensively treated in many reviews and textbooks, we only give the main clues to understand the shape of the voltammogram, skipping most of the mathematical details. The easiest case of a reversible (fast) electron transfer is discussed first. Then, the effect of kinetic limitations is introduced, first considering a single electron transfer and then the case of some more complex mechanisms. The possibilities here are very large, but we will

discuss only the simpler cases and we refer the interested reader to the vast bibliography in this respect. In the second part we describe those voltammograms obtained in the presence of electrosorption processes. The scheme here follows the same used for diffusion limited processes. We derive first the equations that describe the voltammetric current for an electrosorption process that follows Langmuir or Frumkin isotherms, in the absence of kinetic limitations. Next we extend the treatment to the case of competitive adsorption between two species. With the knowledge gathered in these two sections, and taking the voltammogram of platinum as an example, we describe the information that can be extracted from the voltammetric experiment in this case. Next, purely capacitive processes in the case of a nearly ideally polarizable electrode are described using as example the case of gold single crystal electrodes. Finally, kinetic effects are considered, and strategies for the calculation of rate constants from voltammetric experiments are discussed.

#### Processes Controlled by the Rate of Mass Transport

There are three mechanism of mass transport: i) Diffusion, ii) Convection and iii) Migration. In the standard cyclic voltammetric experiment convection is avoided by maintaining a stagnant solution. True stagnant conditions are sometimes difficult to attain since, very often, small vibrations can cause movement of the solution. However, taking some precautions to prevent vibrations, in a short time scale (less than one minute), convection can be considered negligible. On the longer time scale, density changes can cause convective movements in the fluid. Migration is also usually avoided by employing an excess of supporting electrolyte that transports the current in the solution without participating in the electrochemical reaction under study.

Under these conditions, the main mass transport mechanism is diffusion. Diffusion of species in a fluid is governed by Fick's laws of diffusion, which, for planar geometry are reduced to: First Fick's Law:

FIRST FICK'S Law:

$$J_i = -D_i \left(\frac{\partial c_i}{\partial x}\right) \tag{1}$$

Second Fick's Law:

$$\left(\frac{\partial \boldsymbol{c}_i}{\partial t}\right) = D_i \left(\frac{\partial^2 \boldsymbol{c}_i}{\partial t^2}\right)$$
[2]

where  $J_i$  is the flux of species i,  $D_i$  is its diffusion coefficient,  $c_i$  its concentration and x is the distance to the electrode surface. Solution of the differential equation resulting from [2], for each electroactive species, subject to appropriate boundary conditions, provides a set of concentration profiles,  $c_i(x)$ , as a function of time. The most important concentration values are those at the surface of the electrode, x = 0, since these are the one governing the rate of the electrochemical reaction. For a simple electrochemical process:

$$Ox + ne \rightleftharpoons R$$
 [3]

the rate of the electrochemical reaction, as a function of the electrode potential, E, is usually given by Butler-Volmer equation:

$$j = nFk^{0} \left[ c_{R}^{sup} \exp\left( \alpha_{a} \frac{F}{RT} \left( E - E^{0} \right) \right) - c_{Ox}^{sup} \exp\left( -\alpha_{c} \frac{F}{RT} \left( E - E^{0} \right) \right) \right]$$

$$[4]$$

where *F* is the Faraday constant,  $k^0$  is the standard rate constant,  $E^0$  is the standard (formal) electrode potential,  $\alpha_a$  and  $\alpha_c$  are the charge transfer coefficients for the anodic and cathodic reaction, respectively, and  $c_{R}^{sup}$  and  $c_{Ox}^{sup}$  are the relevant concentrations measured at the surface of the electrode:

$$c_R^{sup} = c_R(x = 0, t) \text{ and } c_{Ox}^{sup} = c_{Ox}(x = 0, t)$$
 [5]

While electrochemical reactions that involve more than one electron transfer need particular attention and will be discussed with more detail in the next section, in the equations that follow we keep the parameter n to give more generality to the discussion, although n will be taken as one in this section. The continuity of the flux at the surface of the electrode gives rise to the following condition:

$$J_{Ox} = -J_R = \frac{J_e}{n} = \frac{j}{nF}$$
[6]

The consistence of the sign of the different magnitudes involved in equation [6] and the sign criteria stablished by the IUPAC for the current (positive for anodic currents and negative for cathodic currents) is illustrated in Figure 2. In this figure, the flux towards the electrode surface is considered as negative and the flux towards the bulk of the solution as positive. For a reduction process, concentration of Ox is depleted at the surface of the electrode while concentration of R is increased. The opposite happens for the oxidation process.

Integration of differential equation [2] needs consideration of appropriate boundary and initial conditions. The initial condition is usually given by the values of bulk concentration:

$$c_i(t=0,x) = c_i^{\text{bulk}}$$
<sup>[7]</sup>



**Figure 2** Illustration of the relationship between the concentration profiles near the electrode surface, located at distance x = 0, and the flux,  $J_{i}$  of the different species participating in the electrochemical reaction for a) reduction process and b) oxidation process.

For the simplest case of planar semiinfinite diffusion, the first boundary condition is also given by the concentration in the bulk of the solution:

$$c_i(t, \mathbf{X} \to \infty) = c_i^{\text{bulk}} \tag{8}$$

The second boundary condition is, in general, given by the combination of equations [4] and [6]. In the particular case of a very fast electron transfer reaction ( $k^0 \rightarrow \infty$ , in practice  $k^0 = 10$  cm s<sup>-1</sup> is a very fast electrochemical reaction), equation [4] reduces to the Nernst equation:

$$E = E^{0} + \frac{RT}{nF} \ln \frac{c_{Ox}^{sup}}{c_{R}^{sup}}$$
[9]

where, again, the relevant concentrations are those at the surface of the electrode. Analytic solution of 2nd Fick's law can only be achieved for relatively simple situations. In the following, we will avoid the complex mathematical treatment and we will explain the shape of the voltammogram using relatively simple arguments that start with the description of the simpler case of a constant potential perturbation.

One of the easiest cases that allows understanding of the variation of the current with time is when the potential is stepped from a value where no electrochemical reaction takes place to a sufficiently high (for an oxidation) or low (for a reduction) potential. This is the chronoamperommetric experiment illustrated in Figure 1(a). From the application of the potential step, the reactive species is consumed at the surface of the electrode, decreasing its concentration while the formed product increases its concentration. The appearance of a concentration gradient triggers the diffusion of the reactant towards the surface of the electrode and the products towards the bulk of the solution. Concentration profiles vary with time as depicted in Figure 3.

One very important consequence of the continuity equation [6] is the relation between the current and the gradient of the concentration profile at the surface of the electrode:

$$j = \frac{nF}{\nu_i} D_i \left(\frac{\partial c_i}{\partial x}\right)_{x=0}$$
<sup>[10]</sup>

where  $\nu_i$  is the stoichiometric coefficient, negative (-1) for Ox and positive (+1) for R. Observation of the curves of Figure 3 reveals that, as time increases, the perturbation of the concentration due to the electrochemical reaction in equation [3] penetrates more and more into the bulk of the solution. The layer where the concentration is different from the value in the bulk is called the diffusion layer. Therefore, the previous observation can also be stated by saying that the thickness of the diffusion layer increases with time.

Let us discuss first the situation of a constant potential value. In the case of a fast electrochemical reaction (Figure 3(a)), the concentrations at the surface are fixed by Nernst law (equation [9]) (in combination with the mass balance (equation [6]). On the other hand, when the reaction rate is not sufficiently fast, concentrations at the surface will evolve with time, approaching progressively the value fixed by the Nernst equation, as shown in Figure 3(b). For a given value of the surface concentration, as the thickness of the diffusion layer increases, the gradient of the concentration profile decreases and, as a consequence of equation [10], the current decreases with time. Figure 4 shows a set of chronoamperommetric curves corresponding to the oxidation of R in the absence of Ox when the potential is stepped to progressively higher values in the particular case of a relatively high value of  $k^0$  (Reversible case).

In this case, solution of the differential equation [2] can be achieved by using Laplace transform technique and it is relatively easy to demonstrate that current is given by Cottrel equation:

$$|I(t)| = \frac{nFD_R^{1/2}Ac_R^{\text{bulk}}}{(\pi t)^{1/2}(1+\xi\theta)} = \frac{|I_d(t)|}{(1+\xi\theta)}$$
[11]

where  $\theta = \frac{c_{R}^{sup}}{c_{Ox}^{sup}} = \exp\left(-\frac{nF}{RT}\left(E - E^{0}\right)\right)$  and  $\xi = \left(\frac{D_{R}}{D_{Ox}}\right)^{1/2}$


**Figure 3** Concentration profiles near the electrode surface corresponding to a chronoamperometric (a,b) or voltammetric (c) experiment: a) Reversible process, constant potential; b) Irreversible process, constant potential; c) Voltammetric experiment (lineal scan) for a reversible process.

The only potential dependence is within the parameter  $\theta$ . Therefore, the curves at different potentials correspond to the value of  $I_d(t)$  scaled by the factor  $\frac{1}{1+\xi\theta}$ . For a potential step of large amplitude,  $E \gg E^0$  and  $\theta \to 0$  and the current does not depend anymore on the potential. At this point, the concentration at the surface of the electrode has dropped to nearly zero and the current is completely governed by the rate of diffusion. A similar result is obtained for the quasireversible situation. The only difference in this case is that current does not tend to infinity at shot times, since the current is limited by the rate of the electrochemical reaction. However, this rate grows with increasing overvoltage and therefore, for a step of sufficient amplitude, the reaction is again limited by the rate of mass transport and the curves for the quasireversible and the reversible situations become identical above a certain potential value.

The set of curves in **Figure 4** allow us to explain qualitatively the shape of the voltammetric curve for a simple process controlled by diffusion. Let us consider, as an example the oxidation of compound R in the absence of Ox in solution. The voltammetric experiment would normally start at a sufficiently low potential where no reaction takes place. Then, the potential would be scanned to progressively higher values. When the potential approaches the value of the standard potential,  $E^0$ , some current would start to flow, causing the depletion of the concentration of R at the surface, as this species is being consumed. This corresponds to curve 1 in



Figure 4 Chronoamperommetric curves for different potential step experiments as a function of the electrode potential. The cross-section bisecting the time-potential plane gives a qualitative description of the voltammetric experiment.

**Figure 3(c)**. As previously discussed, for a reversible system, the surface concentration is fixed by Nernst law. Hence, increasing the potential decreases the surface concentration of R and increases the surface concentration of Ox so equation [9] is satisfied. As the concentration of Ox on the surface decreases, the concentration gradient increases, and according to equation [10] the current increases. This effect can be seen in curves 1-4 in **Figure 3(c)**. However, when the concentration on the surface reaches zero, the gradient can no longer increase, regardless of the value of the potential. In fact, because the thickness of the diffusion layer increases, the gradient decreases, and so does the current. This is the situation for curves 6 to 8 in **Figure 3(c)**. The characteristic maximum observed in the voltammetric sweep is due to the balance between two opposing trends affecting the concentration gradient. On the one hand, the increase of the overpotential decreases the gradient. At the beginning of the sweep the decrease of the surface concentration dominates the shape of the curve, however when the surface concentration reaches its minimum value, the increase of the diffusion layer with time dominates. In fact, at potentials above the peak current, the curve shape is dominated by time and the sweep of the potential has no effect. This description can be better understood by considering again the set of chronoamperommetric curves of **Figure 4**. The potential scan can be seen as equivalent to performing a cross-section in the surface defined by these curves as we traverse the *E-t* plane diagonally. Hence, reaction rate is dominated by electron transfer at low potentials and by mass transport at high potentials.

Figure 5 shows a set of voltammetric scans performed at different scan rates,

$$v = \frac{dE}{dt}$$
[12]

for the oxidation of R, having the shape predicted in the above qualitative discussion. The important parameters that can be extracted from this curve are peak potentials and currents and their variation with the scan rate.

The previous discussion provides only a qualitative explanation for the voltammetric shape but for the exact mathematical description of the curve, finding a solution of the differential equation given by Fick's law is necessary. This can be achieved by the use of Laplace transformation techniques. For the oxidation of R the following expression is obtained

$$\int_{0}^{t} j(x)(t-x)^{-1/2} dx = \frac{nFD_{R}^{1/2}\sqrt{\pi}C_{R}^{bulk}}{1+\xi\theta}$$
[13]

Where  $\theta = \exp\left(-\frac{nF}{RT}\left(E - E^{0}\right)\right)$ ,  $\xi = \left(\frac{D_{R}}{D_{0x}}\right)^{1/2}$  and x is a dummy variable for the integration. To obtain j(t) it is necessary to solve the integral equation above.

This integral is in fact a convolution between the current and  $t^{-1/2}$  and can also be expressed in terms of a semiintegral, which is a concept from fractional calculus:

$$\frac{d^{-1/2}}{dt^{-1/2}}j(t) = \frac{1}{\sqrt{\pi}} \int_0^t j(x)(t-x)^{-1/2} dx$$
[14]

With this notation, the following rather simple equation is obtained:

$$\frac{d^{-1/2}}{dt^{-1/2}}j(t) = \frac{nFD_R^{1/2}\pi C_R^{bulk}}{1+\xi\theta}$$
[15]



**Figure 5** Set of voltammetric experiments recorded at different scan rates. Obtained with Digisim for the following parameters:  $k^0 = 10^4$  cm s<sup>-1</sup> (totally reversible process),  $\alpha = 0.5$ ,  $D_{ox} = D_R = 10^{-5}$  cm<sup>2</sup>s<sup>-1</sup>.  $C_{ox} = 0$ ;  $C_R = 10^{-3}$  M. n = 1. Labels indicate the scan rate in mV s<sup>-1</sup>.

The similarity between equations [15] and [11] is remarkable. Because the function  $1/(1 + \xi\theta)$  gives a sigmoidal curve when plotted as a function of the potential, it is usually stated that the semiintegration of the current (or convolution with  $t^{-1/2}$ ) recovers the typical shape for a stationary process (for instance, as obtained with a rotating disk electrode).

Equation [13] is more conveniently expressed in terms of adimensional variables:

$$\int_0^\tau \frac{\chi(\mathbf{z})}{\sqrt{\tau - \mathbf{z}}} d\mathbf{z} = \frac{1}{1 + \xi\theta}$$
[16]

Where  $\tau$  is the adimensional time given by

$$\tau = \frac{Fv}{RT}t$$
[17]

And  $\chi$  is the adimensional current, given by:

$$\sqrt{\pi}\chi = \frac{j}{nFD_R^{1/2}C_R^{bulk}\sqrt{\frac{F_V}{RT}}}$$
[18]

Moreover,  $\xi\theta$  can be more conveniently written as:

$$\xi\theta = \exp\left(-\frac{nF}{RT}\left(E - E^{h}\right)\right)$$
[19]

Where

$$E^{h} = E^{0} + \frac{RT}{nF} \ln\left(\frac{D_{R}}{D_{Ox}}\right)^{1/2}$$
[20]

Equation (16) can be solved to obtain the function  $\chi(\tau)$ . Because time and potential are related by:

$$\epsilon = \frac{nF(E - E^h)}{RT} = \frac{nF(E_i - E^h)}{RT} + \tau$$
[21]

Where  $\varepsilon$  is the adimensional potential, it is customary to express  $\chi(\varepsilon)$  instead of  $\chi(\tau)$ . Both functions only differ on a horizontal translation. Different approximations have been used to obtain  $\chi(\varepsilon)$ . One of the most convenient representation is given by the following series (Given by Oldham et al.):

$$\sqrt{\pi}\chi(\varepsilon) = \frac{149}{392} + \frac{54\varepsilon}{455} - \frac{13\varepsilon^2}{296} + \sqrt{\frac{\pi}{2}} \sum_{n=1,3}^{19} \left\{ \frac{(\varepsilon_n + 2\varepsilon)\sqrt{\varepsilon_n - \varepsilon}}{\varepsilon_n^3} - \frac{8n^2\pi^2 + 12n\pi\varepsilon - 15\varepsilon^2}{8(n\pi)^{7/2}} \right\}$$
[22]

Where  $\varepsilon_n = \sqrt{\varepsilon^2 + n^2 \pi^2}$ 

The maximum in function  $\chi(\varepsilon)$  is obtained for  $\varepsilon_{\rho} = 1.109$  with a value of  $\sqrt{\pi}\chi(\varepsilon_{\rho}) = 0.4463$ . Substituting this value into equation (21), the following expression for the peak potential is obtained:

$$E_{\rho} = E^{o} + \frac{RT}{nF} \ln\left(\frac{D_{R}}{D_{Ox}}\right)^{1/2} + 1.109\left(\frac{RT}{nF}\right)$$
[23]

for the oxidation process. An important characteristic of this equation is that peak potential for a reversible process controlled by diffusion is independent of the scan rate or the concentration.

Another important information contained in the voltammetric current is given by the peak current. For a reversible process, the peak current is given by:

$$j_{p} = 0.4463nFD_{R}^{1/2}C_{R}^{bulk}\sqrt{\frac{nFv}{RT}}$$
[24]

The most significant feature of equation (24) is that peak current is proportional to the square root of the scan rate. A plot of peak current as a function of the square root of the scan rate allows calculation of the diffusion coefficient.

To measure the peak current for the cathodic peak a correction has to be done to take into account that the cathodic peak is overlapped with the oxidation current remaining from the anodic peak. As discussed above, the decay after the peak is due to the predominance of mass transport limitation and follows  $t^{-1/2}$  law:

$$j_{masstransport} = \frac{B}{\left(t - t_0\right)^{1/2}}$$

where  $t_0$  is, in general, not known. However, it can be easily determined by plotting  $1/j^2$  as a function of t, according to:

$$\frac{1}{j^2} = \frac{t - t_0}{B^2}$$



**Figure 6** Illustration of the method to extract the  $t^{-1/2}$  decay of the mass transport limited current.

The result of such plot is shown in Figure 6. Although the  $t^{-1/2}$  dependence at long times is not evident in equation [22], alternative expressions for  $\chi(\varepsilon)$  clearly show such dependence.

The treatment of the non-reversible situation, that is, when Nernst law is not satisfied on the surface of the electrode, runs parallel to what has been described in previous paragraphs, although now the boundary condition at the surface of the electrode is equation [4] instead of [9]. In this case, concentrations at the surface are not only function of the potential but depend also on time, as shown in **Figure 3(b)** for the chronoamperommetric case. We skip the mathematical details to jump to the most important result, that is, the equations that describe peak potential and current. For a totally irreversible process the following relationships are obtained:

$$j_{p} = 0.4958F \left(\frac{\alpha_{a}F}{RT}\right)^{1/2} D_{R}^{1/2} c_{R}^{bulk} v^{1/2}$$
[25]

And

$$E_{p} = E^{o} + \frac{RT}{\alpha_{a}F} \left[ 0.78 + \ln\left(\frac{D_{R}^{1/2}}{k^{o}}\right) + \ln\left(\frac{\alpha_{a}Fv}{RT}\right)^{1/2} \right]$$
[26]

From these equations, current is still proportional to the square root of the scan rate but the peak potential depends on scan rate (and also on the concentration). It should be remarked that these equations are deduced for a single electron transfer, n = 1. Extension to a multiple electron transfer, n > 1, is not straightforward, since the result will depend on the particular mechanism, as discussed in the next section. Comparison of equation [24] and [25] for a single electron transfer and considering a typical value of  $\beta = 0.5$  reveals that peak current for an irreversible process is ca. 78% of the value for a reversible process. For a quasireversible process, peak current is between these two limiting values. Figure 7(a) illustrates this behaviour by plotting simulated curves obtained for different values of the rate constant  $k^0$ . It has to be stressed that peak current does not depend on the rate constant for a totally irreversible process. Decreasing the rate constant shifts the peak position but does not decrease further the peak height. In a normal experiment, the rate constant cannot be varied and what is varied is the scan rate. Increasing scan rate (faster transport) is equivalent to decreasing rate constant. Figure 7 shows this behaviour. The following adimensional parameter has been defined as a measure of the degree of reversibility:

$$\Lambda = k^0 \sqrt{\frac{RT}{FvD}}$$
[27]

According to equation [26] a plot of peak potential as a function of log (v) can provide  $\beta$  from the slope and  $k^0$  from the intercept. Estimation of diffusion coefficients from peak current is dubious unless the system is totally reversible.

#### **Complex Mechanims**

As mentioned previously, equations [25] and [26] are only valid for a single electron transfer. It is generally accepted that the simultaneous transfer of more than one electron is statistically very unlikely. For this reason, when more than one electron is involved in



**Figure 7** Cyclic voltammograms for an irreversible process. a) Different rate constant ( $k^0$ /cm s<sup>-1</sup>=10<sup>4</sup>, 1, 0.1, 5 · 10<sup>-3</sup>, 2 · 10<sup>-3</sup>, 10<sup>-3</sup>, 5 · 10<sup>-4</sup>, 2 · 10<sup>-4</sup>, 10<sup>-4</sup>, 10<sup>-4</sup>, 10<sup>-5</sup>) The resulting values of  $\Lambda$  according to equation [27], are indicated in the figure. Scan rate = 100 mV s<sup>-1</sup>. b) different scan rates, as indicated in the figure (in mV/s).  $k^0 = 10^{-3}$  cm/s. The other parameters, common for the two plots are:  $D_{\rm R} = D_{\rm 0x} = 10^{-5}$  cm<sup>2</sup>/s;  $\beta = 0.5$ ;  $c_{\rm 0x} = 0$ ;  $c_{\rm R} = 10^{-3}$  M; n = 1.

the electrochemical reaction, it is necessary to consider a mechanism that involves several electron transfer steps. It is rather usual that the mechanism involves also one or more chemical reactions. To describe these complex mechanisms it is customary to use the E&C nomenclature, where E stands for an electron transfer step and C for a chemical step. In this way, EE means the consecutive transfer of two electrons while EC means that the electron transfer step is followed by a homogeneous chemical reaction. Sometimes, subindices *r*, *q* or *i* are added to classify the steps as reversible, quasireversible or totally irreversible, respectively. Increasing the number of electron transfer steps, grows the number of possible mechanisms, and so does the complexity of the mathematical treatment necessary for the calculation of the voltammetric curve. Although the analytical solution of a given problem always offers a deeper understanding of the parameters that affect the solution, nowadays it is a much more practical approach to use numerical simulations for the calculation of the voltammetric current for each problem. For this purpose, different software have been developed, such as Digisim (Provided by BASi), DigiElch (Provided by Gamry Instruments), CV Sim (provided by BioLogic) or ESP (Freely available from Carlo Nervi). These programs not only simulate the voltammetric current for a given a set of parameters but can also fit the parameters to experimental data, allowing the determination of rate constants, among other variables, that affect the shape of the voltammetric current. As selected examples, we discuss the main aspects that characterise the cyclic voltammograms obtained in the simplest cases: the EE and EC mechanism.

Figure 8 shows cyclic voltammograms simulated for a two electron process:

$$R \rightleftharpoons I + e E_1^0$$

$$I \rightleftharpoons Ox + e E_2^0$$
[28]

When  $E_1^0 < E_2^0$  the two electron transfers appear as two separate peaks in the voltammogram and there is a potential region,  $E_1^0 < E < E_2^0$ , where the intermediate product I is stable. However, when  $E_1^0 > E_2^0$ , the first electron transfer to form the intermediate species, I, takes place in a potential range,  $E > E_1^0 \gg E_2^0$  where the second electron transfer is totally displaced towards the formation of Ox and therefore, the intermediate species I is very unstable and is transformed immediately into Ox. In this case, the voltammogram appears as if the two electron transfers would take place simultaneously, with a standard potential that is the mean value between  $E_1$  and  $E_2$ . If both transfers are very fast ( $E_rE_r$  mechanism), equation [24] is valid with n=2. When one of the electron transfer steps is slow, extension of equation [25] by introducing a factor n=2 should be done with caution since this would only be valid if the first electron transfer is the limiting step. This is illustrated in Figure 9 where the voltammograms for mechanisms  $E_iE_r$  (Figures (a) and (b)) and  $E_rE_i$  (Figures (c) to (e)) are compared. In the latter case, it can be seen (Figure 9(e)) that at sufficiently fast scan rates the two electron transfer steps can be decoupled. Figure 9(f) shows the plot of peak current as a function of the square root of scan rate. The plot is linear for the  $E_iE_r$  but clearly deviates from linearity in the case  $E_rE_i$ 



**Figure 8** Cyclic voltammograms for a ErEr mechanism. Effect of standard potential. The other parameters are:  $c_{0x}=0$ ;  $c_R=0.001$  M,  $D_{0x}=D_R=D_I=10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>  $E_2^0=0V$ .



**Figure 9** Calculated cyclic voltammograms for a two electron transfer process: a) and b) First electron transfer is the rate limiting step  $(E_i E_r)$ .  $k_1^0 = 10^{-4} \text{ cm s}^{-1}$  and  $k_2^0 = 10^4 \text{ cm s}^{-1}$ . c) and d) Second electron transfer is rate limiting step  $(E_r E_i)$ .  $k_1^0 = 10^4 \text{ cm s}^{-1}$  and  $k_2^0 = 10^{-4} \text{ cm s}^{-1}$ . In b) and d) the current has been normalised by the square root of the scan rate. Scan rates, in V s<sup>-1</sup>, are: 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1. e) as in C but with scan rate of 10 V s<sup>-1</sup>. F) Plot of peak current as a function of the square root of scan rate for a)  $E_i E_r$  and b)  $E_r E_i$ . Other parameters are:  $E_1^0 = 0.1 \text{ V}$ ;  $E_2^0 = 0 \text{ V}$ ;  $D = 10^{-5} \text{ cm}^2 \text{s}^{-1}$  (for all species).  $C_R = 10^{-3} \text{ M}$ .



**Figure 10** a) Calculated cyclic voltammograms and b) normalized currents by the square root of the scan rate for an EC mechanism for different values of the scan rate, in V s<sup>-1</sup>: 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1. Other parameters are:  $D = 10^{-5} \text{ cm}^2 \text{s}^{-1}$  (for all species).  $C_R = 10^{-3} \text{ M}$ ,  $K_2 = 10^4$ ,  $k_f = 1 \text{ s}^{-1}$ ,  $k_b = 10^{-4} \text{ s}^{-1}$ .

Finally, we show in Figure 10 the voltammograms calculated numerically for a ErC mechanism.

$$R \rightleftharpoons Ox + eE_1^0$$

$$Ox \to \text{Products}$$
[29]

If the chemical transformation that follows the first electron transfer is irreversible, then the existence of this chemical step is reflected in a diminution of the peak in the reverse scan. This effect depends very much on the scan rate. For slow scan rate, there is enough time to complete the transformation of Ox into the final products and the peak in the reverse scan completely disappears. However, at faster scan rates, the transformation of Ox is incomplete and the fraction of Ox not transformed into the final products can reduced back to R in the reverse scan. Hence, a plot of  $I_{p,c}/I_{p,a}$  as a function of the scan rate will be useful to identify this mechanism, since a deviation from unity at different scan rates will immediately become apparent.

One message to take home from the previous paragraphs: validity of the equations described above varies significantly depending on the applicability of the particular mechanism considered. Therefore, before jumping into the automatic application of equations one has to carefully decide what is the correct mechanism. Application of the incorrect equations to extract kinetics parameters from voltammetric data may lead to completely meaningless results.

#### Cyclic Voltammetry in the Presence of Adsorption Processes

**Figure 11** shows the cyclic voltammogram recorded with a polycrystalline platinum electrode immersed in a sulphuric acid solution. This voltammogram is clearly very different from those discussed above for a process dominated by diffusion of species from solution. Some distinctive characteristics of this voltammogram are:

- Peaks are essentially triangular in shape.
- There are peaks of different width. Peaks at the low potential region are sharper while peaks at the high potential region are broader.
- Some of the peaks are very symmetric with respect to the potential axis. Other peaks (the ones at higher potentials) are rather asymmetric.
- Peak current varies linearly with the scan rate, not the square root of the scan rate, as discussed above for a diffusion controlled process.
- Stopping the potential scan causes the current to drop suddenly to zero (in the time scale of milliseconds) while for a diffusion controlled process, the current drops with the square root of time (equation (11)).

The reason for the very different behaviour is that processes causing the peaks in the voltammogram of Figure 11 are due to electrosorption of species from solution with little diffusion limitation. As we will discuss below, the different voltammetric features are



Figure 11 Cyclic voltammogram corresponding to a polycrystalline platinum electrode immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Scan rate: 50 mV s<sup>-1</sup>.

responding to the particular adsorption isotherm that controls the electrosorption process. In the particular example of Figure 11, it is generally accepted that the peaks at low potentials correspond to hydrogen adsorption/desorption on different platinum surface sites, according to the reaction

$$\mathsf{Pt} + \mathsf{H}^+ + \mathsf{e} \rightleftharpoons \mathsf{Pt} - \mathsf{H}$$
[30]

The observation of different peaks is due to the fact that different adsorption sites on the different facets on the polycrystalline electrode possess different adsorption energies. Although generally neglected for polycrystalline platinum, careful studies with well-defined platinum surfaces have revealed a significant contribution in the peaks at low potentials of a charge transfer process due to anion adsorption (sulphate, in this case) according to:

$$Pt + HSO_4^{-} \rightleftharpoons Pt - SO_4 + H^+ + 2e$$
[31]

On the other hand, processes at high potentials correspond to platinum oxide formation according to

$$Pt + xH_2O \rightleftharpoons Pt - O_x + 2xH^+ + 2xe$$
[32]

And involving the anion desorption step at the beginning of the process. Let us consider first the voltammetric shape for a reversible processes. Similar to what was discussed above for diffusion controlled processes in the case of a reversible reaction, the concentration (activity) of species at the surface is related with the electrode potential by Nernst Law. In the case of adsorbed species, the activity should be expressed in terms of surface coverage,  $\theta$ , or surface excess,  $\Gamma$ . Both magnitudes are related by:

$$\theta = \frac{\Gamma}{\Gamma_{max}}$$
[33]

Moreover, the charge involved in the electrosorption process is related to the surface coverage by the following expressions:

$$q = -nF\Gamma = -nF\Gamma_{max}\theta = q_{ml}\theta$$
[34]

Where  $q_{ml}$  is the charge involved in the formation of one monolayer of the electrosorbed species. The voltammetric current would be given by the partial derivative of the charge, according to:

$$j = \frac{\mathrm{d}q}{\mathrm{d}t} = -nF\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = q_{ml}\frac{\mathrm{d}\theta}{\mathrm{d}t}$$
[35]

The current (and the charge) will be positive for an oxidative adsorption process, like the adsorption of an anion, according to:

$$A^- + M \rightleftharpoons A - M + e \tag{36}$$

In this case, *n* has to be taken as negative, for the sign of equation [34] to work. Conversely, charge and current will be negative for the reductive adsorption of a cation, like hydrogen adsorption:

$$H^+ + M + e \rightleftharpoons H - M \tag{37}$$

For a reversible electrosorption process, the surface excess can be considered only a function of the potential. This is a significant difference with the previously discussed diffusion controlled processes, where surface concentrations are also a function of time. In this case,

$$j = q_{ml} \frac{d\theta}{dE} \frac{dE}{dt} = q_{ml} \frac{d\theta}{dE} v$$
[38]

As previously stated, a linear dependence exists between the current and the scan rate. This is a consequence of the assumption that the coverage only depends on the potential. Under these circumstances, it is convenient to define the pseudocapacity according to:

$$C_{ads} = q_{ml} \left(\frac{\partial \theta}{\partial E}\right)_{\mu_i}$$
[39]

Therefore, the voltammetric current is related with the pseudocapacity by:

$$j = C_{ads}v$$
<sup>[40]</sup>

And the coverage can be obtained from the current by integration, according to:

$$\theta = \theta^* + \frac{1}{q_{ml}} \int_{E^*}^{E} \frac{j}{v} dE$$
[41]

We will now consider how the voltammetric profile should be in the case of a particular adsorption isotherm. The most simple, but still useful, and widely used, isotherm is the Langmuir isotherm (ideal situation with homogeneous distribution of adsorption sites and absence of lateral interactions). This can be derived from the equality of the rates of adsorption and desorption. In the case of an electrosorption process, both rates of adsorption and desorption will depend on the potential. For instance, for hydrogen adsorption, equation [37], we will have:

$$v_{ads} = k^0 c_{H^+} (1 - \theta) \exp\left[-\beta \frac{nF}{RT} \left(E - E^0\right)\right]$$

$$v_{des} = k^0 \theta \exp\left[(1 - \beta) \frac{nF}{RT} \left(E - E^0\right)\right]$$
[42]

Imposing the equilibrium condition  $v_{ads} = v_{des}$  we obtain:

$$\frac{\theta}{1-\theta} = Kc_{H^+} \exp\left(-\frac{nFE}{RT}\right)$$
[43]

And:

$$\theta = \frac{Kc_{H^+} \exp\left(-\frac{nFE}{RT}\right)}{1 + Kc_{H^+} \exp\left(-\frac{nFE}{RT}\right)}$$
[44]

with the equilibrium constant given by:

$$\mathcal{K} = \exp\left(\frac{n\mathcal{F}E^{0}}{RT}\right) = \exp\left(-\frac{\Delta G^{0}}{RT}\right)$$
[45]

where  $\Delta G^0 = -nFE^0$  represents the energy of adsorption. From equation [43], it is possible to obtain an expression for the pseudocapacity,  $C_{ads}$ :

$$C_{ads} = q_{ML} \left(\frac{\partial \theta}{\partial E}\right)_{\mu_i} = -q_{ML} \frac{nF}{RT} \left\{ \frac{Kc_{H^+} \exp\left(-\frac{nFE}{RT}\right)}{\left[1 + Kc_{H^+} \exp\left(-\frac{nFE}{RT}\right)\right]^2} \right\}$$
[46]

Equations above can be adapted for the case of adsorption of an anion, equation [36], by taking n = -1 and replacing  $c_{H^+}$  by  $c_{A^-}$ . **Figure 12** shows plots of the pseudocapacity and the coverage as a function of the electrode potential. The voltammetric current can be obtained through the capacitance using equation [40]. The pseudocapacity (and the current] shows a peak centred at  $E^0$ . The position of the peak is therefore a measure of the energy of adsorption,  $\Delta G^0$ , according to equation [45]. The peak current coincides with the condition  $\theta = 0.5$ . This can be easily seen in the plot and demonstrated taking the derivative of equation [46] and equating it to zero.

The value of the pseudocapacity at the peak potential is given by:

$$C_{\rm ads,max} = -q_{m/} \frac{nF}{4RT}$$
[47]



**Figure 12** Plot of the pseudocapacity,  $C_{ads} = j/\nu$ , and coverage,  $\theta$ , as a function of the electrode potential for an electrosorption process that follows the Langmuir isotherm; c = 1 M,  $q_{ML} = 240 \ \mu \text{Ccm}^{-2}$  and T = 298 K.

Finally, another important parameter is the width of the peak at half height which is given by:

$$\Delta E_{1/2} = \frac{2.3RT}{nF} \log \left(\frac{2+\sqrt{2}}{2-\sqrt{2}}\right)^2 \cong 90.3 \,\text{mV} \text{ at } T = 298 \text{K}$$
[48]

Remarkably, the width of the peak does not depend on any parameter, except the temperature. As previously mentioned when discussing the example of **Figure 11**, in reality voltammetric peaks have variable widths. To take it into account, additional parameters need to be included in the isotherm. The easiest extension is to consider that the energy of adsorption is a function of the coverage. Possible reasons for such dependency would be the existence of lateral interactions between adsorbed species or the existence of an intrinsic heterogeneity on the surface. In the latter case, calculation of the adsorption isotherm requires assumptions about a particular distribution function for the energy of different sites on the surface. A homogeneous distribution leads to Temkin isotherm.

However, the easiest function to consider is a linear variation of the energy of adsorption with coverage, leading to Frumkin adsorption isotherm:

$$\Delta G^0 = \Delta G^0_{\theta=0} + r\theta \tag{49}$$

where  $\Delta G_{\theta=0}^{0}$  would be the adsorption energy at infinite dilution and *r* is called the lateral interaction parameter. With this definition, positive values of *r* makes the adsorption less favourable [the energy of adsorption more positive], and therefore correspond to lateral repulsions. Conversely, negative values of *r* correspond to attractive lateral interactions. Introducing [49] into [45] and [43]

$$\frac{\theta}{1-\theta} = Kc_{H^+} \exp\left(-\frac{nFE + r\theta}{RT}\right)$$
[50]

Where, in this case,

$$\mathcal{K} = \exp\left(-\frac{\Delta G_{\theta=0}^{0}}{RT}\right)$$
[51]

To obtain the voltammetric current from equation [50], we need, as before, to calculate the derivative  $\frac{d\theta}{dE}$ . In this case the algebra is slightly more complicated, since it is not possible to solve explicitly equation [50] for  $\theta$ . To overcome this difficulty, we either take implicit derivative or we use the mathematical trick shown below:

$$C_{ads} = q_{ml} \left( \frac{d\theta}{dE} \right) = q_{ml} \frac{1}{\left( \frac{dE}{d\theta} \right)} = -\frac{q_{ml} nF}{RT} \left\{ \frac{\theta(1-\theta)}{1 + \frac{r}{RT} \theta(1-\theta)} \right\}$$
[52]

This expression, together with

$$E = -\frac{RT}{nF} \ln \frac{\theta}{1-\theta} - \frac{r}{nF} \theta + \frac{RT}{nF} \ln (Kc_{H^+})$$
[53]

give a parametric representation of the voltammetric current. To plot  $C_{ads}$  as a function of E values to  $\theta$  between 0 and 1 can be substituted into equations [52] and [53], respectively. Figure 13 shows the result of such plots. In this case, the maximum current is no longer centered around  $E^0$  but it is still satisfied that  $\theta = 0.5$  at the peak, as can be shown by differenciating [52] and equating to 0. Hence, the maximum pseudocapacity is given by:

$$C_{ads,max} = -\frac{q_{ml}nF}{4RT} \left(\frac{1}{1 + \frac{r}{4RT}}\right) = -\frac{q_{ml}nF}{4RT} \left(\frac{4}{4 + g}\right)$$
[54]

where we have defined  $g = \frac{r}{RT}$  as the adimensional parameter measuring the magnitude of lateral interactions. The peak potential is:

$$E_{peak} = \frac{RT}{nF} \log(Kc_{H^+}) - \frac{r}{2nF}$$
[55]

Another important characteristic, evident in the plot of Figure 13, is that the width of the peak varies significantly with the lateral interaction parameter, *r*. Positive values of *r*, that is, repulsive interaction, result in broader peaks while negative values of *r*, that is, attractive lateral interaction, results in narrower peaks. There is a mathematical discontinuity for  $g = \frac{r}{RT} = -4$ , since  $C_{ads,max}$  tend to infinity at this value. For g < -4 the isotherm is no longer a single valued function, as can be seen in Figure 13(c) (inset) and the system can undergo a phase transition. The relation between the width at half height and the lateral interaction parameter is given by:

$$\Delta E_{1/2} = 2\frac{RT}{F} \ln \left[ \frac{\sqrt{g+8} + \sqrt{g+4}}{\sqrt{g+8} - \sqrt{g+4}} \right] + \frac{r}{F} \sqrt{\frac{g+4}{g+8}}$$
[56]



**Figure 13** Plot of the pseudocapacity,  $C_{ads} = j/v$  (a), and coverage,  $\theta$ , (b) as a function of the electrode potential for different values of the lateral interaction parameter, g = r/RT, for an electrosorption process that follows Frumkin isotherm. (c) adsorption isotherm for g = -6. Other parameters are: c = 1 M,  $q_{ML} = 240 \ \mu Ccm^{-2}$  and T = 298 K.



**Figure 14** Plot of peak width at half height for a pseudocapacity peak that follows a Frumkin isotherm as a function of the lateral interaction parameter, g = r / RT.

Figure 14 shows a plot of  $\Delta E_{1/2}$  as a function of the adimensional parameter, *g*. The plot shows that while the functional relationship is rather complex, the actual result is an almost linear relationship which allows to easily calculate the value of the lateral interaction parameter from the measured width of the peak.

#### **Coadsorption Phenomena**

In the previous section we considered the case of the adsorption of only one species, taking as representative example hydrogen adsorption. Nowadays, it is known that the so called hydrogen peaks for the voltammetry of platinum (Figure 11) involve also anion adsorption, as explained above. Many times these two species compete for the same surface sites and, during a positive potential excursion, adsorbed hydrogen is displaced by the anion adsorption involving charge transfer, in a coupled process. The adsorption isotherm for hydrogen and anion competing for the same sites, are given by the following equations:

$$\frac{\theta_H}{1-\theta_H-s\,\theta_A} = c_H \exp\left[-\frac{F}{RT}\left(E-E_H^0\right) - g_H\,\theta_H\right]$$
[57]

$$\frac{\theta_A}{\left(1-\theta_H-s\,\theta_A\right)^s}=c_A \exp\left[\frac{F}{RT}\left(E-E_A^0\right)-g_A\,\theta_A\right]$$
[58]

Where  $E_A^0$  and  $E_H^0$  are the standard potentials for the processes of anion and hydrogen electrosorption, respectively,  $g_A$  and  $g_H$  are the dimensionless lateral interaction parameters, *s* is the number of surface atoms occupied by one anion and the rest of symbols have the same meaning as above. We have not considered the possibility of crossed lateral interaction terms,  $g_{AH}\theta_H\theta_A$  to simplify the algebra. These equations can be solved numerically to obtain  $\theta_H$  and  $\theta_A$  as a function of potential. Then, the current will be given by:

$$j = \frac{dq}{dt} = \frac{dq}{dE} \frac{dE}{dt} = v \frac{dq}{dE} = vq_{ML} \left(\frac{d\theta_A}{dE} - \frac{d\theta_H}{dE}\right)$$
[59]

since an increase in the coverage involves positive currents for the anion but negative currents for the hydrogen. Figure 15 shows an example of this situation for a case where hydrogen adsorption has a repulsive lateral interaction but the anion experiences attractive lateral interactions. Different anion concentrations are considered to exemplify the effect of the overlapping of both adsorption steps. For the lowest anion concentration both processes are well separated. However, as anion concentration increases, the peak shifts to more negative potentials and the two processes overlap. Figure 15B illustrates in more detail the situation for the highest anion concentration by plotting separately  $d\theta_A/dt$  and  $d\theta_H/dt$  as well as  $\theta_A$  and  $\theta_H$  as a function of potential. It can be seen how anion adsorption induces hydrogen desorption resulting in a change of slope in the curve  $\theta_H$  vs *E* and a peak in  $d\theta_H/dt$ . This example is interesting to illustrate that the deconvolution of the two adsorption processes is not a simple task.

An extreme situation is obtained when the peak potential for anion adsorption is lower than that for hydrogen desorption. In this case, the two processes merge into one peak and equations [57] and [58] can simplified considering that

$$\theta_H + \mathbf{s}\theta_A = \mathbf{1} \tag{60}$$

In this case, by dividing [57] by [58] and substituting [60] we obtain:

$$\frac{\theta_A}{\left(1-s\,\theta_A\right)^s} = \frac{c_A}{c_H^s} \exp\left[\frac{(1+s)F}{RT}\left(E-E^0\right) - g'_A\,\theta_A\right]$$



**Figure 15** a) Model cyclic voltammograms obtained by solving the set of equations (57)-(58) with the following values of the parameters:  $g_H = 6$ ,  $E_H^0 = 0.15$  V,  $c_H = 0.1$  M,  $g_A = -3$ ,  $E_A^0 = 0.1$  V and  $c_A$  varying from 0.001 to 1 M. b) variation of coverage of H (black line) and A (red line) as a function of potential and their contribution to the overall current, for the particular case of  $c_A = 1$  M.

Where

$$E^{0} = \frac{E^{0}_{A} + sE^{0}_{H} - sg_{H} \frac{RT}{F}}{1 + s}$$

And

$$g'_A = g_A + s^2 g_H$$

This means that the situation reduces to a simple Frumkin isotherm with parameters that are combination of those of hydrogen and anion and the process can be represented by:

$$M-H + A^{-} \leftrightarrows M-A + H^{+} + 2e$$

This case is illustrated in Figure 16. When  $E_H^0 < E_A^0$  the two processes are well separated, giving two well resolved peaks. However, when  $E_H^0 > E_A^0$ , the two processes merge into a single peak. Same conclusion is obtained from Figure 16(b), observing the variation of the hydrogen and anion coverage as well as their independent contribution to the overall current.

#### Cyclic Voltammetry of Platinum Single Crystal Electrodes. Voltammetry as a Surface Sensitive Characterization Technique

The voltammetry of platinum provides a representative example of the different phenomena that characterise the voltammetric response in the presence of adsorption processes, as discussed in the previous paragraphs. Figure 17 shows the voltammetry of the three platinum basal planes in sulphuric and perchloric acid solutions. The single crystal surfaces are obtained by cutting a crystal in a well-defined orientation with respect to the crystallographic axis as indicated in the insets of Figure 17. The first remarkable



**Figure 16** a) Model cyclic voltammograms for the competitive adsorption of hydrogen and anion, obtained by solving the set of equations (57)-(58) with the following values of the parameters:  $g_H=6$ ,  $c_H=0.1$  M,  $g_A=-3$ ,  $c_A=0.1$  M,  $E_A^0=0.1$  V and  $E_H^0$  varying from -0.2 to 0.4 V, as indicated in the figure. B) variation of coverage of H (black line) and A (red line) as a function of potential and their contribution to the overall current, for the particular cases of  $E_H^0 = -0.2$  V and  $E_H^0 = 0.4$  V.

observation is that the voltammetric profile is very sensitive to the crystallographic orientation of the electrode. This turns cyclic voltammetry into a very sensitive surface characterisation. The second observation is that the voltammetric profile is also very sensitive to the composition of the electrolyte. Different peaks are observed in the voltammograms that, as discussed above, correspond to different adsorption processes. The effect of the anion is to 'compress' the hydrogen adsorption states towards lower potentials. Let's start discussing first the voltammogram corresponding to Pt(111) in perchloric acid (red curve in Figure 17(a)). Two well differentiated adsorption regions are observed, between 0.06 V and 0.40 V and between 0.55 V and 0.85 V. The first one corresponds to hydrogen adsorption/desorption and the second one corresponds to OH adsorption/desorption. While the



Figure 17 Cyclic voltammograms corresponding to three platinum single crystal electrodes in 0.5 M sulphuric (blue) and 0.1 M perchloric acid (red) solutions: a) Pt(111); B) Pt(100) and C) Pt(110). Scan rate: 50 mV s<sup>-1</sup>.

hydrogen adsorption is a relatively featureless broad peak, the OH adsorption is characterised by a very sharp peak at 0.8 V overlapped with a broader adsorption state that extends to 0.55 V. The existence of two processes in this region have been explained in terms of the existence of two water states in the bulk electrolyte, structured and unstructured water, originated from the interaction between the water molecules and the anion species. An alternative explanation is that the sharp peak corresponds to a disorder – order phase transition. Integration of the current provides the charge involved in the adsorption process, which, as discussed above, allows an easy measure of the H and OH coverage on the surface, as a function of the potential, because, at single crystal electrodes adequately handled, the number of surface atoms is well known.

When sulphuric acid is used instead of perchloric acid, the hydrogen region remains unaffected while the OH region is substituted by a new adsorption state located at lower potentials, between 0.30 and 0.60 V, overlapping with the hydrogen region. These states correspond to sulphate adsorption, as has been identified by IR spectroscopy and thermodynamic analysis. Similarly to the case of OH adsorption on Pt(111), sulphate adsorption also features a very sharp spike at 0.45 V. In this case, there is wide agreement that this spike correspond to a phase transition in the sulphate adlayer from a disorder adlayer to an ordered  $\sqrt{3} \times \sqrt{7}$  adlayer. The structure of the latter has been identified with STM. Formation of the ordered adlayer is very sensitive to the quality of the surface and therefore, the height of this peak is a good measure of this quality. The peaks at around 0.75 V have been attributed to an order – disorder transition forming a disordered sulphate adlayer at potentials higher than the peak that involves a further increase of sulphate coverage.

In the case of Pt(100) in perchloric acid hydrogen and OH adsorption processes are not so well separated. It is usually assumed that the broad wave between at 0.50 V and 0.70 V correspond to OH adsorption/desorption while currents below 0.50 correspond to hydrogen adsorption/desorption. In the case of sulphuric acid electrolyte, a sharp peak at 0.38 V is observed, corresponding to the desorption of hydrogen coupled with sulphate adsorption. Then, when the potential is scanned positively, it is the sulphate anion which forces the desorption of the hydrogen in what is effectively a displacement reaction:

$$Pt - H + HSO_4^- \leftrightarrows Pt - SO_4 + 2H^+ + 3e$$

The small peak at 0.30 V corresponds to adsorption processes on small amount of surface defects which are intrinsic to this particular surface orientation. The situation is very similar for Pt(110), although this surface is less well defined. In perchloric acid, although two peaks are observed it is usually assumed that both correspond to the coupled desorption of hydrogen and OH adsorption, on surface sites of different geometries. In sulphuric acid only a large peak is observed for Pt(110) corresponding to the coupled hydrogen desorption and anion adsorption processes.

Stepped surfaces can be prepared by cutting the crystal at orientations between two basal planes. In this way, when the crystal is cut in an orientation between (111) and (110), stepped surfaces with (111) terraces and (110) steps are obtained as depicted in the inset of **Figure 18**. The length of the terrace can be selected by changing the angle during cutting the crystal. This example has been selected here since it provides an excellent illustration of the use of cyclic voltammetry as a surface characterisation technique. When the length of the terrace is decreased, a new peak arises around 0.12 V. By measuring the charge corresponding to this peak, as illustrated by the shadowed region in the voltammogram of Pt(775), it can be demonstrated that the charge under this peak is proportional to the step density (number of steps per unit length measured perpendicular to the step), as shown in **Figure 19**.



Figure 18 Cyclic voltammograms recorded with different Platinum stepped surfaces in 0.1 M sulphuric acid. n indicates the number of atomic rows on the terrace: Pt(S)[n(111)x(111)]. 50 mV s<sup>-1</sup>.



Figure 19 Plot of charge associated to step sites as a function of the step density.

The deviations observed at large step densities are likely due to the interaction between adjacent steps. Therefore, by measuring the charge under this peak one can easily calculate the contribution of (110) steps present on the surface. In this case, hydrogen adsorption is used as a surface sensitive probe but the idea can be extended to other probes such as metal underpotential deposition or the irreversible adsorption of adatoms such as bismuth or germanium. The first one has been demonstrated to be an excellent probe for (111) sites while the second is valid for (100) sites. Another interesting observation in **Figure 18** is that the sharp peak at 0.50 V, due to the sulphate phase transition, disappears as soon as some steps are introduced on the surface. The peaks are still visible for n = 14 but disappear for n < 10, giving an idea about the length of the terrace necessary to obtain the  $\sqrt{3} \times \sqrt{7}$  structure.

## Fit of Voltammetric Peaks to Adsorption Peaks

The equations discussed above can be used to fit Frumkin adsorption isotherm to some real experimental data. The easiest way is to measure directly from the peak the relevant parameters such as charge, peak potential and width. Then, with the equations above, some model voltammetric data can be calculated and compared with the experimental data. Figure 20 shows examples of such calculations. Alternatively, one can manipulate the data to obtain a linear representation that allows to use a linear least square fitting procedure to extract the interaction parameter. The most convenient way of doing this is to integrate the data to extract coverage following equation [41]. With these data, adsorption energies can be calculated using

$$\Delta G = -nFE = \Delta G^{0'}(\theta) + RT \ln \frac{\theta}{1-\theta}$$
[61]



**Figure 20** Fit of a Frumkin isotherm to the cyclic voltammogram of a) Pt(111) and B) Pt(100) in 0.1 M HClO<sub>4</sub>. Scan rate: 50 mV s<sup>-1</sup>. Positive and negative currents have been averaged and double layer currents subtracted. Fitting parameters are: a) g=11.8;  $E^0=0.28$  V;  $q_{ML}=240 \ \mu \text{Ccm}^{-2}$  b) g=5.5;  $E^0=0.43$  V,  $q_{ML}=209 \ \mu \text{Ccm}^{-2}$ .

Where  $\Delta G^{0'}$  is a formal adsorption energy which is, in general, a function of the coverage. This equation has been called a generalized adsorption isotherm. It derives from Langmuir isotherm considering that all deviations from the ideal behaviour are included in the term  $\Delta G^{0'}$ . Frumkin isotherm would be a particular case where

$$\Delta G^{0'} = \Delta G^0_{\theta=0} + r\theta \tag{62}$$

Then,  $\Delta G^{0'}$  can be calculated from

$$\Delta G^{0'}(\theta) = -nFE - RT \ln \frac{\theta}{1-\theta}$$
[63]

and plotted as a function of the coverage. If the plot turns outs to be linear, it would be a proof that the Frumkin adsorption isotherm is satisfied and the slope will give a measure of the lateral interaction parameter.

When there are multiple peaks in the voltammogram, there are two possibilities:

- -they can be originated from individual adsorption states such as the overall current is just the addition of different processes following identical equations as described above. This would be the case of a polycrystalline surface with independent contributions from different facets.
- -Or they can be due to different processes competing for the same adsorption states, as would be the case of hydrogen and anion adsorption on platinum. In this case, starting with the surface covered with a monolayer of hydrogen, as the potential is increased, hydrogen is oxidatively desorbed. When the surface sites are freed, if the applied potential is sufficiently high, anions can be oxidatively adsorbed. Hydrogen desorption and anion adsorption can take place in separate potential ranges as occur on the Pt(111) surface or they can overlap, in which case competitive adsorption has to be taken into account, as discussed previously.

The case of non-competing multiple adsorption states has been used in the past to explain the voltammetry of polycrystaline platinum and platinum nanoparticles, even single crystal platinum electrodes. To simplify the fitting process the use of Lorentzian peaks instead of the equation [52] has been proposed. Figure 21 gives one example of this.

#### **Ideally Polarizable Electrodes**

Another situation worth mentioning is the case where the electrode surface can be considered ideally polarizable, that is, no faradaic process takes place and only the capacitive charge flows during the potential scanning. The electrochemical interphases always behaves as a capacitor storing charge that varies as a function of the potential. An excess or defect of electronic charge in the metal side of the interphase is balanced by ionic charge of opposite sign on the electrolytic side. As the potential is increased, the charge



Figure 21 Fit of the voltammetric current for a polycrystalline platinum to several pseudo capacity peaks following a Frumkin adsorption isotherm. Taken from J Solla-Gullon et al. (2008) Phys.Chem.Chem.Phys, 10, 1359–1373.

separation increases. There is one particular potential value where the charge separation cancels and this is the potential of zero charge. In the absence of kinetic effects, the charge separation is only a function of the electrode potential and therefore:

$$j = \frac{dq}{dt} = \frac{dq}{dE} \frac{dE}{dt} = v \frac{dq}{dE}$$
[64]

In general, the charge is also function of the composition of the solution, but the voltammetric experiment is performed at constant composition and therefore the derivative above is, strictly speaking, a partial derivative.

$$j = v \left(\frac{\partial q}{\partial E}\right)_{\mu_i} = v C_d \tag{65}$$

where  $C_d$  is the differential capacity. The latter is more usually calculated with electrochemical impedance spectroscopy (EIS) methods, because these allow to discriminate the existence of kinetic effects. EIS experiment is usually performed potentiostatically and therefore a set of discrete values of  $C_d$  are obtained for different potentials. In the absence of kinetic effects, identical results should be obtained with cyclic voltammetry and EIS, with advantage of the former that it is usually a faster experiment providing a continuous function of  $C_d$  vs. potential.

**Figure 22** shows some cyclic voltammograms for a Au(111) electrode in perchloric acid solutions. Gold, as a difference with platinum, does not adsorb hydrogen. In addition, perchlorate anions adsorbs only very weakly and therefore, the voltammograms shown in **Figure 22** can be considered a good example of an ideally polarizable interphase. The increase of the current at high potentials corresponds to the oxidation of the surface and therefore, they mark the limit of the potential region where the interphase can be considered ideally polarizable. One interesting feature of the voltammogram in **Figure 22** is the minimum observed around 0.22 V, which corresponds to the minimum in the differential capacity predicted by Gouy-Chapman-Stern theory of the double layer. According to this theory, a minimum in the differential capacity should be observed at the potential of zero charge.

#### Kinetic Effects in the Adsorption Pseudocapacity

So far we have considered reversible processes where the rates of adsorption and desorption are equal. The equality of rates leads to the adsorption isotherms as we have discussed in the previous section. In this case, it is assumed that rates of adsorption and desorption are so fast that the equilibrium adapts almost immediately to the potential scan and the system is always in equilibrium. However, when scan rate is too fast or rate constant is too low, the process cannot adapt to the fast change of potential and the adsorption equilibrium is broken. This is reflected in the voltammogram as a lack of symmetry through the potential axis as seen in the platinum oxidation process in Figure 11.

The kinetic effect on adsorption processes can also be introduced into the approach described above based on the Frumkin isotherm. For the case of the oxidative adsorption of an anion:

$$A^- + M \rightleftharpoons A - M + e \tag{66}$$



**Figure 22** Cyclic voltammograms corresponding to a Au(111) single crystal electrode in HClO<sub>4</sub> solutions of different concentration as labelled in the figure.

by considering the following differential equation:

$$\left(\frac{d\theta}{dt}\right) = k^0 \left[\frac{c}{c^0}(1-\theta)\exp\{(1-\alpha)fE - \beta g\theta\} - \theta \exp\{-\alpha fE + (1-\beta)g\theta\}\right]$$
[67]

While for the reductive adsorption of a cation, hydrogen adsorption, for example, we would write:

$$H^{+} + M + e \rightleftharpoons H - M \text{ and } \left(\frac{d\theta}{dt}\right) = k^{0} \left[\frac{c}{c^{0}}(1-\theta)\exp\{-\alpha f E - \beta g\theta\} - \theta \exp\{(1-\alpha)f E + (1-\beta)g\theta\}\right]$$
[68]

In these equations,  $k^0$  represent the standard rate constant for the adsorption/desorption process and  $\alpha$  and  $\beta$  are Bronsted type symmetry factors considering the effect of potential and lateral interactions, respectively, on the energy barrier for the transition between reactants and products. Under equilibrium conditions  $\frac{d\theta}{dt} = 0$  and the equations [67] and [68] reduces to the Frumkin isotherm, equation [50]. For a cyclic voltammetric experiment, the electrode potential varies linearly with time and this time dependence impedes the exact solution of the differential equation. However, this can still be easily solved by numerical methods. **Figure 23(a)** shows some cyclic voltammograms obtained by solving equation [67] for g=0 (Langmuir isotherm) and different values of the ratio  $k^0/v$ . It is clear that introduction of kinetic limitations results in breaking the symmetry of the voltammogram across the potential axis and a displacement of the peak potential. **Figure 23(b)** shows the effect of different values of the lateral interaction parameter. An interesting effect of the lateral interaction parameter is revealed when the upper limit of the potential scan is limited in such a way that completion of the adlayer is not achieved. In this case, the peak potential of the subsequent negative scan depends on the value of lateral interaction, as shown in **Figure 24**. Lateral repulsive interactions (**Figure 24(a)**) makes the desorption of the adlayer easier (peak potential more positive) when the coverage attained in the positive scan is higher while the opposite is observed for attractive interactions (**Figure 24(b**)).

The most important information in the voltammograms of Figure 23(a) is obtained from the dependence of the peak potential with the scan rate. The following treatment closely follows that proposed by Laviron. Equations [67] and [68] can be rewritten in terms of adimensional parameters to show that the adimensional current, defined by:

$$\psi = \frac{jRT}{q_{ML}vF}$$
[69]



**Figure 23** Kinetic effects on the pseudocapacity peak: A) effect of the rate constant for the absence of lateral interactions (Langmuir isotherm) and B) effect of the lateral interaction parameter (Frumkin isotherm) for  $\log(\nu/k^0) = 1$ .  $q_{ml} = 240 \ \mu \text{Ccm}^{-2}$  in both plots.



**Figure 24** Effect of upper potential limit on the pseudocapacity peak for the case of A) repulsive lateral interactions (g = 5) and. B) attractive lateral interactions (g = -3).  $q_{ML} = 240 \ \mu C cm^{-2}$ , log ( $\nu/k^0$ ) = 1.



**Figure 25** Plot of peak potential as a function of log(v) for an electrosorption process (circles). Solid lines represent theoretical curves calculated from equation 68 No se encuentra el origen de la referencia. plotted as a function of the adimensional variable –log(m). The theoretical curves allow calculation of the rate constant from the horizontal displacement between experimental and theoretical values.

is a function of the adimensional parameter *m* defined as:

$$m = \frac{k^0 RT}{vF}$$
[70]

and not on the independent values of  $k^0$  and v. In this way, the following strategy can be followed to calculate  $k^0$  from experimental values of peak potential measured for different scan rates. A theoretical plot of peak potential as a function of log (*m*) can be elaborated from the numerical solution of equation [67] or [68]. Experimental values of peak potential can be plot also in this graph as a function of log(*v*). Figure 25 shows the result of this plot. Because

$$-\log(m) = \log(v) - \log\left(\frac{RTk}{F}\right)$$
[71]

Plotting as a function of log(v) or plotting as a function of log(m) differ only on a horizontal displacement of -log(RTk/F). Hence, the value of  $k^0$  can be calculated from the displacement between the experimental points and the theoretical curve, as shown in Figure 25

## **Oxidation of Small Organic Molecules**

In the previous paragraphs we have made a clear separation between two main groups of processes: those processes where the reactant comes from solution and therefore, the process is limited by its diffusion to the electrode surface, and those processes that are limited by the availability of free adsorption sites on the surface and determined by an adsorption isotherm. We consider in this section a new group of processes where the distinction between the two situations described above is not so clear. We take as an example the oxidation of small organic molecules. These reactions are very relevant for their application in the anode of fuel cells. **Figure 26** shows as an example the oxidation of methanol on a platinum single crystal surface, Pt(100). The situation is very similar for other organic molecules such as formic acid, ethanol, ethylene glycol, etc. or other platinum surfaces. In this case, methanol, usually at quite high concentration, proceeds from the bulk of the solution to be oxidised at the surface of the electrocatalyst:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e$$
<sup>[72]</sup>

However, the reaction is not limited by its diffusion as can be verified by recording the voltammogram under conditions of force convection (rotating disk electrode). Under these conditions, the peak at 0.75 V is still present and current almost does not change with the rotation rate. Therefore, the reason for the decay of the current at high potentials is not the limit of mass transport. In addition, current are much lower than those predicted from equations [24] or [25] (for a single electron transfer current should



Figure 26 Oxidation of methanol on Pt(100) electrode surface in 0.1 M HClO<sub>4</sub> + 0.1 M CH<sub>3</sub>OH. Scan rate: 50 mV s<sup>-1</sup>.

be above 14 mA cm<sup>-2</sup>). Current is also nearly invariant with the scan rate, indicating that the process is clearly different from what has been discussed above. Other striking feature of this voltammogram is the existence of positive currents (oxidation) in the negative going sweep. In fact, the electrode works always as an anode, irrespective of the sweep direction. In this regards, the often employed terminology that uses the term 'cathodic sweep' to refer to the negative scan would be misleading.

Reaction [72] involves the transfer of six electrons and therefore must imply a rather complex mechanism. In addition, in the case of the oxidation of organic molecules at platinum the following dual path mechanism is usually considered:

$$CH_{3}OH \rightarrow intermediates \xrightarrow{E_{1}^{0}} CO_{2}$$

$$CH_{3}OH \rightarrow CO \xrightarrow{E_{2}^{0}} CO_{2}$$

$$(73)$$

Because  $E_2^0 > E_1^0$ , carbon monoxide is considered as a poisoning intermediate, since it blocks the surface and inhibits the oxidation through the more active first route. In this way, when the scan is started at low potentials, the surface is almost completely blocked by adsorbed CO and therefore, shows little activity. When a sufficiently high 'ignition potential' is attained, adsorbed CO is oxidised, freeing some surface sites that become immediately active for the oxidation of methanol through the first route and the current grows very fast. However, when the potential is further increased, a maximum is attained after which the current decreases again. The inhibition of the reaction at potentials above 0.75 V is due to the competition of adsorbed species that blocks the surface. There is some debate in the literature about the exact nature of this adsorbed species, but these could be OH adsorption, water adsorption or oxide formation, depending of each particular experimental situation. When the scan direction is reversed, these inhibiting species are desorbed and the current grows again. Because CO formation does not take place at high potentials, current remains higher in the negative sweep than in the positive one, until CO formation takes place and the electrode is blocked again. The relative height of the peaks in the positive and negative sweep depend on the interplay of variables like rate of CO formation, CO oxidation and of methanol oxidation through the active (first) route.

#### **Concluding Remarks**

In a cyclic voltammetric experiments the current is recorded as a function of the electrode potential, while this is scanned at constant rate between two potential limits. Two main groups with different behaviour can be distinguished.

- For those processes where mass transport is a significant factor, a peak in the voltammogram is obtained, caused by the increase of the thickness of the diffusion layer.
- For reversible processes, equilibrium condition (Nernst Law) is satisfied at the surface of the electrode. In this case, peak potential does not depend on the scan rate, while peak current varies linearly with the square root of the scan rate.
- When kinetic limitations are significant, calculation of the relevant parameters of the voltammetric curve needs a detailed knowledge of the operating mechanism. In the case of single electron transfer (or first electron transfer limiting the rate of the reaction) and very slow kinetics, the peak current is again proportional (although with a slope that is different than that of the

reversible situation) to the square root of the scan rate. Peak potential is, in this case, also a function of the scan rate. Variation of peak potential with scan rate allows determination of the rate constant while peak current does not depend on the rate constant.

• For electrosorption processes, the voltammetric shape is determined by the adsorption isotherm. For a reversible process, symmetric peaks are obtained. Peak potential gives a measure of the energy of adsorption. Peak widths are related with the existence of lateral interactions (for homogeneous surfaces). The charge under the peak allows determination of amount of adsorbed species (coverage). When kinetic limitations exist, the peaks become asymmetric and peak potential depends on scan rate. As before, from the variation of peak potential with the scan rate, the value of the rate constant can be determined.

Cyclic voltammetry is a very powerful electrochemical technique that allows a fast, easy and affordable study of the reactivity of electroactive species. However, we have to emphasize once more that analysis of voltammetric data requires knowledge of the particular mechanism taking place. Application of the equations described above without ensuring their applicability may lead to meaningless results. The study of the variation of the voltammogram with different parameters like scan rate, concentration of reactants or even a change in hydrodynamic conditions (not treated in this review) can provide information about the mechanism. However, most of the time, voltammetric information needs to be complemented with other, non-electrochemical, techniques with chemical or structural specificity. In particular, spectroscopic methods can be coupled to electrochemical experiments to provide very valuable information about nature of reaction intermediates as a function of the electrode potential in the course of the electrochemical reaction.

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# **Differential Capacitance Measurements on Passive Films**

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## Glossary

 $C_{\rm d}(\omega, U_{\rm E})$  Differential capacitance in F cm<sup>-2</sup>. **DOS**/N(E) Density of electronic states distribution in  $eV^{-1}$  cm<sup>-3</sup>.  $E_{CL} E_V$  Conduction, valence band (mobility) edge in crystalline (amorphous) SC. *E*<sub>F</sub> Fermi Level.  $E_f^0$  (El) Fermi level of the c-SC in the electrochemical scale.  $E_{g}$  Band gap (mobility gap) of c-SC (a-SC) in eV.  $E_{\omega}$  Cutoff energy level in eV.  $F(\Delta \Phi, \omega)$  First-order coefficient with respect to  $\tilde{\varphi}$  in the Taylor's expansion of  $\delta \rho$ .  $f_{\omega}(\mathbf{x}(\Delta \Phi_{\rm SC}))$  Trial functions to fit  $C_{\rm d}(\omega, U_{\rm E})$ .  $G_{SC}(\omega, U_E)$  SC conductance in S cm<sup>-2</sup>.  $g_{\omega}(x(\Delta\Phi_{SC}))$  Trial functions depending on the electrode potential and angular frequency to fit the conductance versus applied potential curves. h Planck's constant.  $k_{\rm B}$  Boltzmann's constant.  $k_{\rm SC}$  Test function of SC spatial homogeneity.  $m^*$  Effective mass for DOS calculation in SC.  $M_{C/V}$  Number of equivalent minima (maxima) in the conduction (valence) band.  $N_{\rm C}$  (and  $N_{\rm V}$ ) Effective DOS at the SC conduction (valence) band edge.  $N_{\rm D/A}$  Donor (acceptor) concentration in cm<sup>-3</sup>.  $Q_{\rm SC}$  Accumulated charge in the space charge region. SC Semiconductor. c-SC Crystalline SC. a-SC Amorphous SC. SSC (Ag/AgCl) Silver/silver chloride reference electrode (Sat. KCl). T Absolute temperature.  $U_{\rm E}$  Electrode potential (in V vs. reference electrode).  $U_{\rm fb}$  Flat band potential (in V vs. reference electrode).  $X^{0}_{SC}$  Space charge width into the SC electrode at 1 V of band bending.  $X_{SC}$  Space charge region in SC.  $Y_{SC}$  Differential admittance of the interface in S cm<sup>-2</sup>.  $\delta \rho(\omega, \phi)$  AC variation of space region charge density.  $\Delta \Phi^*$  The potential drop equal to  $\Delta \Phi_{SC}$  when  $\Delta \Phi_{SC} > \Delta \Phi_{er}$  otherwise it is equal to  $\Delta \Phi_{ec}$ .  $\boldsymbol{\varepsilon}$  Dielectric permittivity of semiconductor in F cm<sup>-1</sup>.  $\rho(\Delta \Phi)$  Volumetric space charge density in the SC.  $\tilde{\boldsymbol{\phi}}$  AC component of the electrode potential.  $\Delta \Phi_{\rm C}$  Band bending at a characteristic point  $x_{\rm C}$ .

 $\Delta \Phi_{g}$  Band bending at  $x_{g}$ .

 $\Delta \Phi_H$  Potential drop across Helmholtz double layer.

 $\Delta \Phi_{\rm SC}$  Potential drop (or band bending) across SC.

 $\Delta \Phi_{
m SC/El.}$  Total potential drop across the SC/El. interface.

 $\tau$  Relaxation time for the capture/emission of electrons from electronic states E below E<sub>F</sub>.

 $\tau_0$  Prefactor  $(10^{-10} - 10^{-14} \text{ s}^{-1})$  in the relaxation time expression  $\tau$ .

 $\omega$  Angular frequency of A.C. signal.

## Introduction

The onset of a passivity condition on the surface of most common metals of low thermodynamic nobleness is the key aspect for the stabilization of metallic surfaces against corrosion processes usually occurring in natural and industrial environments. It is now worldwide accepted that such a kinetic protection of the underlying metallic surfaces is essentially dependent on the protection action of a thin or thick surface protective layer that, in many cases, is formed by simple exposure to the electrolytic environment or intentionally grown to by anodizing in suitable electrolytic solutions. Regardless of the growth process, the ultimate corrosion resistance of the underlying metallic surfaces strongly depends on the physicochemical properties of the passive films formed in each environment, so that it is not surprising that the study of the passive films has been one of the most fertile fields of research since the initial observations on the existence of a "peculiar voltaic condition of iron" reported in 1836 by C. T. Schoenbein in his letter to M. Faraday.<sup>1</sup>

In the attempt to reach a deeper knowledge on the corrosion protection action of the passive film, a large research effort has been devoted to gather useful information on the nature and properties of passive films by using numerous in situ and ex situ techniques. At these aims very powerful ex situ techniques (Auger, ESCA, XPS, SIMS, RBS, GDOES, etc.) have been employed to characterize the passive film grown on different metals and alloys. However, it exists a large agreement that in situ techniques, allowing a potentio-static control during the physicochemical characterization of the passive film, are preferable by considering that, in many cases, very thin passive films (1–2 nm thick) may be altered in the transfer process from an electrochemically controlled environment to vacuum conditions. According to this electrochemical analytical techniques are welcome in passivity studies also in the characterization of solid-state properties of passive films.<sup>2–15</sup>

It is a matter of fact that in many cases the passive films and corrosion layer grown on metallic substrates in different environments display semiconducting or insulating behavior with few, but important exceptions, of transition metal oxides showing metallic conductivity. According to this some of the techniques typical of the semiconductors electrochemistry have been exploited to get information on the semiconducting behavior of passive films and corrosion layers. In this article we will describe the differential admittance technique (DAT), a well-established technique in the field of semiconductor electrochemistry, aimed to the characterization of electronic properties of passive film having semiconducting and/or insulating properties.<sup>15–26</sup> The use of such technique is mainly aimed at locating the characteristic energy levels of the semiconductor/electrolyte (SC/EL) junction: the Fermi energy level,  $E_{\rm F}$ , and the correlated energy band edge (conduction band edge,  $E_{\rm C}$ , or valence band edge,  $E_{\rm V}$ , for n- and p-type SC, respectively).

The location of these characteristic energy levels, in a suitable energy scale (electrochemical and/or absolute scale), is a preliminary task for a better understanding of the possible mechanisms of electrons and ions transfer processes, occurring at the metal/passive film and passive film/electrolyte interfaces. In fact both these processes play a fundamental role in the mechanism of film dissolution and breakdown as well as in determining the rate of localized corrosion process too.<sup>27–34</sup> As for the dissolution processes of a semiconducting film the thermodynamic predictions based on the theory of SC/El. interface can help to predict the possible reactions occurring at this interface with the participation of the surface film itself. In the case of localized corrosion the rate of electrons transfer process, necessary to sustain the cathodic reactions coupled to anodic localized process, depends on a complex interplay between the nature of redox couple (through the redox potential,  $E_{red/ox}$ , as well as the exchange current density parameter, i<sub>0</sub>) present in solution, the corrosion potential,  $U_{corr}$ , and the flat band potential,  $U_{fb}$ , of the semiconducting passive film and its conductivity (p- or n-type).<sup>35–38</sup>

The use of DAT for the location of characteristic energy levels rests on the validity of the underlying theory of metal/semiconductor junctions based, in the case of crystalline semiconductors (c-SCs), on the classical theory of Mott and Schottky.<sup>39,40</sup> This last approach, initially used for solid-state Schottky barrier, has been validated also for the electrolyte/semiconductor junction by the classical papers of Boddy, Brattain, and Dewald.<sup>41–44</sup> This last author studied extensively the structure of single crystal c-ZnO/electrolyte interface by testing the validity of M-S plots and so opening a new route to the characterization of SC/electrolyte interface.<sup>43,44</sup>

In the case of passive films further complications must be taken into account due to the disordered or amorphous nature of such films as well as to their extreme thinness. Both these aspects are peculiar of the passive films so that, in the following, after a brief description of the classical theory of the c-SC/electrolyte interface a more detailed description of the amorphous semiconductor (a-SC)/electrolyte interface will be carried out together with the presentation of some recent studies pertaining to such an interface.<sup>45–49</sup>

#### **SC/EI.** Interface

As aforementioned most of passive layers grown on metals and alloys behave like semiconducting or insulating materials. Accordingly, a widespread use of the theory of c-SCs has been made to discuss the behavior of passive film/electrolyte junction. Such an extension is not always critically checked by taking into account whether the hypothesis underlying the theory of bulk crystalline materials is also valid in the case of the thin passive films investigated. Moreover, in spite of the existing evidence that, in many cases, the passive films are amorphous or strongly disordered such an information is not usually taken into account to explain the admittance behavior of the junction neither to modify the traditional approach to the study of the interface by using the more pertinent theory of a-SC Schottky barrier. For a better understanding of the influence of amorphous nature on the differential admittance behavior of passive films a brief introduction on the general structure of SC/El. interface will be given to derive the most important properties of such an interface.

The main differences between the metal/electrolyte interface and the SC/electrolyte interface are related to the different electronic structures of the electrode.<sup>16–26</sup> In fact, differently than in a metal, a space charge region in the semiconductor is formed in order to neutralize the excess of charge lying in the solution side. In Fig. 1 we report the schematic Galvani potential distribution across an n-type SC/El. interface in absence of specific absorption of ions in solution. According to Fig. 1 the total potential drop across the SC/El. interface is given by:

$$\Delta \Phi_{\rm SC/EL} = \{ \Phi_{\rm SC}(\infty) - \Phi_{\rm SC}(0) \} + \{ \Phi_{\rm SC}(0) - \Phi_{\rm El}(-\infty) \}$$
(1)

where the first term in the bracket of Eq. (1) represents the Galvani potential drop from the bulk (zero electric field) to the surface of SC/El. junction, while the term in the second bracket is the Galvani potential drop occurring into the compact and diffuse double layer (if any) of the electrolytic solution. In presence of concentrated electrolyte the diffuse double layer is negligible and we can rearrange the previous equation as:

$$\Delta \Phi_{\rm SC/EL} = \Delta \Phi_{\rm SC} + \Delta \Phi_H \tag{2}$$

where  $\Delta \Phi_{SC}$  and  $\Delta \Phi_{H}$  represent the potential drop in the space charge region of the semiconductor and the Helmholtz double layer, respectively. The fundamental property of the interface is the differential capacitance,  $C_d$ , which is defined as the relation between the variation of accumulated change in the space charge region and the variation of polarization potential:

$$C_{\rm d} = \frac{\partial Q_{\rm SC}}{\partial \Delta \Phi_{\rm SC/EL}} \tag{3}$$

where  $Q_{SC}$  is the accumulated charge in the space charge region. The differential capacitance can be divided in two contributions, one coming from the semiconductor,  $C_{SC}$ , and one coming from the electrolyte,  $C_{H}$ :

$$\frac{1}{C_{\rm d}} = \left(\frac{\partial Q_{\rm SC}}{\partial \Delta \Phi_{\rm SC/EL}}\right)^{-1} = \left(\frac{\partial Q_{\rm SC}}{\partial \Delta \Phi_{\rm SC}}\right)^{-1} + \left(\frac{\partial Q_{\rm SC}}{\partial \Delta \Phi_{\rm H}}\right)^{-1} = \frac{1}{C_{\rm SC}} + \frac{1}{C_{\rm H}}$$
(4)



Fig. 1 Schematic Galvani potential distribution across an n-type SC/El. interface in absence of specific absorption of ions in solution.

The static (zero frequency) differential capacitance of the space charge region of the semiconductor can be calculated from the equation<sup>50</sup>:

$$C_{\rm SC} = -\varepsilon \frac{d}{d\Delta \Phi_{\rm SC}} \left( \frac{d\Delta \Phi}{dx} \Big|_0 \right) \tag{5}$$

where  $\Delta \Phi$  is equal to  $\Phi_{SC}(\infty) - \Phi_{SC}(x)$ . In real experimental conditions, the electric response of the interface is measured by superimposing a small ac potential perturbation,  $\tilde{\varphi}$ , to the DC component of the polarization, as it is done in the DAT. The dynamic response of the system,  $\tilde{i}$ , can be used to calculate the differential admittance of the interface, which is given by<sup>50</sup>:

$$Y_{\rm SC}(i\omega) = -i\omega \frac{\varepsilon}{\widetilde{\varphi}} \frac{\partial \widetilde{\varphi}}{\partial x} \Big|_0 \tag{6}$$

In general, the dynamic response of the system may be composed by a resistive and a capacitive component. The latter may result different from the differential capacitance as expressed by Eq. (5), due to the finite response of the electrons in the electronic structure of the semiconductor (see later a-SCs). The correlation between differential admittance and the electronic structure of the semiconductor is given by the correlation between the variation of the electric field at the interface and the variation of electric potential, as shown in Eqs. (5) and (6). As anticipated, in order to obtain such correlation, the Poisson equation is used

$$\frac{\partial^2 \Delta \Phi}{\partial x^2} = \frac{\rho(\Delta \Phi)}{\varepsilon} \tag{7}$$

where  $\rho(\Delta \Phi)$  is the volumetric space charge density, and  $\varepsilon$  is the dielectric constant of the semiconductor. Eq. (7) is valid for the static component of the potential. In order to describe the dynamic component of the potential,  $\tilde{\varphi}$ , Eq. (7) is coupled to<sup>37,50</sup>:

$$\frac{\partial^2 \widetilde{\varphi}}{\partial x^2} = \frac{\delta \rho}{\varepsilon} \tag{8}$$

According to Ref. 50, in the small signal approximation it is possible to develop in series of Taylor the term  $\delta \rho$ , which represent the AC variation of the charge density:

$$\delta\rho = -F(\Delta\Phi,\omega)\cdot\widetilde{\varphi} \tag{9}$$

where  $F(\Delta \Phi, \omega)$  is the first-order coefficient with respect to  $\tilde{\varphi}$  in the Taylor's expansion of  $\delta \rho$ , and it is an implicit function of the spatial coordinates, *x*, through the electric potential drop,  $\Delta \Phi$  and eventually of the angular frequency,  $\omega$ . We will show later that different electronic structure lead to different solutions of Eqs. (7), (8).

#### **C-SC/EI.** Interface

In the hypothesis of a c-SC with a single completely ionized donor level, which is the underlying assumption seldom explicitly discussed in the literature of passive films, the following analytical expressions can be derived from Eqs. (7) to  $(9)^{37,50}$ :

$$\rho(\Phi) = |e| \cdot N_D \cdot \left[ 1 - \exp\left(-\frac{|e| \cdot \Delta \Phi}{k_B \cdot T}\right) \right]$$
(10)

$$F(\Phi,\omega) = -\frac{|e|^2 \cdot N_D}{kB \cdot T} \cdot \exp\left(-\frac{|e| \cdot \Delta \Phi}{k_B \cdot T}\right)$$
(11)

After substitution in Eq. (6) it is possible to derive the expression for the differential admittance of c-SC with single donor level completely ionized at any electrode potential  $U_E \ge U_{FB}$ .

$$Y_{\rm SC}(i\omega\Delta\Phi_{\rm SC}) = i\omega\sqrt{\frac{\varepsilon \cdot |e| \cdot N_{\rm D}}{2}} \cdot \frac{1 - \exp\left(-\frac{|e| \cdot \Delta\Phi_{\rm SC}}{k_{\rm B} \cdot T}\right)}{\sqrt{\Delta\Phi_{\rm SC} - \frac{k \cdot T}{|e|} \cdot \left[1 - \exp\left(-\frac{|e| \cdot \Delta\Phi_{\rm SC}}{k_{\rm B} \cdot T}\right)\right]}$$
(12)

where  $N_D$  is the number of donors (for n-doped semiconductors),  $k_B$  is the Boltzmann constant, *e* the elementary charge, and *T* the absolute temperature. As the function *F* is independent from the angular frequency,  $\omega$ , the differential admittance is composed only by a frequency independent capacitive in agreement with absence of any lag effect in the electrical answer of the c-SC. The frequency independence of Y<sub>SC</sub> in Eq. (12) is an important aspect in the study of c-SC/El. junction because from Eq. (12) we derive the expression for the frequency independent differential capacitance of c-SC<sup>37,43,44,50</sup>:

$$\frac{1}{C_{\rm SC}(\Delta\Phi_{\rm SC})} = \sqrt{\frac{2}{\varepsilon \cdot |e| \cdot N_D}} \cdot \frac{\sqrt{\Delta\Phi_{\rm SC} - \frac{k \cdot T}{|e|}} \cdot \left[1 - \exp\left(-\frac{|e| \cdot \Delta\Phi_{\rm SC}}{k_{\rm B} \cdot T}\right)\right]}{1 - \exp\left(-\frac{|e| \cdot \Delta\Phi_{\rm SC}}{k_{\rm B} \cdot T}\right)}$$
(13a)

At high band bending,  $\Delta \Phi_{SC} \gg k_B T/e$  ( $\geq 3k_B T/e$ ), from Eq. (12) it is possible to derive the Mott–Schottky equation of a c-SC as:

$$C_{\rm SC}^{-2}(\Delta\Phi_{\rm SC}) = \frac{2}{\varepsilon \cdot |e| \cdot N_{\rm D}} \cdot \left(\Delta\Phi_{\rm SC} - \frac{k_{\rm B} \cdot T}{|e|}\right) = \frac{2}{\varepsilon \cdot |e| \cdot N_{\rm D}} \cdot \left(U_{\rm E} - U_{\rm fb} - \frac{k_{\rm B} \cdot T}{|e|}\right)$$
(13b)

where  $N_D$  ( $N_A$ ) is the donor (or acceptor) concentration in cm<sup>-3</sup> for n-type (p-type) SC,  $\varepsilon = \varepsilon_{SC}\varepsilon_0$  is the SC dielectric permittivity, and  $\Delta \Phi_{sc}$  is the potential drop within the SC. This last term can be written as:

$$\Delta\Phi_{\rm SC} = U_{\rm E}({\rm ref}) - U_{\rm fb}({\rm ref}) \tag{14}$$

where  $U_{\rm E}$  is the electrode potential measured with respect to a reference electrode and  $U_{\rm fb}$  (ref) represents the flat band potential measured with respect to the same reference electrode in the electrochemical scale. The previous equation holds for a p-type material, with the minus sign in front of  $\Delta \Phi_{\rm SC}$  and  $N_{\rm A}$  instead of  $N_{\rm D}$ .

The first task to get the energetics of a-SC/El. interface is to derive the flat band potential of the junction, corresponding to the condition of zero potential drop inside the SC (flat band condition). A common practice in electrochemistry of semiconductor is to get such a parameter, by assuming  $1/C_H \ll 1/C_{SC}$ , and measuring the differential capacitance of the junction defined as above as a function of the electrode potential.

The extrapolation to zero of the first term in M-S equation provides the value of the intercept with voltage axis  $U_0$ , while from the slope of Eqs. (13a), (13b) it is possible to derive the concentration of donor (or acceptor) in the SC.

The assumption of neglecting the contribution of Helmholtz capacitance to  $C_m$  can seriously affect the value of flat band potential. In fact the following relationship exists between the intersection of the M-S plot with potential axis,  $U_0$ , and the flat potential value<sup>51–53</sup>:

$$U_{\rm fb} = U_0 - \frac{kT}{e} + \frac{\varepsilon_{\rm ox}\varepsilon_0 eN_{\rm D}}{2C_{\rm H}^2} \quad \text{for } n - \text{type semiconductor}$$
(15a)

$$U_{\rm fb} = U_0 + \frac{kT}{e} - \frac{\varepsilon_{ox}\varepsilon_0 e N_{\rm A}}{2C_{\rm H}^2} \quad \text{for } p - \text{type semiconductor}$$
(15b)

The required correction in the  $U_{\rm fb}$  value remains negligible as long as the dielectric constant value and donor density are small but it becomes important as  $\varepsilon_{\rm ox}$  or  $N_{\rm D}$  (or both) increase close to values as those sometimes reported for passive films (see later). The location of the Fermi level of the c-SC, in the electrochemical scale, is carried out by means of the equation:

$$E_f^0(\text{El}) = -|e|U_{\text{fb}}(\text{ref}) \tag{16}$$

The conversion from the electrochemical scale to the absolute scale<sup>54,55</sup> is usually carried out by assuming a value of  $4.45 \pm 0.1$  V for the NHE reference electrode with respect to the vacuum so that we can locate the characteristic energy levels of the junction with respect to the absolute scale according to the following relationship:

$$E_f^0(\text{El}) = -|e|U_{\text{fb}}(nhe) - 4.45 \pm 0.1 \ eV \tag{17}$$

The region of SC necessary for screening the potential drop  $\Delta \Phi_{SC}$  defines the space charge region. However, it is possible to define, in a generalized way, the width of the space charge region,  $X_{SC}$ , by means of the relationship:

$$X_{\rm SC}(\Delta\Phi_{\rm SC}) = \frac{\varepsilon}{C_{\rm SC}(\Delta\Phi_{\rm SC})} \tag{18}$$

Under the conditions above depicted for c-SC the width of the space charge region in c-SC changes with the potential drop according to the following equation:

$$X_{\rm SC} = X_{\rm SC}^0 \left( \left| \Delta \Phi_{\rm SC} \right| - \frac{kT}{e} \right)^{0.5} \tag{19}$$

where  $X_{SC}^{0}$  represents the space charge width into the SC electrode at 1 V of band bending ( $\Delta \Phi_{SC} = 1$  V) and its value depends on the concentration of mobile carriers into the SC. The expression for such a characteristics length is given by:

$$X_{\rm SC}^0 = \left(\frac{2\varepsilon_{\rm SC}\varepsilon_0}{eN_{\rm D/A}}\right)^{0.5} \tag{20}$$

where  $N_{\text{D/A}}$  is the donor (or acceptor) concentration in cm<sup>-3</sup>,  $\varepsilon_{\text{SC}}$  and  $\varepsilon_0$  are the SC dielectric constant and the vacuum permittivity, respectively. By assuming for the passive film dielectric constant a typical value of ~10 and a donor concentration of  $10^{19}$  cm<sup>-3</sup> we get for  $X_{\text{SC}}^{0}$  a value around 100 Å V<sup>-0.5</sup>.

In Fig. 2A and B we report the schematic diagram of an n-type SC/electrolyte junction in energy–distance coordinates at flat band conditions ( $X_{SC} = 0$ ) and under slight depletion ( $X_{SC} > 0$ ).  $\Delta \Phi_{SC} = 0$  (no potential drop within the SC) corresponds to the special flat band condition reported in Fig. 2A, while an anodic  $\Psi_{SC} > 0$  (n-type SC) polarization corresponds to the conditions depicted in Fig. 2B. In the case of p-type material a space charge layer develops inside the SC for  $\Psi_{SC} < 0$ .



**Fig. 2** Schematic diagram of an n-type SC/electrolyte junction in energy–distance coordinates at (A) flat band conditions ( $X_{SC} = 0$ ) and (B) under slight depletion ( $X_{SC} > 0$ ).

The location of the remaining energy levels of the junction is carried out by means of the usual relationships for n- and p-type semiconductors:

$$E_{\rm C} = E_{\rm F}^0 + kT \ln\left(\frac{N_{\rm C}}{N_{\rm D}}\right) \quad \text{for } n - \text{type SC}$$
(21a)

$$E_{\rm V} = E_{\rm F}^0 + kT \ln(N_{\rm V}/N_{\rm A}) \quad \text{for } p - \text{type SC}$$
(21b)

$$E_{\rm g} = E_{\rm C} - E_{\rm V} \tag{21c}$$

where  $N_{\rm C}$  (and  $N_{\rm V}$ ) is the effective density of states (DOS) at the bottom (top) of the SC conduction (valence) band,  $E_{\rm C}$  and  $E_{\rm V}$  are the conduction and valence band edges, respectively, and  $E_{\rm g}$  is the band gap of the SC. As for the effective DOS at conduction (valence) band edge for n-type (p-type) SC it is given by:

$$N_{\rm C} = 2M_{\rm C/V} \left(\frac{2\pi m^* kT}{h^2}\right)^{\frac{3}{2}}$$
(22)

where  $M_{C/V}$  is the number of equivalent minima (maxima) in the conduction (valence) band,  $m^*$  is the effective mass for the DOS in the corresponding band, and the other symbols have their usual meaning. By assuming  $M_C = 1$  and  $m^*$  equal to the mass of free electron,  $m_0$ , we get  $N_C = 2.5 \times 10^{19}$  cm<sup>-3</sup> at room temperature. By taking into account that Eqs. (21a), (21b) hold on the hypothesis that the following relationship:

$$(E_V + 3kT) \le E_F \le (E_C - 3kT) \tag{23}$$

is satisfied, we can estimate for an hypothetical donor (acceptor) density equal to  $10^{19}$  cm<sup>-3</sup> an effective electron (holes) mass for DOS in the conduction (valence) band  $m^* \ge 7$ .

The simplified method reported above and based on the use of classical M-S theory for locating the energy levels at the SC/El. interface is very popular among the corrosion scientists. However, we have to mention that although the validity of Eq. (8) has been tested rigorously for several SC/El. interfaces, <sup>56-60</sup> since the seminal work of Dewald<sup>43,44</sup> on single crystal ZnO electrodes, in many cases a misuse of such an equation has been made.

In order to highlight this last aspect we summarize the following limitations included in the use of the earlier reported equations:

- (a) c-SC electrode homogeneously doped under depletion regime;
- (b) fully ionized single donor (or acceptor, for p-type SC) level;
- (c) negligible contribution of surface states and minority carriers to the measured capacitance;
- (d) width of space charge layer much lower than the semiconductor thickness;
- (e) absence of Faradaic processes at the SC/El. interface;
- (f) absence of deep-lying donor (acceptor) levels in the forbidden gap of the SC.

The points (a)–(c) reported have been assumed in deriving the expression for the differential capacitance and M-S relationship so that these assumptions need a preliminary test in the analysis of the experimental results derived by using the M-S approach to the study of SC/El. junction specially if these equations are used to analyze the data of thin passive film/El. junction.

As for the value of  $m^*$  above estimated it is not unusual for transition metal oxides so that we can also estimate the corresponding space charge thickness of the semiconducting oxide by means of Eq. (19) reported. According to the previous calculations and by assuming  $\Delta \Phi_{SC} = 0.5$  V a value of space charge length of ~ 9 nm for iron oxide ( $\varepsilon_{ox} = 15$ ) and ~ 8 nm for nickel oxide ( $\varepsilon_{ox} = 12$ ) is estimated. Both these values are larger than the oxide film thickness usually reported for passive iron (3–5 nm), nickel (2–3 nm), chromium and stainless steels (2–3 nm), in different solutions, before the onset of the transpassive region, <sup>61–66</sup> so that the hypothesis of SC space charge width much lesser than the thickness of SC could be untenable and the electrical equivalent circuit of the junction should be modified by adding a further capacitance in parallel with the  $C_{SC}$  term which accounts for the metal contribution to the total stored charge.<sup>46,67</sup>

Moreover, donor or acceptor concentration larger than  $10^{20}-10^{21}$  cm<sup>-3</sup> for passive films on iron, nickel, and stainless steel have been, frequently, reported<sup>68-77</sup> and up to  $10^{22}$  cm<sup>-3</sup> in several cases (including TiO<sub>2</sub> and some chromium carbon steel).<sup>78,79</sup> At such high doping levels the applicability of classical M-S theory to the study of a degenerate SC/El. interface is open to serious doubts. By considering that, in this case, the Fermi level should be located well above (below) the conduction (valence) band edge, the passive film/electrolyte interface becomes now more similar to a semimetal/electrolyte interface for which a different theoretical approach has been suggested.<sup>32,80,81</sup> In presence of such large density of donor (acceptor) concentration the experimental data should be taken with caution and the electrical equivalent circuit, employed to extract the space charge capacitance data, carefully scrutinized in order to verify if the restrictions underlying the simple M-S analysis are satisfied specially in absence of an ideally polarizable interface (see also later).

More importantly at such high doping levels, neglecting the contribution of the capacitance of the Helmholtz double layer to the measured capacitance is no more acceptable. For highly doped materials, in fact, the values of  $U_{\rm fb}$  can differ considerably from the intercept value  $U_0$ . By substituting in Eqs. (15a), (15b) the value of dielectric constant usually reported for passive iron ( $\varepsilon_{\rm ox} = 15$ ) and  $N_{\rm D}$  values in the range  $5 \times 10^{20}$ – $5 \times 10^{21}$  cm<sup>-3</sup> we obtain a difference between the flat band potential and the intersection voltage  $U_0$  ranging from  $\approx 0.13$  V up to  $\approx 1.3$  V by assuming for C<sub>H</sub> values around 20 µF cm<sup>-2</sup>. Such a difference grows to values comprises between 0.4 and 3.9 V in the case of TiO<sub>2</sub> anodic films showing dielectric constant values  $\varepsilon_{\rm TiO} \approx 45$ .

The absence of Faradaic processes at the SC/El. interface is an important, but rather neglected, assumption in the analysis of the M-S plots usually employed to characterize the semiconducting properties of thin passive film. The assumption of an ideally polarizable interface is often a rather difficult condition to be observed, at the most common metal/passivefilm/electrolyte interfaces, in presence of a variable electrode potential spanning a sufficiently large range of electrode potential values where to carry out the impedance measurements. This aspect has been discussed in a recent work<sup>82</sup> showing that the presence of a knee point in the M-S plots of passive metals, sometimes attributed to the existence of p–n junction originated by the excess of metal cation or oxygen anion in the different regions of the film, could be instead related to the onset of a region of nonideally polarizable behavior of the interface in the same range of electrode potential values where the differential capacitance measurements are carried out. Should this suggestion be confirmed, then some of previously proposed models of passive films would have to be, consequently, revised.

Although the presence of a single ionized dopant is implicitly assumed when talking about c-SCs, this is in general not the case. In fact, the electronic structure of c-SCs may include the presence of multiple dopants, or deep level dopants, <sup>50</sup> which are not fully ionized and they behave as traps for electrons and holes, as well as recombination centers. The presence of these deep traps changes the expression of the charge density<sup>37</sup> which can be rewritten as:

$$\rho(\Phi) = |e| \cdot N_{\rm D} - |e| \cdot N_{\rm C} \cdot \exp\left(-\frac{\Delta E_{\rm C}}{k_{\rm B} \cdot T}\right) \cdot \exp\left(-\frac{|e| \cdot \Delta \Phi}{k_{\rm B} \cdot T}\right) + \sum_{i} |e| \cdot N_{T,i} \cdot \left[\frac{1}{1 + \exp\left(-\frac{E_{T,i} - E_{\rm F} + |e| \cdot \Delta \Phi}{k_{\rm B} \cdot T}\right)} - \frac{1}{1 + \exp\left(-\frac{E_{T,i} - E_{\rm F}}{k_{\rm B} \cdot T}\right)}\right]$$
(24)

$$F(\Phi,\omega) = -\frac{|e|^2 \cdot N_{\rm C}}{k_{\rm B} \cdot T} \cdot \exp\left(-\frac{\Delta E_{\rm C}}{k_{\rm B} \cdot T}\right) \cdot \exp\left(-\frac{|e| \cdot \Delta \Phi}{k_{\rm B} \cdot T}\right) + \sum_{i} \frac{|e|^2 \cdot N_{T,i}}{k_{\rm B} \cdot T} \cdot \frac{1}{1 + i \cdot \omega \cdot \tau_0 \cdot \exp\left(\frac{E_{\rm C} - E_{\rm T,i}}{k_{\rm B} \cdot T}\right)} \cdot \frac{\exp\left(-\frac{E_{\rm T,i} - E_{\rm F} + |e| \cdot \Delta \Phi}{k_{\rm B} \cdot T}\right)}{\left[1 + \exp\left(-\frac{E_{\rm T,i} - E_{\rm F} + |e| \cdot \Delta \Phi}{k_{\rm B} \cdot T}\right)\right]^2}$$
(25)

The function *F* is now dependent upon the angular frequency,  $\omega$ , owing to the presence of a time lag effect in the electrical answer of deep-lying donor level of c-SC. According to this the differential admittance will contain resistive and capacitive elements which will be dependent on the frequency of ac signal originating the frequently observed frequency dispersion in admittance data. In reference<sup>37</sup> we took into account these aspects in order to fit the experimental Mott–Schottky plots of a thick (160 nm) Nb<sub>2</sub>O<sub>5</sub> anodic oxide film aged in vacuum at 250°C and showing a large frequency dispersion in the exploited frequency range (10 Hz–10 kHz). In order to solve Eqs. (7), (8) using the **expressions (24)** and (25), a numerical algorithm was developed. The results of this study have shown that both the frequency-dependent behavior and the presence of a double slope in the Mott–Schottky plots are not explained by the simplified model of existence of two donor levels within the gap of otherwise perfect crystalline material (see Fig. 3). The detailed study carried out in Refs. 37,83 has shown that the use of the simplified M-S approach is rather misleading in terms of determination of the two important parameters,  $U_{\rm fb}$  and  $N_{\rm D}$ , necessary to locate correctly the characteristic energy levels of the anodic oxide/electrolyte interface. Moreover, in order to fit the experimental results, multiple donor levels were used, thus mimicking, in some extent, the physics of DOS distribution in a-SCs (see later).

We have to add that in some studies pertaining to c-SC/El. junctions, and the possible physical cause of the observed frequency dependence in the M-S plots has been attributed to the presence of an external (disordered or amorphous) layer, which after



**Fig. 3** Mott–Schottky plot and fitting curves at different frequencies in 0.5 M H<sub>2</sub>SO<sub>4</sub>, relating to aged 50 V anodic films on Nb. The parameters of the fitting curves are  $U_{\rm fb} = -0.46$  V vs. SSC;  $N_{7,1} = 7.8 \times 10^{18}$  cm<sup>-3</sup>,  $E_{\rm C} - E_{\rm T,1} = 18k_{\rm B}$ T,  $N_{7,2} = 1.1 \times 10^{20}$  cm<sup>-3</sup>,  $E_{\rm C} - E_{\rm T,2} = 28.5k_{\rm B}$ T. ( $\Delta E_{\rm F} \approx 278$  meV). Adapted from La Mantia, F., Habazaki, H., Santamaria, M., Di Quarto, F. *Russ. J. Electrochem.* **2010**, *46*, 1306 (Fig. 9).

a suitable chemical etching of the surface of c-SC could be removed to restore the expected behavior.<sup>84</sup> In the case of passive films the presence of a frequency-dependent differential capacitance is intrinsic to the formation of a layer having an amorphous or strongly disordered nature, so that the use of interpretative models accounting for such a specific feature must be taken into consideration. In this frame the present authors advocated<sup>37,45–49,83,85</sup> the use of the theory of a-SC Schottky barrier to provide an unified approach to the theory of electrical admittance of SC/El. junction by showing that the behavior of c-SC junction containing a distribution of donor (acceptor) levels in the forbidden energy gap of the SC<sup>37</sup> can be treated as a particular case of the theory of amorphous Schottky barrier by leaving the traditional M-S approach to the limiting case of ideal c-SC/electrolyte junction. The theory and the results of such studies will be presented and discussed in the next section.

## a-SC/El. Interface

The differences in the differential admittance response of a-SC Schottky barrier with respect to the c-SC Schottky barrier are caused by the difference in DOSs distribution. We stress that usually amorphous materials maintain the same short-range order than their crystalline counterparts and that the main differences come out from the absence of the long-range order, which is typical of crystalline phases.<sup>86–91</sup> It is now generally accepted that the band structure model retains its validity also in absence of the long-range lattice periodicity.<sup>92</sup> This means that the long-range disorder perturbs but does not annihilate the band structure: its main effect is the presence of a finite DOS within the so-called mobility gap, between  $E_{\rm C}$  and  $E_{\rm V}$ , of the a-SC or insulator.

In Fig. 4 we report the model of DOS distribution versus energy for generic crystalline and amorphous materials. Although the general features of DOS distribution are preserved, especially if we compare Fig. 4A with Fig. 4C, some differences are evident and they strongly affect the response of a-SC/El. junction under AC electrical as well under light stimulus (see later). The DOS distribution of Fig. 4B, initially proposed by Cohen–Fritzsche–Ovshinsky (CFO model),<sup>86</sup> takes into account the possible existence of lattice defects inside the semiconductor which originate a continuous distribution of electronic states within the mobility gap (like in a-Si:H).

On the other hand the DOS distribution of Fig. 4C, due to Mott and Davis,<sup>88</sup> has been proposed for an ideal amorphous material in which only the long-range lattice disorder is taken into account. Other models have been suggested for explaining the behavior of different classes of amorphous materials, but they involve only minor modifications to those of Fig. 4, when the existence of specific defects in the investigated material is considered. As evidenced in the Fig. 4, the general features of the DOS of crystalline materials are preserved also for disordered phases, but some differences are now evident with respect to the c-SC and these can be summarized as follows:

- (1) Existence of a finite DOS within the mobility gap, defined by two mobility edges,  $E_C$  and  $E_V$ , in the conduction band (CB) and in the valence band (VB), respectively.
- (2) For energy levels below  $E_{\rm C}$  or above  $E_{\rm V}$ , the free-electron-like DOS, N(E) versus  $E^{1/2}$ , is no more generally valid. For explaining the optical properties of different amorphous materials the presence of a tail of states, exponentially or linearly<sup>88</sup> decreasing, has been suggested below (above)  $E_{\rm c}$  ( $E_{\rm v}$ ) by different authors.<sup>92</sup>
- (3) Different mechanisms of charge carriers transport are invoked in extended (above  $E_{\rm C}$  or below  $E_{\rm V}$ ) or localized (within the mobility gap) electronic states. A free-carrier-like mechanism of transport is involved in the first case, while a transport by hopping (thermally activated) is assumed in localized states.<sup>93</sup>



Fig. 4 Model of the electronic structure for a crystalline semiconductor (A), amorphous semiconductor following the Cohen–Fritzsche–Ovshinsky model (B), and amorphous semiconductor following the Mott–Davis model (C).

#### Admittance Equations for a-SC/EI. Junction

Based on the work of Abram et al.<sup>94–96</sup> and Lang et al.<sup>97,98</sup> and as discussed in previous papers<sup>37,45–49,83,85,99,100</sup> the impedance of an a-SC Schottky barrier is influenced by the existence of deep tails of electronic states within the mobility gap, usually absent in the case of ideal c-SC. This point is well explained in Fig. 5 where the energetics of n-type a-SC/El. interface is sketched, under the simplifying hypotheses of constant DOS and spatially homogeneous material. The main difference with respect to the case of c-SC is that the net space charge depends on both the ionized impurities and the localized states within the mobility gap. The electronic states lying into the gap (see Fig. 5) do not follow instantaneously the imposed ac signal, but they need a finite response time. The latter depends on the energy position with respect to the Fermi level, and it can be much longer than the period of the ac signal having angular frequency  $\omega$ . According to the theory,<sup>97,98</sup> the relaxation time,  $\tau$ , for the capture/emission of electrons from electronic states *E* below  $E_{\rm F}$  (Fermi Level) is described by the relationship:

$$\tau = \tau_0 \cdot \exp\left(\frac{E_C - E}{k_{\rm B} \cdot T}\right) \tag{26}$$

where at constant temperature,  $\tau_0$  is a constant characteristic of each material usually ranging between  $10^{-14}$  and  $10^{-10}$  s. This means that by changing  $\omega$  at constant band bending the levels able to follow the signal change. On the other hand, by changing the



Fig. 5 Electronic structure (A) and band banding distribution (B) across an n-type SC/El. interface.

band bending at constant AC frequency, deeper levels of depleted region lying below a critical level will not change the occupancy with ac signal. According to Eq. (14), by decreasing the energy of the localized state in the gap,  $\tau$  increases sharply so that deep states (for which  $\omega \tau \gg 1$ ) do not respond to the ac signal. By assuming a full response for states satisfying the condition  $\omega \tau \ll 1$  and a null response for states having  $\omega \tau \gg 1$ , a sharp cutoff energy level,  $E_{\omega}$ , separating states responding from those not responding to the signal, can be defined from the condition:  $\omega \tau = 1$ , as:

$$E_{\rm C} - E_{\omega} = -k_{\rm B} \cdot T \cdot \ln(\omega \cdot \tau_0) \tag{27}$$

According to Fig. 5 the intersection of  $E_{\omega}$  with the Fermi level  $E_F$  of material determines a characteristic point in the barrier,  $x_{C}$  at which corresponds a potential drop  $\Delta \Phi_C$  given by:

$$|e| \cdot \Delta \Phi(x_C) = |e| \cdot \Delta \Phi_C = -k_B \cdot T \cdot \ln(\omega \cdot \tau_0) - \Delta E_F$$
(28)

where  $\Delta E_F = (E_C - E_F)_{\text{bulk}}$ .  $x_C$  is now a distance in the barrier increasing with increasing frequency at constant polarization or with increasing polarization at constant frequency. As consequence of this phenomenon, the charge density can be now written as<sup>97,98</sup>.

$$\rho(\Phi) = |e| \cdot \int_{E_{\rm F}}^{E_{\rm F}} N(E) \cdot dE$$
(29)

$$F(\Phi,\omega) = \frac{|e|^2 \cdot N(E_{\rm F} - |e| \cdot \Delta \Phi)}{1 + i \cdot \omega \cdot \tau_0 \cdot \exp\left(\frac{\Delta E_{\rm F} - |e| \cdot \Delta \Phi}{k_{\rm B} \cdot T}\right)}$$
(30)

The differential admittance response for the general case is composed by a resistive and a capacitive component, which take the form<sup>97,98</sup>:

$$\frac{1}{C_{\rm SC}(\Delta\Phi_{\rm SC},\omega)} = \frac{\sqrt{-\frac{2}{e}} \int_0^{\Delta\Phi_c} \rho(\Delta\Phi) \cdot d\Delta\Phi}{\rho(\Delta\Phi_c)} + x_{\rm C}(\Delta\Phi_{\rm SC},\omega)$$
(31)

$$G_{\rm SC}(\Delta\Phi_{\rm SC},\omega) = \frac{k_{\rm B}\cdot T\cdot\pi}{2} \cdot \omega \cdot C_{\rm SC}^2(\Delta\Phi_{\rm SC},\omega) \cdot \frac{\sqrt{-\frac{2}{\epsilon}} \int_0^{\Delta\Phi_{\rm C}} \rho(\Delta\Phi) \cdot d\Delta\Phi}{\rho^2(\Delta\Phi_{\rm C})} \cdot |e| \cdot N(E_{\omega})$$
(32)

Eqs. (31), (32) are valid analytical approximations for sufficiently high polarization potential, that is,  $\Delta \Phi_C \ge 3 k_B \cdot T/|e|$  and  $\Delta \Phi_{SC} > \Delta \Phi_C + 3 k_B \cdot T/|e|$ . If the distribution of states, N(E), is known, Eqs. (30), (31) can be very easily used in order to calculate the differential admittance response of the a-SC Schottky barrier as a function of polarization potential and frequency. However, deconvoluting the shape of N(E) from the differential admittance measurements is not such an easy task, as several parameters have to be taken into account.

Under the hypothesis of constant DOS distribution, N(E) = N, and space charge width much less than a-SC thickness the admittance of the a-SC Schottky junction, Eqs. (30), (31) give as result:

$$\frac{1}{C_{\rm SC}(\Delta\Phi_{\rm SC},\omega)} = \frac{1}{\sqrt{\varepsilon \cdot |e|^2 \cdot N}} \cdot \left\{ \ln\left(\frac{\Delta\Phi^*}{\Delta\Phi_C}\right) + \sqrt{1 + \frac{2}{\Delta\Phi_g} \cdot (\Delta\Phi_{\rm SC} - \Delta\Phi^*)} \right\}$$
(33)

$$G_{\rm SC}(\Delta\Phi_{\rm SC},\omega) = \frac{k_{\rm B}\cdot T\cdot\sqrt{\varepsilon\cdot|e|^2\cdot N}}{|e|\cdot\Delta\Phi_{\rm C}}\cdot\frac{\pi}{2}\cdot\omega\cdot\left\{\ln\left(\frac{\Delta\Phi^*}{\Delta\Phi_{\rm C}}\right) + \sqrt{1+\frac{2}{\Delta\Phi_{\rm g}}\cdot\left(\Delta\Phi_{\rm SC}-\Delta\Phi^*\right)}\right\}^{-2}$$
(34)

provided that  $\Delta \Phi_{SC} \ge \Delta \Phi_C \ge 3 k_B T/|e|$ .  $\varepsilon = \varepsilon_{SC} \varepsilon_0$  is the SC dielectric permittivity,  $\omega$  is the angular frequency of ac signal, and *N* is the value of the DOS ( $eV^{-1}$  cm<sup>-3</sup>) distribution in the a-SC assumed as constant. As for the other symbols (see also Fig. 4):

(a)  $\Delta \Phi_g$  represents the electric potential drop at  $x_g$  and it corresponds to the point at which the quasi Fermi level,  $E_F$ , inside the a-SC ceases to be constant and it marks the beginning of the high band bending regime. In the hypothesis of constant capture/ emission rate of electrons and holes, from localized state to their respective band,  $\Delta \Phi_g$  is given by the expression:

$$|e| \cdot \Delta \Phi_g = \frac{E_g}{2} - \Delta E_F \tag{35}$$

(b)  $\Delta \Phi^*$  is equal to  $\Delta \Phi_{SC}$  when  $\Delta \Phi_{SC} < \Delta \Phi_{g'}$  otherwise it is equal to  $\Delta \Phi_{g}$ .

At high band bending ( $\Delta \Phi_{SC} > \Delta \Phi_g$ ) it has been shown that the contributions to the total capacitance can be attributed to three contributions coming from<sup>37,83</sup>:

- (1) the region  $0 < x < x_g$  which behaves as a dielectric, frequency independent, but which widens with increasing potential;
- (2) the region  $x_g < x < x_C$  (null response region) which behaves as a dielectric and whose response is frequency and potential depending;
- (3) the  $x > x_C$  (total response region) region of the a-SC which is frequency dependent and independent from the potential until the restriction  $\Delta \Phi_{SC} > \Delta \Phi_C$  is respected.

On the other hand the contribution to the conductance of a-SC Schottky barrier comes mainly from the region around  $x = x_C$ , which divides the total response from null response regions and it shows a spectroscopic character with respect to the local DOS distribution, as discussed in Refs. 45,94–99.

At variance with the case of c-SC the location of conduction (valence) band mobility edge  $E_C$  ( $E_V$ ) for n-type (p-type) a-SC it is now carried out according to Eq. (16) once the flat band potential, and then the Fermi level location in the energy scale, has been determined. An evaluation of the energy–distance  $\Delta E_F$  is obtained from the values of  $\psi_C$  at different frequencies. An extrapolation to the angular frequency,  $\omega_0$ , for which  $\psi_C = 0$  can be used in the determination of  $\Delta E_F$ . It results

$$\Delta E_{\rm F} = -k_{\rm B} \cdot T \cdot \ln(\omega_0 \cdot \tau_0) \tag{36}$$

In absence of further information, an average  $\tau_0$  value around  $10^{-12}$  can be used in Eq. (28) to estimate the term  $\Delta E_{\rm F}$ . This leaves an uncertainty of <0.12 eV in the  $E_{\rm C}$  ( $E_{\rm V}$ ) location which is an acceptable value by taking into account the absence of any sharpness in the mobility edge of a-SC separating electronic extended states from localized ones.<sup>88</sup>

Fitting of experimental data for various amorphous anodic films on valve-metals, according to the earlier reported equations for a-SC Schottky barriers, has been carried out in several previous works.<sup>37,45–49,83,85,99</sup> In Fig. 6 we report the fitting of the experimental data of a 157 nm thick a-Nb<sub>2</sub>O<sub>5</sub>/El. junction. The fitting procedure is now carried out by a trial and error procedure and by imposing a flat band potential which is independent from frequency.

The details of the procedure can be found in Refs. 37,83 but the fitting parameters are now reported in the caption of Fig. 6. The range of frequencies is the same previously used (see Fig. 5) for fitting the data by numerical simulation and according to the theory of M-S for crystalline.<sup>37</sup> It is noteworthy that the location of the characteristic energy level of the junction,  $E_{\rm C}$ , calculated by means of Eqs. (33), (34) for a-SC Schottky barriers and that obtained by computer simulation, in the hypothesis of double ionized donor level in c-SC, are in fair agreement between them but at variance with the value obtained by using Eqs. (13a), (13b) and the simplified approach based on the M-S equation. As for the flat band potential, appreciable differences were observed in the  $U_{\rm fb}$  value derived by the different approaches.<sup>37,83</sup>

The previous expressions for the differential admittance of a-SC/El. junction were obtained in closed analytical form by assuming a constant density of states and spatially homogeneous SC. It was suggested in Ref. (22) that the capacitance,  $C_{SC}$ , of a-SC/metal barrier is weakly influenced by a DOS distribution variable in energy provided that changes of DOS are small for energy changes in the order of  $k_BT$ . In this case an average value of DOS is obtained from  $C_{SC}$  and a local value of DOS is obtained from  $G_{SC}$ :



**Fig. 6** Fitting of the experimental data of a 157 nm thick a-Nb<sub>2</sub>O<sub>5</sub>/El. junction.  $U_{fb} = -0.377 \pm 0.015$  V vs. SSC ( $\Delta_{EF} \approx 373$  meV;  $E_C = -0.75$  V vs. SSC). Adapted from La Mantia, F., Habazaki, H., Santamaria, M., Di Quarto, F. *Russ. J. Electrochem.* **2010**, *46*, 1306 (Fig. 11).

$$\frac{1}{C_{\rm SC}(\Delta\Phi_{\rm SC},\omega)} = \frac{1}{\sqrt{\varepsilon \cdot |e|^2 \cdot N_{av}}} \cdot \left\{ \ln\left(\frac{\Delta\Phi^*}{\Delta\Phi_C}\right) + \sqrt{1 + \frac{2}{\Delta\Phi_g} \cdot (\Delta\Phi_{\rm SC} - \Delta\Phi^*)} \right\}$$
(37)

$$G_{\rm SC}(\Delta\Phi_{\rm SC},\omega) = \frac{k_{\rm B}\cdot T}{|e|\cdot\Delta\Phi_{\rm C}}\cdot\frac{\pi}{2}\cdot\omega\cdot\sqrt{\frac{\varepsilon\cdot|e|^2}{N_{av}}}\cdot N(E_{\omega})\cdot\left\{\ln\left(\frac{\Delta\Phi^*}{\Delta\Phi_{\rm C}}\right) + \sqrt{1+\frac{2}{\Delta\Phi_{\rm g}}\cdot(\Delta\Phi_{\rm SC}-\Delta\Phi^*)}\right\}^{-2}$$
(38)

The  $C_{SC}$  and  $G_{SC}$  equations, earlier reported, contain as limiting case the hypothesis of constant DOS ( $N_{av}(E) = N$ ), for which case the analytical expressions derived in (33) and (34) coincide. In Eqs. (37), (38),  $N_{av}$  represents an averaged DOS between  $E_F$  and  $E_{\omega}$  for  $C(\Delta\Phi_{SC}\omega)$  and N is the DOS at  $x_C$  and energy  $E_{\omega} = E_F - |e| \cdot \Delta\Phi_C$  (the conductance has a more spectroscopic character than the capacitance).

#### Thick Films With Variable DOS

The previous equations have been obtained in closed form for the case of constant DOS or in presence of a spatially homogeneous DOS weakly dependent on energy. In order to take into account a possible variation of DOS distribution along the energy or the spatial coordinate (spatially inhomogeneous a-SC) we suggested in previous papers<sup>45,100</sup> to carry out the fitting process with a slightly modified expression of Eqs. (33), (34):

$$\frac{1}{C_{\rm SC}(\Delta\Phi_{\rm SC}\omega x(\Delta\Phi_{\rm SC}))} = \frac{1}{C_{\rm SC}(\Delta\Phi_{\rm SC},\omega)} \cdot f_{\omega}(x(\Delta\Phi_{\rm SC}))$$
(39)

$$G_{\rm SC}(\Delta\Phi_{\rm SC},\omega,x(\Delta\Phi_{\rm SC})) = G_{\rm SC}(\Delta\Phi_{\rm SC},\omega) \cdot g_{\omega}(x(\Delta\Phi_{\rm SC}))$$
(40)

where  $\frac{1}{C_{SC}(\Delta\Phi_{SC},\omega)}$  and  $G_{SC}(\Delta\Phi_{SC},\omega)$  are given by Eqs. (33), (34),  $f_{\omega}(x(\Delta\Phi_{SC}))$  and  $g_{\omega}(x(\Delta\Phi_{SC}))$  are, respectively, two different trial functions depending on the electrode potential and angular frequency.<sup>100</sup> This approach allowed an improvement in the fitting procedure by leaving, however, an uncertainty as for the limits within which to force the fitting procedure and the physical meaning of the function  $f_{\omega}$  and  $g_{\omega}$ . As long as the assumption of a-SC of infinite length holds the spatial dependence of DOS could be obtained by plotting the DOS distribution average value  $N_{av}$ , derived from fitting of  $1/C_{sc}(x(\Delta\Phi_{SC}),\omega,\Delta\Phi_{SC})$  as a function of space charge region  $X_{SC}$ , while the energy dependence can be derived by plotting the *Nav*( $\omega$ ) values derived from the fitting of  $G_{sc}(x(\Delta\Phi_{SC}),\omega,\Delta\Phi_{SC})$  conductance plots at various frequencies, but at fixed  $x_C$  (see Fig. 7).

Unfortunately this procedure can be seriously misleading in the case of a-SC having a finite thickness so that, at higher band bendings, possible contribution to the measured capacitance, derived from the surface charge located at the metal/a-SC interface rather than from the volumetric charge density located close to the a-SC/electrolyte interface, can pass unobserved in the fitting process. This fact is particularly relevant in the case of passive films, usually having a very limited thickness, and where large contribution to the measured capacitance can derive from the underlying metal surface charge already at very low band bendings.<sup>46</sup>

At this aim in order to disentangle, in the DOS distribution, a possible spatial dependence from the energy dependence, in more recent works,<sup>48,49</sup> we tested the limits of validity of the analytical equations derived for spatially homogeneous a-SC, reported



**Fig. 7** Plots of DOS distribution as a function of  $x_c$  at different frequencies for anodic film grown on pure Nb to 50 V at 5 mA cm<sup>-2</sup> in 0.1 M ammonium pentaborate and heat treated in vacuum at (0.5–1) 10<sup>-5</sup> Torr and 523 K for 1 h. From La Mantia, F., Santamaria, M., Di Quarto, F., Habazaki, H. *J. Electrochem. Soc.* **2010**, *157*, C258–C267 (Fig. 10).

earlier, by using numerical simulations to solve Eqs. (7), (8) and to obtain the differential admittance from the definition in Eq. (6). We tested what happens when different DOS distributions variable in energy, but spatially homogeneous, are used. Moreover, we varied the thickness of a-SC with respect to the width of the space charge region, in order to check the onset of any appreciable divergence between the computer simulated values and those derived from the analytical solutions. Finally, an equation allowing checking the spatial homogeneity of the a-SC was derived by using the analytical expressions for the impedance of the junction. As described in details in these more recent works,<sup>46,48</sup> the ac signal response of the space charge region in a-SC/metal junction was modeled through the impedance, which is expressed by a frequency-dependent series capacitance,  $C_{SC}$ , and a frequency-dependent series resistance,  $R_{SC}$ :

$$\frac{1}{C_{\rm SC}(\Delta\Phi_{\rm SC},\omega)} = \frac{\sqrt{-\frac{2}{e}} \int_0^{\Delta\Phi_c} \rho(\Delta\Phi) \cdot d\Delta\Phi}{\rho(\Delta\Phi_c)} + x_{\rm C}(\Delta\Phi_{\rm SC},\omega)$$
(41)

$$R_{\rm SC}(\Delta\Phi_{\rm SC},\omega) = \frac{k_{\rm B}\cdot T\cdot\pi}{2\cdot\omega} \cdot \frac{\sqrt{-\frac{2}{\varepsilon} \int_{0}^{\Delta\Phi_{\rm C}} \rho(\Delta\Phi) \cdot d\Delta\Phi}}{\rho^{2}(\Delta\Phi_{\rm C})} \cdot |e| \cdot N(E_{\omega})$$
(42)

In obtaining Eqs. (41), (42), the same assumptions as in obtaining Eqs. (31), (32) were done and they are consistent with equations presented by Abram et al.<sup>94–96</sup> and Lang et al.<sup>97,98</sup> to model the admittance of an a-SC Schottky barrier by means of the equivalent electrical circuit consisting of a parallel frequency-dependent electrical capacitance and conductance. In fact the  $C_{SC}$  and  $G_{SC}$  expressions in Eqs. (31), (32) can be obtained from the earlier reported relationships by a simple parallel/series transformation and by assuming that  $R_{SC} \ll (\omega \cdot C_{SC})^{-1}$  as in Refs. 46,48.

Moreover, it is now possible to define a new parameter,  $k_{SC}$ , as given by the equation<sup>46,48</sup>:

$$k_{\rm SC}(\Delta\Phi_{\rm SC},\omega) = \frac{2\cdot\omega}{\pi} \cdot \frac{|e|\cdot\Delta\Phi_{\rm C}}{k_{\rm B}\cdot T} \cdot R_{\rm SC}(\Delta\Phi_{\rm SC},\omega) \cdot C_{\rm SC}(\Delta\Phi_{\rm C},\omega) = \frac{|e|^2 \cdot N(E_{\omega})}{\rho(\Delta\Phi_{\rm C})}$$
(43)

where  $C_{SC}(\Delta\Phi_C,\omega)$  is the  $C_{SC}$  value calculated at  $U_E = U_{fb} + \Delta\Phi_C$ , and it depends only on frequency, while  $R_{SC}$  is the measured series resistance of the a-SC/El. junction corrected for the electrolyte and contact resistance in the hypothesis of ideally polarizable interface. For a spatially homogenous thick a-SC the term  $k_{SC}$  depends only on frequency but not from the band bending. In fact, according to the last term in Eq. (43), we expect that, fixing the frequency,  $k_{SC}$  remains constant with the electrode potential provided that the constraints used to obtain Eqs. (41), (42) are satisfied. As precendently, in order to get the equations describing the dependence of  $R_{SC}$  and  $C_{SC}$  on potential we need to solve Eqs. (41), (42) which, in turn, is possible once we know the DOS distribution as a function of energy and distance from the metal/oxide interface. In order to account for a DOS changing in energy, in Refs. 46,48 we solved Eqs. (21a), (21b), (21c) by assuming a constant DOS and we multiplied by a trial function, similar to Eq. (39), to account for possible energy variation in the DOS function:

$$\frac{1}{C_{\rm SC}(\Delta\Phi_{\rm SC},\omega)} = \frac{1}{\sqrt{\varepsilon \cdot |\varepsilon|^2 \cdot \overline{N}}} \cdot \left\{ \ln\left(\frac{\Delta\Phi^*}{\Delta\Phi_{\rm C}}\right) + \sqrt{1 + \frac{2}{\Delta\Phi_g} \cdot (\Delta\Phi_{\rm SC} - \Delta\Phi^*)} \right\} \cdot f_{\omega}(\Delta\Phi_{\rm SC}) \tag{44}$$

$$f_{\omega}(\Delta\Phi_{\rm SC}) = \left(\frac{|e|\cdot\Delta\Phi_{\rm SC}}{k_{\rm B}\cdot T}\right)^{\alpha(\omega)} \tag{45}$$

In Eq. (44)  $\overline{N}$  is a frequency-dependent empirical parameter related to the average value of the DOS between  $E_F$  and  $E_{\omega}$ , while  $\alpha(\omega)$  is an empirical parameter derived from the best fitting of  $C_{SC}(\omega, \Delta\Phi_{SC})$  and the other symbols have been defined before.

The best fitting procedure of the  $C_{SC}^{-1}$  versus  $\Delta \Phi_{SC}$  curves provides the average DOS distribution,  $\overline{N}$ , to be used in deriving the spectroscopic value of DOS at  $E_{\omega}$ ,  $N(E_{\omega})$ , once that the  $k_{SC}$  value, at a fixed band bending  $\psi_{A}$ , is known. According to this, the value of DOS at different frequencies (energies) can be derived by using the following relationship:

$$N(E_{\omega}) = k_{\rm SC}(\Delta\Phi_{\rm A},\omega) \cdot f^{-2}(\Delta\Phi_{\rm A},\omega) \cdot \overline{N}$$
(46)

where  $\Delta \Phi_A = (\Delta \Phi_C + 3 k_B T/e)$  is the lowest potential at which Eqs. (43), (44) are valid. In order to test the validity of the proposed approach in Ref. 48, we presented a detailed study of the fitting process of simulated numerical data obtained for thick films showing a spatially homogeneous DOS but different DOS distributions variable in energy. In Fig. 8 we report the fitting of  $1/C_{SC}(\omega, \Delta \Phi_{SC})$  for the case of a constant DOS as well as for the case of a Gaussian DOS distribution located at different energy-distance from the Fermi level of the a-SC. The reported results confirmed the validity of the use of Eqs. (44)–(46) for deriving the DOS distribution and the numerical values of N(E), at different energies, provided that the width of space charge region remains well below the thickness of the a-SC. Moreover, the results agree with the suggested interpretation of using Eq. (43) as a test for the spatial homogeneity of the DOS distribution indicating that, regardless of the energy dependence of DOS distribution, a constant and potential-independent  $k_{SC}$  value is obtained for a spatially homogeneous SC provided that the space charge region remains well below the thickness (Fig. 8) of a-SC and  $\Delta \Phi_{SC} > \Delta \Phi_C + 3 k_B \cdot T$ . Further support to this interpretation was obtained


**Fig. 8** (A) Simulated and fitted inverse capacitance vs.  $\Delta \Phi_{SC}$  at 10 and 10,000 Hz. (B) Value of the DOS distribution extracted from the fitting of the capacitance at different frequencies. (C) Value of the parameter  $k_{SC}$  as a function of  $\Delta \Phi_{SC}$  at different frequencies. (D) Simulated and fitted inverse capacitance vs.  $\Delta \Phi_{SC}$  at 10 and 10,000 Hz. (E) Value of the DOS distribution extracted from the fitting of the capacitance at different frequencies. (F) Value of the parameter  $k_{SC}$  as a function of  $\Delta \Phi_{SC}$  at different frequencies. (F) Value of the parameter  $k_{SC}$  as a function of  $\Delta \Phi_{SC}$  at different frequencies. The thickness of the semiconductor is 141 nm. Adapted from La Mantia, F., Fan, M., Stojadinovich, J., Santamaria, M., Miraghaei, S., Di Quarto, F. *Electrochim. Acta*, **2015**, *179*, 460, (Figs. 2, 3, 4).

by the experimental results reported for anodic film grown on titanium foil in different conditions (see Fig. 10–11). These results will be discussed in the next section to highlight the role of space charge width and a-SC thickness on the ac response of the thin a-SC/El. junction.

#### Thin Films Variable DOS

On going from the thick film condition ( $X_{SC} \ll D_{SC}$ ) to the thin film condition ( $X_{SC} \approx D_{SC}$ ) new features emerged in the fitting procedure, based on Eqs. (43)–(46), of numerically calculated capacitance plots. As reported in Fig. 9 the fitting of the simulated capacitance data displays a shorter or longer electrode potential region of fitting as a function of the frequency of the ac signal owing to the fact that the space charge width is a function of the total DOS distribution as well as of the ac frequency. Fig. 9A,D shows that lower frequencies allow to probe a larger region of electrode potentials before the simulated data plot and the fitting curve, based on the use of Eq. (44), start to diverge. As a matter of fact we found that as long the relationship  $X_{SC} < 0.7 D_{SC}$  holds, that is, the space charge width is smaller than the 70% of the a-SC, Eq. (44) can be used to fit the capacitance data by using the analytical expression valid for spatially homogeneous a-SC. It is noteworthy that within this constraint ( $X_{SC} < 0.7 D_{SC}$ ) the value of DOS  $N(E_{\omega})$  derived from the fitting of capacitance is in good agreement with that assumed for the a-SC (see Fig. 9B,E).



**Fig. 9** (A) Simulated and fitted inverse capacitance vs.  $\Delta\Phi_{SC}$  at 10 and 10,000 Hz. (B) Value of the DOS distribution extracted from the fitting of the capacitance at different frequencies. (C) Value of the parameter  $k_{SC}$  as a function of  $\Delta\Phi_{SC}$  at different frequencies. (D) Simulated and fitted inverse capacitance vs.  $\Delta\Phi_{SC}$  at 10 and 10,000 Hz. (E) Value of the DOS distribution extracted from the fitting of the capacitance at different frequencies. (F) Value of the DOS distribution extracted from the fitting of the capacitance at different frequencies. (F) Value of the parameter  $k_{SC}$  as a function of  $\Delta\Phi_{SC}$  at different frequencies. The thickness of the semiconductor is 28.2 nm. From La Mantia, F., Fan, M., Stojadinovich, J., Santamaria, M., Miraghaei, S., Di Quarto, F. *Electrochim. Acta* **2015**, *179*, 460, (Fig. 6).

However, it is important to stress that if we look to the behavior of  $k_{SC}$  versus potential plots; it is now evident that the finite thickness of the a-SC affect sensibly the behavior of  $k_{SC}$  as a function of polarization potential.

These results help to better understand the capacitance behavior of semiconducting passive film/El. junction as reported, also, in very recent papers pertaining the characterization of thin passive films grown on Ti metal in different solutions and after different initial treatments. In Fig. 10 we report the experimental data and fitting curves based on the use of Eq. (44) for a film of TiO<sub>2</sub> about 20 nm thick grown on a Ti foil submitted only to a chemical etching. The fitting of  $(C_{SC})^{-1}$  versus  $U_E$  curves (Fig. 10A), in a quite wide range of frequencies (10 Hz-5 kHz), shows that such a film behaves as a thick a-SC as long as the electrode potential spans a range of values obeying the above reported constraint ( $X_{SC} < 0.7 D_{SC}$ ). Moreover, the typical frequency dependence of a-SC/El. junction is reflected in the M-S plots showing both a frequency-dependent shape as well as a typical nonlinear behavior in a wide range of electrode potentials. The thick film behavior has been attributed to the existence of a quite large value of DOS showing a superimposed Gaussian-like distribution on an almost constant value (Fig. 10C). The value of  $k_{SC}$  versus potential is also in large agreement with the expected behavior previously described for thick films simulated data (Fig. 10B).

On the other hand, a different initial treatment of the Ti foil is able to modify the electronic properties of the passive  $TiO_2$  film grown on an identical substrate but at lower potential and different electrolytic solutions. In fact the experimental data seem to suggest that the passive film formed in these conditions displays electronic properties typical of thin a-SC/El. junction, owing to the presence of a lower electronic DOS distribution (Fig. 11A–C).



**Fig. 10** (A) Fitting of C<sup>-1</sup> vs.  $U_E$  relating to anodic film grown on Ti to 5 V vs. Ag/AgCl on Ti in NaBB solution, recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (B)  $k_{SC}$  vs.  $U_E$  curves and (C) DOS distribution vs. distance in energy. Fitting parameters:  $U_{FB} = -0.21 \pm 0.025$  V vs. Ag/AgCl,  $\varepsilon = 50$ ,  $d_{OX} = 180$  Å. From Di Quarto, F., Di Franco, F., Miraghaei, S., Santamaria, M., La Mantia, F. J. Electrochem. Soc. **2017**, *164*(9) C516–C525, (Figs. 5-6).



**Fig. 11** (A) Fitting of C<sup>-1</sup> vs.  $U_E$  relating to anodic film grown on Ti by Pedeferri's treatment, recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (A)  $k_{SC}$  vs.  $U_E$  curves and (B) DOS distribution vs. distance in energy. Fitting parameters:  $U_{FB} = -0.215 \pm 0.025$  V vs. Ag/AgCl,  $\varepsilon = 50$ ,  $d_{OX} = 110$  Å. From Di Quarto, F., Di Franco, F., Miraghaei, S., Santamaria, M., La Mantia, F. *J. Electrochem. Soc.* **2017**, *164*(9) C516–C525, (Figs. 9-10).

#### Conclusions

A theoretical framework for the analysis of the differential capacitance data, usually employed for the characterization of SC/EL. interface, has been provided together with possible explanation for the frequently reported incongruencies in the use of classical Mott–Schottky approach. It has been shown that such a classical approach must be reserved to very special (and rarely checked) conditions underlying to the mathematical treatment used to derive the famous M-S equation. It has been shown that the frequently reported data on rather, improbably, high doping levels in passive films of very limited thickness could be an artifact due to the participation of the metal contribution to the measured differential capacitance. Analogously the frequency dependence observed in many M-S plots pertaining to passive films and attributed to several possible mechanisms needs to be carefully discussed and, possibly, interpreted on the basis of a more general approach based on the theory of a-SC Schottky barriers. It should be avoided, in any case, the practice of presenting M-S plots at only one frequency in absence of any control on the frequency independence of the measured differential capacitance data.

We like to conclude this work by recalling that in the seminal work of Dewald<sup>43</sup> on the characterization of single crystal ZnO/ electrolyte interface, by means of differential capacitance measurements, it is possible to read the following sentence:" In very good approximation the data are frequency independent, as shown for a typical case in Table II." For the sake of completeness, we like to stress the reported extent of variation in the slope ( $629/625/\mu$ F<sup>-2</sup> cm<sup>4</sup> V<sup>-1</sup>) and in the intersect with electrode potential axis ( $U_0 = -0.467 \pm 0.025$  V/SCE) of the experimental M-S plots. It is a pity that, more than 50 years after such a sentence and remarkable series of experiments, the younger generations of electrochemists seem still reluctant to face with such scientific legacy.

See also: Passivity and Passivity Breakdown; Passivity Breakdown: Development and Application of Local Chemical and Electrochemical Probe Methods; Photocurrent Spectroscopy in Passivity Studies.

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# EIS Technique in Passivity Studies: Determination of the Dielectric Properties of Passive Films

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## Glossary

**Cole–Cole plot** The imaginary part of the complex permittivity or relative permittivity as a function of the real part in orthonormal linear coordinates.

**Complex Capacitance** Representation of impedance in which the complex capacitance is given by  $C(\omega) = \frac{1}{i\omega(Z-R_c)}$ .

**Constant-Phase Element** Mathematical representation of frequency or time-constant dispersion for which impedance may be expressed as  $Z = \frac{1}{(i\omega)^{\alpha}Q}$ .

**Electrochemical Impedance Spectroscopy** A frequency-dependent transfer-function relating the electrical input and output for a given system.

**Nyquist plot** The imaginary part of the complex impedance as a function of the real part in orthonormal linear coordinates. **Power-Law Model** A model accounting for a power-law distribution of resistivity within a film that yields constant-phase frequency dispersion.

**Young impedance** A model accounting for an exponential distribution of resistivity within a film that yields frequency dispersion. The frequency dispersion associated with a Young impedance is frequency-dependent (i.e., it cannot be represented as a constant-phase element).

## Nomenclature

<u>C</u> *	$C_{\rm employ} = 100$ $E_{\rm employ} = 100$ $E_{\rm employ} = 100$
C.	Complex capacitance, see Eq. (12), F or F/cm
С	Capacitance, $F/cm^2$ or $F(1 F=1C/V)$
C <sub>dl</sub>	Double-layer capacitance, F/cm <sup>2</sup>
Coxide	Capacitance of the oxide film, F or F/cm <sup>2</sup>
Coxide,PL	Capacitance of the oxide film based on power-law model, see Eq. (20), F or F/cm <sup>2</sup>
F	Faraday's constant, 96,487 C/equiv
f	Frequency, Hz
$f_0$	Characteristic frequency, $f_0 = 1/2\pi\rho_0\varepsilon\varepsilon_0$
$f_{\delta}$	Characteristic frequency, $f_{\delta} = 1/2\pi\rho_{\delta}\varepsilon\varepsilon_0$
fc	Characteristic frequency, see Eq. (22)
8	Dimensionless parameter used for the power-law model, see Eq. (18)
j	Imaginary number, $j = \sqrt{-1}$
Q	CPE coefficient, see Eq. (16), $F/s^{1-\alpha}cm^2$
R	Resistance, $\Omega \text{ cm}^2$
R <sub>e</sub>	Ohmic resistance, $\Omega \text{ cm}^2$
Roxide	Resistance of the oxide film, $\Omega \text{ cm}^2$

<i>r</i> <sub>0</sub>	Radius of disk electrode, cm
Ŷ	Spatial coordinate perpendicular to electrode surface, cm
Ζ	Impedance, $\Omega \text{ cm}^2$
$Z_{\rm F,mo}$	Faradaic impedance at the metal-oxide interface, $\Omega$ cm <sup>2</sup>
$Z_{\rm F,oe}$	Faradaic impedance at the oxide-electrolyte interface, $\Omega \text{ cm}^2$
Zoxide	Impedance of the oxide film, $\Omega \text{ cm}^2$
Z <sub>Y,oxide</sub>	Young impedance of the oxide film, $\Omega \text{ cm}^2$
α	CPE exponent, see Eq. (16)
γ	Exponent in power-law model, see Eq. (14)
δ	Film thickness, cm
ε	Dielectric constant
$\boldsymbol{\varepsilon}_0$	Permittivity of vacuum, $8.8542 \times 10^{-14}$ F/cm
κ	Conductivity, S/cm
λ	Parameter used in Young model, see Eq.(6)
ξ	Dimensionless position, $\gamma/\delta$
π	3.14159265359
ρ	Resistivity, $\Omega$ cm
$ ho_0$	Resistivity at position $\gamma = 0$ , see Eq. (6) for a Young model and Eq. (14) for the power-law model, $\Omega$ cm
$ ho_{\delta}$	Resistivity at position $\gamma = \delta$ , see Eq. (14), $\Omega$ cm
$\pmb{\Phi}_{ m me}$	Potential difference between the metallic electrode and a reference electrode in the electrolyte, V
$\pmb{\Phi}_{ m mo}$	Potential drop at the metal-oxide interface, V
$\Phi_{ m oe}$	Potential drop at the oxide-electrolyte interface, V
$\pmb{\Phi}_{ ext{oxide}}$	Potential drop through the oxide, V
$\varphi$	Phase angle
ω	Angular frequency, s <sup>-1</sup>

## Introduction

Different descriptions of oxide layers were presented in the literature, including the ion-migration mechanism,<sup>1</sup> the generalized high field model,<sup>2</sup> and, more recently, the point defect model (PDM) introduced by Digby MacDonald.<sup>3,4</sup> The PDM describes the main properties of the oxide layer in terms of kinetics and transport processes, but application of the model is complicated by the large number of parameters. Generally, the experimental electrochemical impedance for oxide-covered metals is very simple and can be reduced to one loop which looks like a depressed semicircle. This leads D. D. Macdonald to use a CPE in the equivalent circuit to represent the geometrical capacitance of the barrier layer.<sup>5</sup> However, even if a CPE is well suited for a fitting purpose, it lacks physical meaning.

In the present chapter, the oxide layer is considered to be a dielectric layer characterized by its resistivity and permittivity. The impedance of an oxide-covered electrode is dominated by the oxide layer under anodic potentials; whereas, for a cathodic potential, a parallel impedance must be taken into account. The impedance of the CPE introduced by D. D. Macdonald<sup>5</sup> is thus considered here to be the impedance of the oxide layer when the potential is anodic.

## Theory

For a homogeneous oxide layer of thickness  $\delta$ , permittivity  $\varepsilon$ , and resistivity  $\rho$ , the impedance per surface unit corresponds to a resistor  $R_{\text{oxide}}$  in parallel with a capacitor  $C_{\text{oxide}}$ , where  $R_{\text{oxide}} = \rho\delta$  and  $C_{\text{oxide}} = \varepsilon\varepsilon_0/\delta$ . The corresponding impedance diagram in the Nyquist plane has the appearance of a semicircle.

If the oxide layer is nonhomogeneous, the resistivity and the permittivity are spatially variant. Under the assumption that the variation of the electrical parameters is in the direction normal to the metal, a local value of resistivity may be designated as  $\rho(\gamma)$ , and a local value of permittivity may be given as  $\varepsilon(\gamma)$ . The resistance associated with a thin differential element d $\gamma$  may be expressed as  $\rho(\gamma)d\gamma$ , and the capacitance may be expressed as  $\varepsilon(\gamma)\varepsilon_0/d\gamma$ . The impedance of this differential element is

$$dZ_{\text{oxide}} = \frac{\rho(\gamma)d\gamma}{1 + j\omega\rho(\gamma)\varepsilon(\gamma)\varepsilon_0} \tag{1}$$



Fig. 1 Equivalent circuit corresponding to an oxide layer with an axial distribution of dielectric and resistive properties.

The corresponding equivalent circuit representation is given in Fig. 1. The impedance of the oxide layer is obtained by integrating over the thickness of the layer, e.g.,

$$Z_{\text{oxide}} = \int_{0}^{\delta} \frac{\rho(\gamma)}{1 + j\omega\rho(\gamma)\varepsilon(\gamma)\varepsilon_{0}} d\gamma$$
(2)

The variation of electrical properties in the film causes a frequency or time-constant dispersion. Such frequency dispersion is frequently observed in impedance measurements for oxide-coated electrodes, and the corresponding impedance diagram is a depressed semicircle in the Nyquist plane.

When the frequency tends toward zero, the resistance  $\rho(y)$ dy in each differential layer is much smaller than the impedance of the corresponding capacitance  $-jdy/\epsilon(y)\epsilon_0\omega$ ; thus, the impedance of the oxide film is a pure resistance

$$R_{\text{oxide}} = \int_0^\delta \rho(\gamma) \mathrm{d}\gamma \tag{3}$$

In contrast, when the frequency tends toward infinity, the resistance  $\rho(\gamma)d\gamma$  in each differential layer can be neglected with respect to the impedance of the corresponding capacitance, expressed as  $-j\epsilon(\gamma)\epsilon_0/\omega d\gamma$ , and the impedance is the impedance of a pure capacitor, i.e.,

$$\frac{1}{C_{\text{oxide}}} = \int_0^\delta \frac{1}{\varepsilon(y)\varepsilon_0} dy \tag{4}$$

In order to extract the capacity of the oxide layer from experimental data, the complex-capacitance representation (sometimes called a Cole–Cole plot) could be useful. The value  $C_{\text{oxide}}$  is the extrapolation at infinite frequency of the complex capacitance,  $C^* = 1/j\omega Z_{\text{oxide}}$ , and this value can be obtained by plotting  $C^*$  in the complex plane.

Derivation of the expression of  $Z_{\text{oxide}}$  (Eq. 2) requires the distribution of  $\varepsilon(\gamma)$  and  $\rho(\gamma)$ . The values of dielectric constant for different oxides,<sup>6–8</sup> shown in Table 1, fall within a relatively narrow range, but the resistivity can vary over many decades, from insulator to conductor.

As the variation in permittivity may be considered insufficient to account for a distribution of time constants extending over several orders of magnitude, the first hypothesis is to consider the permittivity to be uniform, i.e., not distributed within the oxide

 Table 1
 Values for dielectric constant for different oxides

Ovide	Reference	Dielectric constant o	
	nererence		
Cu <sub>2</sub> O	6	7.6	
CuO	6	18.1	
Fe <sub>2</sub> O <sub>3</sub> -α	6	12	
Nb <sub>2</sub> O <sub>5</sub>	7,8	42	
ZrO <sub>2</sub>	6	12.5	

layer. Thus, the variation in time constant is attributed to a resistivity distribution. Under the assumption of a uniform permittivity, Eq. (2) becomes

$$Z_{\text{oxide}} = \int_{0}^{\delta} \frac{\rho(\gamma)}{1 + j\omega\rho(\gamma)\varepsilon\varepsilon_{0}} d\gamma$$
(5)

Two different resistivity distributions have been proposed in the literature: an exponential resistivity distribution corresponding to the Young model and a resistivity distribution following a power law.

## **Exponential Resistivity Distributions: Young Model**

Young assumed that the nonstoichiometry of the oxide layer resulted in an exponential variation of the conductivity with respect to the normal distance to the electrode.<sup>2,9</sup> This assumption may be expressed in terms of resistivity as

$$\rho(\gamma) = \rho_0 \exp(-\gamma/\lambda) \tag{6}$$

where  $\rho_0$  is the resistivity of the oxide at the metal–oxide interface, i.e.,  $\rho_0 = \rho(0)$ . A normalized resistivity  $\rho(\gamma)/\rho_0$  is presented in Fig. 2 as a function of the dimensionless position  $\gamma/\delta$ .

For the resistivity distribution presented in Eq. (6), the corresponding impedance can be derived by integration of Eq. (5).<sup>9,10</sup> This impedance is generally called the Young impedance,

$$Z_{\rm Y,oxide} = \frac{\lambda}{j\omega\varepsilon\varepsilon_0} \ln\left(\frac{1+j\omega\rho_0\varepsilon\varepsilon_0}{1+j\omega\rho_0\varepsilon\varepsilon_0\exp(-\delta/\lambda)}\right)$$
(7)

When  $\omega \rightarrow 0$ , application of L'Hopitals rule yields

$$Z_{\text{Y,oxide}}(0) = \lambda \rho_0 (1 - \exp(-\delta/\lambda))$$
(8)

which corresponds to a resistor. This result could be obtained as well by a direct integration of resistivity, i.e.,

(

$$Z_{\rm Y,oxide}(0) = \int_0^\delta \rho_0 \exp(-\gamma/\lambda) d\gamma$$
(9)

In the high-frequency limit,

$$Z_{\rm Y,oxide}(\infty) = -j \frac{\delta}{\omega \varepsilon \varepsilon_0} \tag{10}$$

Eq. (10) corresponds to the impedance of the capacitor

$$C_{\text{oxide}} = \frac{\varepsilon \varepsilon_0}{\delta} \tag{11}$$

given as Eq. (4) in the general case.



**Fig. 2** Normalized resistivity from Eq. (6) as function of dimensionless position with  $\delta/\lambda$  as a parameter.

An example of the Young impedance is presented in Fig. 3 in Nyquist format with  $\delta/\lambda$  as a parameter. The solid black line represents the impedance response of an oxide layer with homogeneous properties  $\rho(\gamma) = \rho_0$  and  $\varepsilon(\gamma) = \varepsilon$ , corresponding to an *RC* circuit. As compared to the solid line, the Young impedance appears as a depressed semicircle. The Nyquist plot, however, is not symmetric, especially for  $\delta/\lambda > 5$ .

A clearer representation of the impedance response is given by the Bode plot, presented in Fig. 4 as a function of frequency. For an RC-circuit (solid lines), the characteristic frequency is equal to  $1/2\pi RC$  or  $1/2\pi\rho_0\varepsilon\varepsilon_0$ . For the Young model (dashed lines), two characteristic frequencies can be defined, one in low frequency where the imaginary part of the impedance is small with respect to the real part and the other in high frequency where the imaginary part is large with respect to the real part. The lower characteristic frequency is defined by the cut-off frequency of the Voigt element at the interface between the metal and the oxide where the resistor is  $\rho_0 dy$  and the capacitor is  $\varepsilon\varepsilon_0/dy$ . The corresponding characteristic frequency is  $f_0 = 1/2\pi\rho_0\varepsilon\varepsilon_0$ . This cut-off frequency has the same definition as the characteristic frequency for a homogeneous layer, but this cut-off frequency is not the characteristic frequency corresponding to the maximum magnitude of the imaginary part (see Fig. 3). The higher characteristic frequency is defined by the cut-off frequency of the Voigt element at the interface between the oxide and the solution where the resistor is  $\rho_0 dy$  and  $\rho_{\delta} = \rho(\delta)$ . As the capacitor is  $\varepsilon\varepsilon_0/dy$ , the associated characteristic frequency is given by  $f_{\delta} = 1/2\pi\rho_{\delta}\varepsilon\varepsilon_0$ . Following Eq. (6),  $\rho_{\delta} = \rho_0 \exp(-\delta/\lambda)$ , and, thus,  $f_{\delta} = 1/2\pi\rho_0\varepsilon\varepsilon_0 \exp(-\delta/\lambda)$ . The phase angle is equal to zero at low frequency and approaches – 90 degrees at high frequency. At no frequency is the phase angle independent of frequency, and, by definition, no constant phase angle is found.

Another representation of the impedance data is in the form of a complex capacitance,<sup>11,12</sup> given as

$$C^* = \frac{1}{j\omega(Z - R_{\rm e})} \tag{12}$$

A plot of the imaginary part of the complex capacitance as a function of the real part of the complex capacitance is referred to as a type of Cole–Cole plot. The Cole–Cole plot corresponding to the theoretical data presented in Figs. 3 and 4, for  $\delta/\lambda = 10$ , is given in Fig. 5. At sufficiently high frequency, the complex capacitance approaches the real value expressed by Eq. (12).

## **Power-Law Distributions**

The exponential resistivity distribution leads to a phase angle that varies with frequency and therefore cannot account for cases where the impedance of oxide layers presents a constant-phase element (CPE). Hirschorn et al.<sup>13,14</sup> identified a relationship between CPE parameters and physical properties by regressing a measurement model<sup>15,16</sup> to synthetic CPE data. Following the procedure described by Agarwal et al.<sup>15,16</sup> sequential Voigt elements were added to the model until the addition of an element did not improve the fit and one or more model parameters included zero within their 95.4% confidence interval.

The concept was to identify the distribution of resistivity that, under the assumption that the dielectric constant is independent of position, would result in CPE behavior. The details of the development are presented in reference [13].

The resistivity associated with a CPE was found to follow a power-law profile, i.e.,

$$\frac{\rho}{\rho_{\delta}} = \xi^{-\gamma} \tag{13}$$



**Fig. 3** Young impedance given by Eq. (7) in Nyquist format with  $\delta/\lambda$  as a parameter. The model parameters were  $\varepsilon = 12$ , and  $\rho_0 = 1 \times 10^9 \Omega$  cm. The solid line ( $\delta/\lambda = 0$ ) represents the impedance response of an RC circuit.



**Fig. 4** Phase angle associated with the Young impedance given by Eq. (7) as a function of frequency with  $\delta/\lambda$  as a parameter. The model parameters were  $\varepsilon = 12$  and  $\rho_0 = 1 \times 10^9 \Omega$  cm. The solid curve ( $\delta/\lambda = 0$ ) represents the phase angle associated with an RC circuit.

where  $\xi = \gamma/\delta$  is the dimensionless position,  $\gamma$  represents the position through the depth of the film, and  $\delta$  is the film thickness. The parameter  $\rho_{\delta}$  is the resistivity at  $\xi = 1$ , and  $\gamma$  is a positive constant indicating how sharply the resistivity varies. A distribution of resistivity that provides a bounded value for resistivity at  $\xi = 0$  was proposed to be

$$\frac{\rho}{\rho_{\delta}} = \left(\frac{\rho_{\delta}}{\rho_{0}} + \left(1 - \frac{\rho_{\delta}}{\rho_{0}}\right)\xi^{\gamma}\right)^{-1}$$
(14)

where  $\rho_0$  and  $\rho_{\delta}$  are the boundary values of resistivity at respective interfaces. A normalized resistivity  $\rho(\gamma)/\rho_0$  is presented in Fig. 6 versus the dimensionless distance  $\gamma/\delta$ .



**Fig. 5** The normalized complex–capacitance plot for a Young impedance with the model parameters:  $\delta/\lambda = 10$ ,  $\varepsilon = 12$ , and  $\rho_0 = 1 \times 10^9 \Omega$  cm: (A) with imaginary impedance on a logarithmic scale and (B) with imaginary impedance on a linear scale.



Fig. 6 Normalized resistivity from Eq. (14) as a function of dimensionless position with  $\gamma$  as a parameter.

A semianalytic solution to Eq. (5) could be found for the resistivity profile given in Eq. (14) that applied under the conditions that  $\rho_0 \gg \rho_{\delta}$  and  $f < (2\pi \rho_{\delta} \varepsilon \varepsilon_0)^{-1}$ . The solution was given as

$$Z_{\text{oxide}} = g(\gamma) \frac{\delta \rho_{\delta}^{1/\gamma}}{\left(\rho_{0}^{-1} + j\omega\varepsilon\varepsilon_{0}\right)^{(\gamma-1)/\gamma}}$$
(15)

where *g* is a function of  $\gamma$ .

Eq. (15) is in the form of a CPE for  $f > 1/(2\pi\rho_0\varepsilon\varepsilon_0)$ , i.e.,

$$Z_{\text{oxide}} = g \frac{\delta \rho_{\delta}^{1/\gamma}}{(j\omega\varepsilon\varepsilon_{0})^{(\gamma-1)/\gamma}} = \frac{1}{(j\omega)^{\alpha}Q}$$
(16)

Inspection of Eq. (16) suggests that

$$\alpha = \frac{\gamma - 1}{\gamma} \tag{17}$$

Numerical integration was used to develop the interpolation formula

$$g = 1 + 2.88(1 - \alpha)^{2.375} \tag{18}$$

A relationship among the CPE parameters, Q and  $\alpha$ , and the dielectric constant  $\varepsilon$ , resistivity  $\rho_{\delta}$ , and film thickness  $\delta$  was found to be

$$Q = \frac{(\varepsilon \varepsilon_0)^{\alpha}}{g \delta \rho_{\delta}^{1-\alpha}} \tag{19}$$

Eqs. (11) and (19) yield an expression for the capacitance as

$$C_{\text{oxide,PL}} = gQ(\rho_{\delta}\varepsilon\varepsilon_0)^{1-\alpha}$$
<sup>(20)</sup>

In addition to the CPE parameters Q and  $\alpha$ ,  $C_{\text{oxide,PL}}$  depends on the dielectric constant e and the smaller value of the resistivity, e.g.,  $\rho_{\delta}$ .

Eq. (20) can also be expressed as

$$C_{\text{oxide PL}} = (gQ)^{1/\alpha} (\delta\rho_{\delta})^{(1-\alpha)/\alpha}$$
(21)

An example of a power-law impedance is presented in Fig. 7 in Nyquist format with  $\gamma$  as a parameter. The solid line represents the impedance response of an oxide with homogeneous properties  $\rho(\gamma) = \rho_0$  and  $\varepsilon(\gamma) = \varepsilon$ , which corresponds to an *RC* circuit. As compared to the solid line, the power-law impedance appears as a depressed semicircle. The Nyquist plot is not symmetric, especially for  $\gamma > 10$  (or  $\alpha < 0.9$ ).

A clearer representation of the impedance response is given by the Bode plot, presented in Fig. 8 as a function of the dimensionless frequency  $f/f_0$ . For an RC circuit (dashed lines), the characteristic frequency is equal to  $1/2\pi RC$  or  $1/2\pi \rho_0 \varepsilon e_0$ .



**Fig. 7** Nyquist plot for a power-law impedance calculated from Eqs. (5) and (14) with exponent  $\gamma$  as a parameter: (A) full scale and (B) zoomed scale showing the behavior at smaller values of impedance.

For the power-law model (solid lines), two characteristic frequencies can be defined, one in low frequency where the imaginary part of the impedance is small with respect to the real part and the other in high frequency where the imaginary part is large with respect to the real part. The lower characteristic frequency is defined by the cut-off frequency of the Voigt element at the interface between the metal and the oxide where the resistor is  $\rho_0 dy$ , the capacitor is  $\epsilon \epsilon_0/dy$ , and  $f_0 = 1/2\pi\rho_0\epsilon\epsilon_0$ . This cut-off frequency has the same definition as the characteristic frequency for a homogeneous layer, but this cut-off frequency is not the characteristic frequency of the Voigt element at the interface between the oxide where the maximum of the imaginary part (see Fig. 7). The higher characteristic frequency is defined by the cut-off frequency of the Voigt element at the interface between the oxide and the solution where the resistor is  $\rho_{\delta} dy$ , the capacitor is  $\epsilon \epsilon_0/dy$ , and  $f_{\delta} = 1/2\pi\rho_{\delta}\epsilon\epsilon_0$ .

The complex capacitance plot corresponding to the theoretical data presented in Figs. 7 and 8 is given in Fig. 9. It should be noted that the extrapolation of the frequency domain in which the impedance behaves as a CPE crosses the origin, shown as a dashed line in Fig. 9.

## Application to Nb<sub>2</sub>O<sub>5</sub> and to Al<sub>2</sub>O<sub>3</sub>

Two examples for the impedance of oxide-covered metals are described in this section:  $Nb_2O_5$  and  $Al_2O_3$ . In Fig. 10A and B, these results are presented in Nyquist format. For the  $Nb_2O_5$  layer, the impedance of the oxide layer is attributed to the high-frequency loop.<sup>17</sup> These results are also plotted in Bode coordinates in Fig. 11.

Figs. 10 and 11, where the impedances are represented in classical coordinates, cannot be used to ascertain whether the impedances follow a CPE behavior in high-frequency range because, in Bode coordinates, the results are obscured by the electrolyte resistance, and, in Nyquist representation, the low impedance values are also obscured. As suggested by Orazem and Tribollet,<sup>18</sup> Ohmic-resistance-corrected Bode plots allow interpretation of the high-frequency behavior.

## Nb<sub>2</sub>O<sub>5</sub> Oxide Layer

Ohmic-resistance-corrected Bode plots are presented in Fig. 12 for the niobium oxide film. The ohmic-resistance-corrected phase angle, presented in Fig. 12 (square symbol), decreases with frequency. As no CPE appears in the experimental data, a Young



**Fig. 8** Bode plot for a power-law impedance calculated from Eqs. (5) and (14) with exponent  $\gamma$  as a parameter: EIS data obtained for the integral relation (5) and the analytical solution of the impedance in the case of a power law (15).  $\rho_0 = 10^{16} \Omega$  cm,  $\rho_{\delta} = 10^6 \Omega$  cm,  $\gamma = 7$ ,  $\varepsilon = 10$ , and a film thickness of 100 nm.



**Fig. 9** Complex-capacitance plot for a power-law impedance with the model parameters:  $\delta = 100$  nm,  $\alpha = 0.85$ ,  $\varepsilon = 12$ ,  $\rho_0 = 1 \times 10^{16} \Omega$  cm, and  $\rho_{\delta} = 1 \times 10^{6} \Omega$  cm.



Fig. 10 Impedance of an Al<sub>2</sub>O<sub>3</sub> oxide layer (A) and of Nb<sub>2</sub>O<sub>5</sub> oxide layer (B) in a Nyquist format.



Fig. 11 Impedance results from Fig. 10 presented in Bode coordinates.

model providing an exponential distribution of resistivity should be considered for the niobium oxide. The regression of the high-frequency loop by the Young impedance needs to take into account the inductive loop which is obviously present in the middle-frequency range. The quality of the regression may be seen in Figs. 12 and 13. The fitted parameters are the following:  $\rho_0 = 6.4 \times 10^{10} \Omega$  cm,  $\lambda = 3.2$  nm, and  $\delta = 59$  nm, which, following Eq. (6), yields a value of  $\rho_{\delta} = 630 \Omega$  cm at  $\gamma = \delta$ . Given a dielectric constant  $\varepsilon = 42$ , the capacitance of the oxide film is 0.63  $\mu$ F/cm<sup>2</sup>. This result is in relatively good agreement with the extrapolation of the Cole–Cole plot presented in Fig. 14. The difference of 10% could be due to the permittivity value and to the estimate of the electrolyte resistance used for the Cole–Cole plot.



Fig. 12 Impedance results for  $Nb_2O_5$  taken from Figs. 10 and 11 and presented as ohmic-resistance-corrected Bode plots. The + represents regressed values.

## Al<sub>2</sub>O<sub>3</sub> Oxide Layer

The ohmic-resistance-corrected Bode plot is presented in Fig. 15 for the impedance of the  $Al_2O_3$  layer. On the corrected phase shift, a clear plateau is evident between 10 and 200 Hz, which corresponds to a CPE behavior. Thus, the power-law model may be used to analyze the data. For a frequency larger than 200 Hz, a decrease of the phase shift is observed. This phenomenon is attributed to the geometric effect corresponding to the nonuniform current and potential distribution.<sup>19,20</sup> This geometric effect appears for frequencies larger than a characteristic frequency



Fig. 13 Impedance response for  $Nb_2O_5$  in Nyquist format showing the comparison between data and model fit.



Fig. 14 Complex-capacitance plot for Nb<sub>2</sub>O<sub>5</sub> showing the extrapolation to a real value.

$$f_c = \frac{\kappa}{2\pi C_{\text{oxide}} r_0} \tag{22}$$

where  $\kappa$  is the conductivity of the solution,  $C_{\text{oxide}}$  is the capacity of the oxide layer, and  $r_0$  is the radius of the disk electrode.

In the present case, the characteristic frequency value is 1100 Hz, as shown in Fig. 15. As the geometric effect was derived by using a numerical derivation of Laplace's equation, it is difficult to introduce this effect in a fitting procedure; therefore, in the following analysis, the impedance data will be regressed for frequencies below 200 Hz.

As is seen in Fig. 15, a frequency of 200 Hz is smaller than the characteristic frequency  $f_{\delta}$ ; thus, the impedance data can be regressed by the analytic formula given as Eq. (15). In this formula, the two parameters  $\rho_{\delta}$  and  $\delta$  appear in a product, and only this product can be obtained by regression. The necessary independent determination of  $\delta$  could be obtained from the complex–capacitance plot (Fig. 16). The shape of this plot for frequencies lower than 200 Hz is similar to the theoretical plot given in Fig. 9. For the frequency range corresponding to CPE behavior, the experimental points are on a straight line crossing the origin. For a frequency larger than 200 Hz, the data points are above this line due to the geometric effect. However, the



Fig. 15 Impedance results for Al<sub>2</sub>O<sub>3</sub> taken from Figs. 10 and 11 and presented as ohmic-resistance-corrected Bode plots.



Fig. 16 Complex-capacitance plots for Al<sub>2</sub>O<sub>3</sub> showing the influence of geometric capacitance and the extrapolation to a real value.

extrapolation of the high-frequency data gives a value between 1.1 and  $2 \mu F/cm^2$  for the capacitance of the oxide layer. Accordingly, the thickness of the oxide layer was obtained from Eq. (11):

$$\delta = \varepsilon \varepsilon_0 / C_{\text{oxide}} \tag{23}$$

where  $\varepsilon_0$  is the permittivity of vaccum ( $\varepsilon_0 = 8.8542 \times 10^{-14} \text{ F cm}^{-1}$ ). With  $\varepsilon = 11.5$ ,<sup>21</sup> a value of 5–9.3 nm is obtained for the oxide film thickness.

With the larger value of 9.3 nm for the oxide layer thickness, the different parameters of the impedance were determined by regression to be  $\rho_0 = 4.8 \ 10^{11} \Omega$  cm,  $\rho_{\delta} = 8.5 \ 10^5 \Omega$  cm, and  $\alpha = 0.72$ . A comparison between the model and data in Nyquist format is presented in Fig. 17.

## **Oxide Layer as an Electrode**

The electrochemical system represented in Fig. 1 comprises a metallic electrode covered by an oxide layer, which is in contact with electrolyte. Thus, the electrochemical system is composed of an oxide dielectric layer between two interfaces. The potential difference between the metallic electrode and a reference electrode in the electrolyte  $\Phi_{me}$  can be written as

$$\Phi_{\rm me} = \Phi_{\rm mo} + \Phi_{\rm oxide} + \Phi_{\rm oe} \tag{25}$$



Fig. 17 Impedance response for Al<sub>2</sub>O<sub>3</sub> in Nyquist format showing the comparison between data and model fit.



Fig. 18 Electrical equivalent circuit showing the parallel contributions of anodic and cathodic reactions.

where  $\Phi_{\rm mo}$  is the potential drop at the metal–oxide interface,  $\Phi_{\rm oxide}$  is the potential drop through the oxide, and  $\Phi_{\rm mo}$  is the potential drop at the oxide–electrolyte interface.

For a passive layer under steady-state conditions, D. Macdonald gave a similar equation in a schematic form.<sup>22</sup> The passive current crosses the electrochemical system, and the corresponding equation for the impedance is

$$Z = Z_{\rm F,mo} + Z_{\rm oxide} + \frac{Z_{\rm F,oe}/j\omega C_{\rm dl}}{Z_{\rm F,oe} + 1/j\omega C_{\rm dl}}$$
(26)

If the dissolution reaction is considered to be very fast,  $Z_{F,mo} \ll Z_{oxide}$ , and, if the reaction at the interface between the oxide and the electrolyte does not exchange electrons,  $Z_{F,oe} = \infty$ .

Eq. (26) becomes

$$Z = Z_{\text{oxide}} + \frac{1}{j\omega C_{\text{dl}}}$$
(27)

As was done in the first part of this chapter, the impedance associated with the double-layer capacitance can be generally neglected as compared to  $Z_{\text{oxide}}$ .

Because Eq. (27) is defined with the passive current, this impedance corresponds to the anodic branch. If a cathodic reaction is taken into account, this reaction occurs at the interface between the electrolyte and the oxide layer, resulting in an impedance that is parallel to the anodic branch as shown in Fig. 18. The electrons are generated at the interface between the electrolyte and the oxide layer and are transferred to the metal through an electronic resistance. It is interesting to note that the resistances which appear in Fig. 1 are similar to ionic resistances because these are due to vacancies. For simple reaction kinetics, the electronic resistance is added to the cathodic charge-transfer resistance, and only the sum of the two can be determined. In case of a tunneling effect, the electronic resistance is very small and negligible for impedance analysis.

## Conclusions

The impedance response of oxide films on metals that show a nonideal capacitive behavior may be interpreted in terms of distributions of electrical properties. In the case of homogeneous oxide films, expressions for impedance derived in terms of exponential and power-law distributions of resistivity can be used to extract film properties such as film thickness and parameters characteristic of the resistivity distribution. Interestingly, the extrapolation of complex–capacitance plots provides a convenient and independent method to extract film capacitance.

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## **Electrochemical Scanning Tunneling Microscopy**

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## Introduction

After the successful experimental verification of the quantum mechanical phenomenon of electron "tunneling" through a vacuum gap by Binnig and Rohrer in 1981, namely an exponential dependence of the tunneling current on the width of a vacuum gap between two metals,<sup>1</sup> these authors immediately demonstrated the enormous analytical power of this discovery by recording the first STM images from a cleaved Si(111) surface in (moderate) vacuum. By making one of the tunnel electrodes a very sharp tip, and scanning it at controlled distance of ~1 nm across the Si(111) surface, they were able to visualize crystallographic steps and even the famous  $(7 \times 7)$ -reconstruction<sup>2</sup> on the terraces between the steps (Fig. 1A). The most important prerequisite for this type of microscopy is the stable mechanical control of the vacuum gap. Corresponding instrumental improvements and numerous further developments, like software development for tip control, data acquisition, and image processing, as well as temperature control not only made STM within short time a most powerful method in ultrahigh vacuum (UHV)-based surface science, but also triggered the development of quite a number of other "proximity"- or scanning probe methods among them atomic force microscopy (AFM).<sup>39</sup> Fig. 1B illustrates the incredible improvement of STM imaging within just a few years.<sup>3</sup>

It was therefore close to test the same technique also under ambient conditions, and nowadays STM and related techniques are most successfully applied to study also solid surfaces in contact with real gas pressures over wide temperature ranges, in liquids or specifically in electrolytes at variable electric potentials.

The first examination of an electrochemically (100)-facetted polycrystalline Pt electrode by Gomez et al.<sup>4</sup> was still done ex situ after emersion of the electrode from the electrolyte and transfer into vacuum. The first report on STM measurements in liquids, namely oil or liquid nitrogen, was published in 1986,<sup>5</sup> and only 1 year later Sonnenfeld et al.<sup>6</sup> managed to image the surface of graphite and a gold film on glass in water and aqueous electrolyte solutions.

In these early experiments, a mere "two-electrode" setup (metallic tip and electrode surface) was used, with a given bias voltage between them. This arrangement lacked the capability to control the electrode potential, and thereby also that of the tip, with respect to a known reference electrode. Since the biased tip may also act as an electrode, this arrangement involves the risk that polarization and even charge-transfer-induced capacitive and exchange currents through the tip may disturb the detection of the actual tunneling current, or even worse, lead to a destruction of the tip. In 1988, Siegenthaler et al.<sup>7</sup> introduced the three-electrode setup by combining the tip and the sample (working electrode) with an unpolarizable reference electrode (in their case Ag/AgCl) and controlling both potentials with a potentiostat. Only shortly afterwards, Itaya et al.<sup>8</sup> added fourth also a counter-electrode, commonly used in electrochemistry to measure Faradaic currents. This arrangement permitted continuous scanning, while the potential of the working electrode is changed. This was the beginning of true in situ EC-STM.



**Fig. 1** Early development of STM: (A) first STM image taken of the reconstructed Si(111)( $7 \times 7$ ) surface in 1982<sup>2</sup>; (B) STM image of a reconstructed Si(111)( $7 \times 7$ ) surface taken just 8 years later.<sup>3</sup> Indicated is the ( $7 \times 7$ ) unit cell, whose diagonals have the lengths 46.56 Å and 26.88 Å.

Since then, several researchers have advanced the field of EC-STM, namely Bard,<sup>9,10</sup> Behm,<sup>11,12</sup> Ertl,<sup>13,14</sup> Kolb,<sup>11,12,15</sup> Magnussen,<sup>16,17</sup> Nichols,<sup>18,19</sup> Soriaga,<sup>20</sup> Itaya,<sup>20</sup> Wandelt,<sup>21,22</sup> Wandlowski,<sup>23</sup> Weaver,<sup>24</sup> etc., and the range of possible electrolytes was expanded even including ionic liquids.<sup>25–29</sup> Furthermore, the enormous progress in computing capacity and microprocessor technology nowadays allows very fast data acquisition. Magnussen and coworkers, for instance, built the first video EC-STM which allowed registering 10–30 images per second.<sup>16</sup> Since then, further successful developments of fast STM instrumentation have been published.<sup>30–32</sup>

## Scanning Tunneling Microscopy

## The Principle of Electron Tunneling

In classical physics, an electron of total energy *E* cannot overcome an energy barrier  $\Phi > E$ . In quantum mechanics on the other hand, the particle can also be described by a wave function  $\psi(x, y, z)$ . This wave function can penetrate into and pass the barrier as long as height and width of the barrier are finite. The wave function continues on the other side of the barrier with smaller amplitude but at the same frequency (Fig. 2). As a consequence, electrons can "tunnel" between two metals which are close enough but have no



**Fig. 2** Quantum mechanical "tunneling" of an electron from metal I through a vacuum barrier of height  $\Phi$  and width z to metal II;  $\psi_{I}$ ,  $\psi_{II}$  are wave functions before and after tunneling.



**Fig. 3** Energy diagram of a tunnel junction between tip (T) and sample (S).  $E_V$  = vacuum level,  $E_F$  = Fermi level,  $\Phi$  = work function, z = tunnel gap,  $U_B$  = applied bias voltage between tip and sample,  $I_T$  = tunnel current, and LDOS = local density of states.

contact. If one of the two metals is designed as a very fine tip, ideally monoatomic, above an extended surface of the other metal, the tunneling process between both metals is spatially confined to the very position of the tip with respect to the surface. This is the basic principle of a tunneling microscope. The only further aspect to consider is the Pauli principle: The electron can only tunnel through the barrier if there are empty "quantum states" on the other side, as illustrated in Fig. 3. As long as the Fermi levels of both metals are aligned, that is,  $U_B = 0$ , all electronic states below  $E_F$  are filled on both sides. In this case, an electron can only tunnel from one metal to the other if simultaneously another electron tunnels in the opposite direction. Thus, a measurable electron current will only occur if there is a net excess flow of electrons in one direction. This can be achieved by applying a small so-called bias voltage  $U_B \neq 0$  between both metals, which causes a relative shift of both Fermi levels of tip (T) and sample (S). Now, electrons from occupied states within the interval  $E_{E,T}-E_{F,S}=\Delta E_F=eU_B$  can tunnel from the left into empty states above  $E_{F,S}$  on the right, causing a measurable tunneling current<sup>39-38</sup>

$$I_{\rm T} \sim U_{\rm B} \cdot e^{(-kz_{\rm V}/\phi)} \rho(E_{\rm F,S}); (eU_{\rm B} \ll \Phi)$$
<sup>(1)</sup>

which depends linearly on the bias voltage  $U_{\rm B}$ , but exponentially on the barrier height  $\Phi$  and barrier width *z*.  $\rho(E_{\rm F,S})$  is the local density of states (LDOS) near the Fermi level of the sample (see below). By far most of the electrons tunnel elastically, that is, into a state of same energy. *z* is the distance between tip and sample, and the barrier height may be approximated by  $\Phi = 1/2(\Phi_{\rm T} + \Phi_{\rm S})$ , with  $\Phi_{\rm T}$ ,  $\Phi_{\rm S}$  being the work functions of tip and sample.

Eq. (1) results from a quantum mechanical treatment<sup>39–38</sup> according to which the tunneling current is given by

$$I_{\rm T} = 2\frac{\pi}{\hbar} \, \mathrm{e} \sum_{\mu,\nu} \left[ f(E_{\nu}) - f(E_{\mu}) \right] \, |\mathsf{M}_{\mu\nu}|^2 \delta(E_{\nu} + \, \mathrm{e} U_{\rm B} - E_{\mu}) \tag{2}$$

with  $U_B$  being the applied bias voltage,  $f(E_{\mu})$ ,  $f(E_{\nu})$  the Fermi functions, and  $M_{\mu\nu}$  the tunneling matrix element between the electron state  $\psi_{\mu}$  and  $\psi_{\nu}$  of sample and tip, respectively.  $E_{\mu}$  is the energy eigenwert of  $\psi_{\mu}$  relative to the Fermi-level  $E_{F,S}$  of the sample, and  $E_{\nu}$  the energy eigenwert of  $\psi_{\nu}$  relative to the Fermi level  $E_{F,T}$  of the tip. Replacing the Fermi functions by their zero-Kelvin values, that is, by step functions and assuming a small bias voltage, Eq. (2) simplifies to

$$I_{\rm T} = 2\frac{\pi}{\hbar} e^2 U_{\rm B} \sum_{\mu,\nu} |M_{\mu\nu}|^2 \delta(E_{\mu} - E_{\rm F}) \delta(E_{\nu} - E_{\rm F})$$
(3)

If the tip is idealized as a mathematical point  $r_s$ ,  $M_{\mu\nu}$  is proportional to the amplitude of  $\psi_{\mu\nu}$  and the tunneling current becomes

$$I_{\rm T} \propto \sum_{\mu} |M_{\mu}(r_{\rm S})|^2 \delta(E_{\mu} - E_{\nu}) \equiv \rho_{\rm S}(r_{\rm S}, E_{\rm F}) \tag{4}$$

where  $\rho_{\rm S}(r_{\rm S}, E_{\rm F})$  represents the LDOS at the Fermi level of the sample surface at the tip position.

Since the representation of the tip by a mathematical point, of course, is unrealistic, Tersoff and Hamann<sup>40,41</sup> introduced the so-called s-wave model, in which the tip apex is modeled by a hemisphere of radius *R*. Under these conditions, Eq. (4) remains valid; however, the tunneling current becomes dependent of *R*. Moreover,  $\text{Lang}^{42}$  could show that also for larger bias voltages and a tip apex of realistic extension, the tunneling current is described by

$$H_{\rm T} \propto \int_{E_{\rm F}}^{E_{\rm F} + eU_{\rm B}} dE \rho_{\rm S} (r_{\rm S}, E) \rho_{\rm T} (E - eU_{\rm B})$$
(5)

with  $\rho_{S}(r_{S}, E) = \rho_{S}(E) T$ , where *T* is the so-called transmission probability. The integration includes all states of tip and sample, which at given bias voltage contribute to the tunneling current, and yields an approximately linear relationship between tunneling current and bias voltage.

It is the exponential dependence of the tunneling current on the barrier width z (tunneling gap) in Eq. (1) which distinguishes a "tunneling contact" from an "ohmic contact," and which, most importantly, is also the reason for the strong spatial confinement of the tunneling process to the shortest distance between surface and tip, the basis of the high spatial resolution of STM. Depending on the polarity of  $U_B$ , the tunneling current can either flow from the tip into empty electron states above  $E_F$  of the sample or, vice versa, from the sample into empty states above  $E_F$  of the tip. A variation of  $U_B$  can, thus, be exploited to probe the local density of electron states at the metal's surface (scanning tunneling spectroscopy (STS)),<sup>43</sup> or of molecules adsorbed on the surface.

The derivative of Eq. (5) with respect to  $U_{\rm B}$  yields

$$\frac{dI_{\rm T}}{dU_{\rm B}} = A\rho_{\rm S}\rho_{\rm T}T + B \frac{\rho_{\rm S}}{U_{\rm B}} + C \frac{dT}{dU_{\rm B}}$$
(6)

with A, B, C proportionality factors. Assuming  $\rho_{\rm T}$  = const and T only weakly dependent on  $U_{\rm B}$  gives the differential conductivity

$$\frac{dI_{\rm T}}{dU_{\rm B}} \propto \rho_{\rm S},\tag{7}$$

which, to first approximation, is proportional to the LDOS at the given surface position.

In the case of absorbed molecules within the tunneling gap, one has to consider that these molecules possess, besides electronic, also mechanical (translation, rotation, vibration) degrees of freedom which may also be excited by the tunneling electrons. Thus, by varying  $U_{\rm B}$  accordingly, electrons may now tunnel also inelastically by loosing characteristic quanta  $\Delta E = eU_{\rm B} = h\nu$  due to excitation of vibrational modes of an adsorbed molecule. This extra "inelastic tunneling channel" leads to measureable changes of the tunneling current at  $U_{\rm B} = h\nu/e$  which enables vibrational spectroscopy of single adsorbed molecules, and thereby chemical identification.<sup>44</sup>

## **Tunneling Through an Electrolyte**

Electron tunneling through an electrolyte is expected to be different from tunneling through a vacuum gap. This is supported by two experimental observations. Firstly, experimentally determined tunneling barrier heights are found to be lower compared to those measured in vacuum. This is consistent with the fact that adsorption of water lowers the work function of metal surfaces.<sup>45,46</sup> Secondly, the dependence of the tunneling current on the distance between tip and surface does not follow a simple exponential decay as in UHV. As seen in Fig. 4, there is a distinct modulation of the tunneling current as a function of distance.<sup>47,48</sup> This modulation has been associated with the layered water structure between tip and surface. As a consequence of the presence of water, the



**Fig. 4** (A) Semi-logarithmic plot of the tunnel current as a function of distance between tip and a Au(111) surface in 0.02 M HClO<sub>4</sub> solution; (B) deviation of the experimental data from a fit linear mean; a = oscillation period (see text).<sup>47,48</sup>

barrier height should also not be constant parallel to the surface, but be modified by an oscillating network of hydrogen and oxygen atoms of the water molecules.<sup>49</sup> However, the time an electron needs to tunnel through a gap of say 1 nm is at least two orders of magnitude faster than the motion of the molecules.<sup>50</sup> Thus, each individual tunneling electron faces a basically static and different barrier. In a real STM experiment, the limited response time of the registration and control electronics will, thus, lead to an average tunneling current instead of individual tunneling events.

As outlined in the previous section, the detection of this current requires the application of a bias voltage between tip and surface, which in the presence of an electrolyte may also cause Faradaic processes within the gap which would add to, and thereby distort, the real tunneling current (Fig. 4). Precautions to minimize this as well as other external disturbances are described in the following section.

## **Instrumental Aspects**

#### Control of the tip position

Above all, the tip apex must be brought to a distance *z* where the wave functions of tip and surface start to overlap (Fig. 3) and tunneling occurs ( $\leq 1$  nm). Secondly, the tip must be moved (scanned) in *x* and *y* directions across the surface which can be done either by holding the tip apex at constant *z* position or by keeping the tunneling current *I*<sub>T</sub> constant. In the first case ("constant height mode"), any surface roughness changes the width of the tunneling gap and thereby the measurable tunneling current (Fig. 5A). This mode should only be applied for flat surfaces in order to avoid tip crash with high surface protrusions. In the second case ("constant current mode"), the *z*-position of the tip apex must be changed by means of a feedback loop in order to keep the current constant (Fig. 5B). Since in this case the tip follows the contours of the surface, tip crashes can be avoided, but due to the continuous height adjustment this detection mode is slower. Typical values of tunneling currents are in the nA range, and typical bias voltages range from a few to a few hundreds of mV depending on the specific system and problem (see literature).

The instrumental realization of these two detection modes, obviously, has to obey the following most important conditions:

- (i) The tip must be brought from a macroscopic distance (mm) to the tunneling distance (nm).
- (ii) The position of the tip at any point above the surface must be controllable with subatomic ( $\approx 0.01-0.001$  nm) precision.
- (iii) The tip should be mechanically stable and as sharp as possible, preferably monoatomic.

While all three conditions need to be met in all types of instruments independent of whether they are operated in UHV, gas atmosphere or liquids, the preparation of tips used in electrolytes requires special attention (see "Tip preparation" section).

The control of the *x*,*y*,*z* positions of the tip (conditions (i) and (ii)) is realized by the use of piezoelectric actuators. The most common technical realization of an STM is the beetle design,<sup>51</sup> as illustrated in Fig. 6A. The plate *P* is carried by three piezo-tubes  $P_1-P_3$  (tripod) standing on the basis G with three ramped 120° sectors on which the piezos can be made to "walk" for coarse tip approach and positional offset taking advantage of the so-called stick and slip mechanism.<sup>51</sup> In the center of plate *P* is a fourth piezo-tube, the actual scanner  $P_4$ , which holds the tip, pointing downwards to the sample in the electrochemical cell between  $P_1$ ,  $P_2$ , and  $P_3$ . All piezo-tubes are coated with separate metal electrodes, four outside and one inside. By applying appropriate voltages  $U_+$ ,  $U_-$  of up to 100 V between any of the outer and the inner electrodes, respectively, the piezo-tubes can be made to bend in -x-, +x-, -y-, +y- or stretch/contract in *z*-direction, thereby scanning or positioning the tip with the necessary precision in a controlled way.<sup>51</sup> The calibration of a scanner, that is, the *x*,*y*,*z*-deflection per applied volt, is best done by imaging known surface structures. The *x*,*y*-deflection can be determined by imaging a surface of known lattice structure, for example, graphite (HOPG). The *z*-deflection can be calibrated by scanning across surface steps of known height. In this latter case, however, caution must be exercised because according to Eq. (1)  $I_T$  does not only depend on the geometric height change (the tunneling gap), but also on the site-specific electronic properties  $\rho(E_{\rm F,S})$  (see Fig. 14).

A more recent alternative to the Besocke-type scanner is a so-called length-extension resonator (LER). This is a stiff sensor which consists of a LER quartz and enables combined STM/noncontact-AFM measurements.<sup>52–55</sup> A "KolibriSensor<sup>TM</sup>"<sup>52,56</sup> as shown in Fig. 6B is based on a rectangular shape piezoelectric quartz LER (L) whose sidewalls are gold-coated. At its center, it is supported by two arms S to a plate *P*, ensuring a highly symmetric geometry of the oscillating rod L. Excitations of oscillations of this quartz rod by applying a sinusoidal voltage ( $U_{osc}$ ) to one of its sidewall electrodes cause not only periodic extension or contraction of the quartz rod across its width due to the piezoelectric effect, but also a periodic change of its length in longitudinal direction with



**Fig. 5** Sketch of (A) the "constant height mode" and (B) "constant current mode" of tunneling microscopy. The thickness of the arrows symbolizes the current strength.



Fig. 6 (A) Beetle-type setup of an STM, and (B) length-extension resonator for combined STM/noncontact AFM measurements.

an amplitude A as low as 1 pm (Fig. 6B). *z*-approach and *x*,*y* scans are effected by piezo scanners moving the sample in this case. If the tip is metallic and separately contacted by a thin wire (Fig. 6B), combined STM ( $I_T$ ) and noncontact AFM ( $\Delta \nu$ ) measurements<sup>52</sup> can be performed providing simultaneously electronic structure and topographic information about the surface, that is, the distance between tip and surface is precisely known. The stiffness of the resonator is particularly useful for measurements under environmental conditions, that is, in gases and liquids.<sup>57</sup>

External mechanical (sound, building vibrations, thermal drift, etc.) as well as electromagnetic perturbations which have a significant effect on the geometry of the tunneling gap and, thus, on the tunneling current, may effectively be suppressed by vibration damping systems, the choice of suitable materials to avoid or compensate for thermal expansion and drift, and electromagnetic shielding (for details see specialized literature<sup>39–38</sup>).

#### Electrochemical STM setup

Fig. 7 shows a dedicated homebuilt electrochemical STM system developed at the University of Bonn.<sup>21,58–60</sup> This microscope is sketched in Fig. 7A and consists of a single-tube scanner in an assembly as shown in Fig. 6A except that the roles of the plate *P* (holding the tripod  $P_1$ – $P_3$ ) and the basis G (now holding the scanner  $P_4$ ) are reversed. The electrochemical cell (Fig. 8) with various electrodes has a volume of 2.5 ml and is mounted into the STM basis. This volume permits cyclic voltammetry (CV) measurements within the same cell. Apart from the sample (working electrode), which is connected to virtual ground potential, a counterelectrode, an internal reference electrode, and a generator electrode for in situ dissolution of defined quantities of a metal into the electrolyte as well as hoses for the electrolyte flow system lead to the cell.<sup>21,58–60</sup> An external reference electrode, for example, a reversible hydrogen electrode, can be connected via a Luggin capillary.

The STM head (Fig. 7B) rests on three spacer bolts ( $B_1$ – $B_3$ ), carries the scanner, and contains the preamplifier, very close to the tunneling tip. The whole system rests on a stack of three brass plates separated by rubber spacers in an aluminum housing (1 in Fig. 7C). The latter serves to shield the STM from acoustic, thermal, and electromagnetic disturbances and can be filled with a specific gas atmosphere, for example, inert argon. This complete setup rests on a rubber mat on a heavy granite slab (2), which is suspended from the ceiling by springs (3). The stack of brass plates inside and the suspended granite slab outside the aluminum cube constitute a very effective damping system.

A detailed description of the system including the electronic setup of the STM controller has been published in.<sup>21,58</sup>

## Potentiostatic, potentiodynamic, and spectroscopic detection methods

The electronics of the Bonn EC-STM is designed for a four-electrode setup (working electrode, counter-electrode, reference electrode, and tip) so that the potential of the STM tip and the sample (working electrode) versus the reference electrode may be controlled independently by a bipotentiostat. In the so-called potentiostatic mode, both the sample potential and the bias voltage are kept constant, leading to classical imaging. Variation of the bias voltage and measuring, at constant sample potential, the resulting tunneling current enables registration of  $dI_T/dU_B$  curves which provide spectroscopic information (Eq. (7)) about the LDOS at a given tip position (STS).<sup>39</sup> Finally, during potentiodynamic measurements, the potential of the working electrode is changed during the acquisition of an STM image. This allows the direct correlation of current waves in a cyclic voltammogram with changes of the surface structure seen in in situ STM images at the same potentials. It is this combined information which is indispensible for an understanding of the "electrochemical double layer."



Fig. 7 (A) Illustration of a tip-sample arrangement in EC-STM; (B) sketch, and (C) photograph of the setup of the Bonn EC-STM.



Fig. 8 (A) Top-view and (B) cross-section of the electrochemical cell of the Bonn EC-STM (see text).

#### **Sample Preparation**

## Flame annealing

A simple and widely used preparation method, originally developed by Clavilier,<sup>61</sup> is flame annealing. The sample is exposed to a butane–air flame and heated to a slightly reddish hue. This procedure removes organic compounds by oxidation and heals surface defects. The hot sample may then be quenched in water<sup>61</sup> or cooled down less drastically in an Argon-flow under careful exclusion of oxygen, in order to avoid surface oxidation. This method is suitable for Au or Pt single-crystal electrodes<sup>62–65</sup> but obviously less so for more reactive and low melting point metals such as copper.

## Electrochemical etching and annealing

Another commonly applied method for the preparation of samples is electrochemical etching in an electrolyte using an AC voltage of several volts. This removes the top layers of the crystal together with any impurities and contaminations. A disadvantage of this method, especially for single crystals, is the removal of material, which leads to a roughening of the surface. Therefore, this method is best applied to surfaces of crystals which show "self-healing" in an electrolyte. This process which has been termed "electrochemical annealing" (but is actually based on chemical transport reactions) has been described, for example, for Au,<sup>66</sup> Cu,<sup>67</sup> Ru,<sup>68</sup> and Fe<sup>69</sup> surfaces as well as conducting organic films<sup>70</sup> and has recently been theoretically described by Schmickler, Ibach, and coworkers.<sup>71,72</sup>

## **UHV-EC** transfer

If flame annealing and electrochemical etching are not successful, the only remaining option is the preparation in UHV by sputtering, for example, with Ar ions, followed by annealing at elevated temperatures and subsequent transfer into the electrolyte. This is obviously best done in a UHV preparation chamber which is directly attached to the electrochemical cell by a buffer chamber in order to avoid contact with air.<sup>73,74</sup> The preparation in UHV has also the significant advantage that the crystallographic perfectness as well as the absence of contaminants can be checked by standard UHV analysis methods such as low-energy electron diffraction, photoelectron or Auger electron spectroscopy (UPS, XPS, AES), or ion scattering spectroscopy (ISS).<sup>75,76</sup>

## Tip preparation

Various protocols have been developed to produce stiff tips as sharp as possible, preferably monoatomic. Stiffness is particularly important if high scan rates are employed (Video-STM), in order to avoid bending,<sup>77,78</sup> and is best achieved by using tungstenor Pt–Ir alloy-tips. Sharpness is actually easy to achieve, no matter how the wire is disrupted. The wire could simply be cut by pliers or torn apart. In both cases, it is likely that after separation one atom sticks out furthest on either end of the rupture. Most commonly, however, STM tips are prepared by electrochemical etching. A gold wire loop as a working electrode is either filled with a lamella or placed in the surface plane of a solution of 2 M KOH for tungsten tips or 2 M KOH/4 M KSCN for Pt–Ir tips (Fig. 9A and B). The wire to be etched is pierced through the lamella or—largely protected by a Kapton<sup>®</sup> tube—immersed into the electrolyte such that contact with the electrolyte is confined to the lamella or the very surface of the bulk solution. Typical etching conditions are 2 V (DC) superimposed by a rectangular AC voltage of 10 V and a frequency of 1 kHz until the lower part of the wire falls off under its own weight into the Teflon base. After carefully removing the Kapton<sup>®</sup> tube, the tip is rinsed with high-purity water and dried.

In order to prevent interferences of the measured tunneling current with possible Faradaic currents through the gap, the tip needs to be largely insulated, for instance, with hot glue (Fig. 9C). Due to the very high curvature, the hot glue retreats from the very tip apex, leaving, after hardening, only the very apex of just a few tens of nanometer in diameter uncovered which reduces any Faradaic current through this open part to be more than two orders of magnitude lower than the actually desired tunneling current.



Fig. 9 Methods of STM-tip etching: (A) in bulk solution; (B) in a lamella of electrolyte, (C) photograph of an etched tip coated with hot glue (see text).

## **Case Studies**

In this section, we demonstrate the analytical power of (in situ) EC-STM in combination with CV by presenting in situ STM images of typical phenomena of interfacial electrochemistry, such as anion adsorption, corrosive surface compound formation, metal underpotential deposition, and molecular self-assembly. We largely concentrate on copper electrode surfaces because interfacial electrochemistry at copper surfaces has become very important in recent years, among others due to its relevance in modern chip production.

## **Anion Adsorption**

Anions and cations in aqueous solution are hydrated, and their interaction with the electrode surface, thus, competes with their hydration strength. While the latter is a given ion-specific quantity, the former depends on the potential applied to the electrode. The stronger the electrostatic attraction to the electrode, the more the ions free themselves from their hydration sphere, and adsorb "specifically," that is, strongly, with direct contact to the metal surface (without water in between) at a distance of the inner Helmholtz plane within the "electrochemical double-layer." If ions adsorb with their hydration sphere because (at given potential) the electrostatic attraction to the surface is weaker than the ion–water interaction, they adsorb "nonspecifically," that is, weakly, and remain mobile on the surface. A very comprehensive review about anion adsorption has been published by Magnussen.<sup>79</sup>

In particular, anions, due to their larger size and therefore lower charge density than corresponding cations, tend to adsorb specifically and form ordered layers on electrode surfaces, predestined for in situ STM investigations.

#### Chloride and iodide adsorption on Cu(111)

Fig. 10 displays the cyclic voltammograms of a Cu(111) electrode in chloride and iodide containing acidic solution, respectively.<sup>80–</sup> <sup>82</sup> A clear pair of adsorption (Ads)- and desorption (Des) peaks is seen with chloride, while with iodide only an adsorption peak is seen at very negative potentials; the desorption peak is actually hidden by the current arising from the cathodic hydrogen evolution reaction (HER). These CVs suggest to find iodide adsorbed on Cu(111) within the whole potential range between HER and the anodic copper dissolution reaction (CDR), but chloride only at potentials after the adsorption and before the desorption peak. The hysteresis between the two peaks actually reflects the activation energy needed to remove the hydration shell before specific adsorption. Fig. 11 shows in situ STM images of the Cu(111) surface in hydrochloric acid solution at positions marked with the arrows 1, 2, and 3 in Fig. 10A. Panel (A) registered at potential 1, indeed, shows the correct symmetry and periodicity of the bare Cu(111) surface (in solution); the distance between the bright spots, assigned to the Cu atoms, is 0.256 nm. Also the image in panel (B) taken at potential 2 shows perfect hexagonal structure, but the distance between the spots is found to be  $\sqrt{3}$ -times longer than in panel (A). Ex situ XPS spectra registered in a "transfer-chamber" (see "UHV-EC transfer" section) after emersion at arrow P2 in Fig. 10A prove that the surface is covered with chloride, thus forming a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure of coverage  $\Theta = 1/3$ . Finally, in Fig. 11C taken near arrow 3 in Fig. 10A, the chloride structure is modulated by a wavy superstructure, which due to the symmetry of the substrate surface occurs in three equivalent domains rotated by  $\alpha = 120^{\circ}$ , two of which are shown in Fig. 11D. At these high potentials, more chloride is adsorbed, that is,  $\Theta > 1/3$ , with the consequence that the chloride structure is compressed (one-dimensionally in  $[\overline{1}10]$  direction) and chloride anions occupy inequivalent substrate sites which makes them appear differently high. Registration of panel B in Fig. 11 with different bias voltages, that is, performing STS (see "Potentiostatic, potentiodynamic and spectroscopic detection methods" section), results for instance in Fig. 12A. This image contains contributions from both the chloride overlayer and from the Cu(111) substrate. Fourier analysis of this image (Fig. 12B) allows to separate both contributions as shown in panels (C) and (D) of Fig. 12, whose superposition proves that the chloride anions reside in the threefold hollow sites of the Cu(111) surface.<sup>81</sup>

It should be mentioned that the steady increase of the current before the adsorption peak in Fig. 10A indicates that chloride starts to adsorb already before the actual adsorption peak (Ads). At these more negative potentials, however, the chloride anions are still



Fig. 10 Cyclic voltammograms of Cu(111) in (A) 10 mM HCl solution and (B) 0.1 mM KI + 5 mM  $H_2SO_4$  solution; scan rate 10 mV/s. Ads and Des denote anion adsorption/desorption current peaks; HER = hydrogen evolution reaction; CDR = copper dissolution reaction. The *arrows* 1, 2, and 3 mark the potentials at which the STM images (A–C) in Fig. 11 were taken.



**Fig. 11** In situ STM images of a Cu(111) surface in hydrochloric acid at different electrode potentials: (A) anion-free, measured near *arrow* 1 in **Fig. 10A**; the distance between neighboring spots agrees with the interatomic distance of 0.256 nm of Cu atoms in a Cu(111) plane; (B) covered with a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  Cl-structure near *arrow* 2 in **Fig. 10A** and **C** at high potentials (*arrow* 3 in **Fig. 10A**); unit cell and crystallographic directions are indicated; (D) two (of three possible) rotational domains of the structure shown in (C);  $\alpha \approx 120^\circ$ .



**Fig. 12** (A) In situ STM image of a ( $\sqrt{3} \times \sqrt{3}$ )*R*30° Cl-covered Cu(111) surface,  $U_B$  = is chosen such that the image includes clear contributions from both the copper substrate and the Cl-overlayer; (B) power spectrum of panel (A); (C) low frequency and (D) high frequency contribution in panel B, representing Cl-overlayer and Cu-substrate lattice (see text). Adapted from Broekmann, P.; Wilms, M.; Kruft, M.; Stuhlmann, C.; Wandelt, K.; *J. Electroanal. Chem.* **1999**, *467*, 307.



**Fig. 13** In situ STM images of a Cu(111) surface covered with (A) an adsorbed ( $\sqrt{3} \times \sqrt{3}$ ) $R30^{\circ}$  iodide layer; (B) and (C) uniaxially, in [ $\overline{1}10$ ] direction compressed, iodide layer, the wave length / decreases with increasing potential (from left to right).<sup>82</sup>

weakly (nonspecifically) bound and mobile and therefore not seen with STM.<sup>79</sup> Only after "locking in" into the  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$  structure and the threefold hollow sites, the anions become visible.

In parenthesis, we mention that on the more open Cu(100) surface chloride forms a strongly bound ( $\sqrt{2} \times \sqrt{2}$ )R45° (or in short  $c(2 \times 2)$ ) structure.<sup>83</sup>

The phenomenon of "electro-compression" as seen in **Fig. 11C** and **D** is fully reversible, and seen even more pronounced with iodide adsorption on Cu(111), as displayed in **Fig. 13**. As suggested by the CV in **Fig. 10B**, iodide adsorbs very strongly near/within the HER regime forming a ( $\sqrt{3} \times \sqrt{3}$ )*R*30<sup>*o*</sup> structure (**Fig. 13A**) and exhibits pronounced electro-compression at all higher potentials (**Fig. 13B** and C).<sup>82</sup> Unlike chloride, the larger iodide anions show also on Cu(100) orthogonal domains of an electro-compressible uniaxially incommensurate *c*(*p* × 2) structure.<sup>82</sup> The wave length *l* (**Fig. 13**) of the uniaxially incommensurate superstructures of iodide on Cu(111) (as well as Cu(100)) varies linearly and reversibly with the electrode potential.

Similarly detailed surface structure determinations using in situ STM are published for other anions. As one further very important example, we show the surface structure of a Cu(111) in contact with dilute pure sulfuric acid (Fig. 14)<sup>85-87</sup> which is a widely



**Fig. 14** In situ STM images of a Cu(111) surface covered with (A) a disordered layer of sulfate  $(SO_4^{2-})$  anions; the beginning formation of a nearly hexagonal Moiré-superstructure (see *arrows*) proceeds in (B) from step edges onto the upper terrace. (C) Close-up of the Moiré structure showing a  $(\sqrt{3} \times \sqrt{7})R30^\circ$  lattice of SO<sub>4</sub> anions (bright spots), zigzag chains of H<sub>2</sub>O molecules (or H<sub>3</sub>O<sup>+</sup>, hydronium, ions), and the Moiré depression (darker regions).<sup>86,87</sup> (D) Model of the  $(\sqrt{3} \times \sqrt{7})R30^\circ$  structure of adsorbed sulfate anions on the reconstructed Cu(111) surface.

used supporting electrolyte for many anion adsorption studies (as, for instance, for the iodide adsorption experiments described above and in "Corrosive Surface Compound Formation" section, in which the more strongly bound iodide anions displace sulfate anions from the surface). As verified by IR spectroscopy, at the chosen potential the whole surface in Fig.14A is fully covered by a disordered, mobile layer of SO<sub>4</sub> anions.<sup>87,88</sup> Beginning in Fig. 14A (see arrows), Fig. 14B shows the growth of a new structure starting from step edges of the Cu(111) surface which has been identified as a Moiré superstructure arising from a sulfateinduced expansion of the first copper layer accompanied by a massive restructuring of the Cu(111) surface.<sup>86,87</sup> A close-up of this Moiré structure is shown in Fig. 14C; the main bright spots correspond to the sulfate anions forming, like on many other fcc(111) metal surfaces, a ( $\sqrt{3} \times \sqrt{7}$ )R30° structure shown in panel (D). The zigzag rows of small spots between the SO<sub>4</sub> anions are H<sub>2</sub>O molecules (or H<sub>3</sub>O<sup>+</sup> hydronium ions). The dark regions in panel C represent the enlarged Moiré superstructure. Detailed discussion of this interesting SO<sub>4</sub>/Cu(111) adsorption system can be found is Refs. 86 and 87.

## **Corrosive Surface Compound Formation**

In the previous section, we described the mere adsorption of chloride and iodide anions on the Cu(111) surface. Already this adsorption is accompanied by some restructuring of the first layer, namely in the form of the "electrochemical annealing" or expansive reconstruction in the case of  $SO_4/Cu(111)$ . Next, we will address the influence of the halide anions on the copper dissolution process. In the case of iodide, more positive potentials lead even to the formation of stable surface CuI compound phases.

Fig. 15 shows the complete cyclic voltammograms of Cu(111) in both blank (full line) and 0.1 mM KI containing 5 mM H<sub>2</sub>SO<sub>4</sub> electrolyte (dashed line).<sup>89</sup> The CV of Cu(111) in the iodide containing electrolyte shows a number of distinct new current features. An almost identical CV is also found for Cu(100) in the same solution. Firstly, the couple of adsorption/desorption peaks (P/P') of sulfate anions on Cu(111) is fully suppressed. As mentioned before, this is due to the fact that iodide anions adsorb stronger on Cu(111) and displace sulfate anions. Secondly, a large and broad anodic peak system close to the onset of the CDR (denoted P1,2) corresponds to the formation of a CuI surface compound.<sup>89</sup> The fact that the same voltammetric behavior was also found for Cu(100)<sup>90–92</sup> shows that the crystallographic orientation has obviously no significant effect on the electrochemical process between copper and iodide. The following EC-STM images prove that the current wave P(1,2) is correlated with the formation of a two-dimensional CuI film. Interestingly, after passing the peak system P(1,2), the anodic current does not drop to zero in Fig. 15, indicating that the reactive copper dissolution may be slowed down but it is not fully suppressed by the presence of the CuI film.

The three current peaks P'1, P'2, and P'3 showing up in the negative potential scan direction have been assigned to the electroreduction and dissolution of the various previously found solid CuI phases which differ in their structural relationship to the copper substrate surface as verified by in situ STM measurements<sup>90</sup> described in the following.

Starting with a well-ordered and electro-compressible layer of merely adsorbed iodide as shown in Fig. 13 and sweeping the electrode potential then to the onset of  $P_{1,2}$  result in a drastic change of the surface structure as shown in Fig. 16. Fig. 16A shows six terraces (T1–T6) of a Cu(111) surface covered with the saturated and uniaxially compressed iodide layer like in Fig. 13B, C. At the onset of  $P_{1,2}$  in Fig. 15, it becomes evident from Fig. 16B that the surface undergoes already a reaction. Copper steps recede



Fig. 15 Cyclic voltammograms of Cu(111) in pure 5 mM  $H_2SO_4$  (black trace) and in 5 mM  $H_2SO_4 + 1$  mM KI (*grey* dashed trace). Scan rate 10 mV/ s. The potential regimes marked in red indicate existence of adsorbed iodide, and the onset of 2D and 3D formation of CuI surface compound.



**Fig. 16** Series of consecutive in situ STM images showing six terraces of a Cu(111) surface covered in (A) and (B) with a compressed  $c(p \times \sqrt{3})$  layer of adsorbed iodide as displayed in **Fig. 13**, note the receding of the step edges indicating copper dissolution; (C) sudden formation of a 2D Cul compound film on terrace T2 (T2  $\rightarrow$  T2') and T3, T1 (see text).<sup>89</sup>

with time (M is a rigid marker, and the white dashed lines in the image indicate the position of the same step in the preceding image in panel (A)), proving local copper dissolution along the step edges. This, however, does not lead to a soluble product which diffuses into the bulk solution like in the case of chloride and bromide, but instead, to a rapid nucleation and growth of a 2D CuI film. This 2D CuI film appears suddenly from one scan line to the next in the STM image of **Fig. 16C** as seen on terrace T2 (as well as T3 and T1); copper terraces already covered by the 2D CuI film are labeled as T1' and T2'. This sudden film formation can be explained as follows: depending on the applied potential, an equilibrium concentration of mobile cuprous species, namely CuI or  $[CuI_2]^-$  monomers, as intermediate products of the copper oxidation reaction, is produced on the surface.<sup>91,93</sup> These diffusing cuprous species are in equilibrium with step edges, which are the sources of copper ions for the formation of these species. With increasing potential, the concentration of these species on terraces increases until a critical threshold is exceeded which gives rise to the surface-confined nucleation and growth of the 2D CuI film.<sup>90</sup>

The 2D CuI film has been interpreted by a post-adsorbed Cu–I bilayer on top of the preexisting layer of adsorbed iodide resulting in an I–Cu–I triple-layer. This interpretation is strongly supported by (1) high-resolution ex situ XPS experiments which clearly distinguish between the preadsorbed iodide and the post-adsorbed CuI species,<sup>89</sup> (2) by a detailed analysis of high-resolution in situ STM images of the 2D film (Fig. 17) whose densely packed rows of anions are rotated by 7 degree with respect to the rows of preadsorbed iodide anions on Cu(111) (or 44 degree on Cu(100)), as well as (3) by similar results for 2D CuI films grown on Cu(111) (and Cu(100)) by dissociative iodine adsorption under UHV conditions.<sup>94</sup>

This 2D CuI film is stable only within a narrow potential window. After passing peak *P*1,2 in Fig. 15, the CuI formation continues as evidenced by the persistently high current in the CV. Obviously, the existing 2D CuI film does not act as an effective passivation layer. This further copper dissolution leads to the nucleation and growth of 3D CuI clusters of enormous height (Fig. 18). STM alone, of course, does not reveal whether the 3D CuI clusters nucleate directly on top of the 2D CuI film or in solution followed by their precipitation onto the 2D CuI film. But their rather irregular appearance and distribution seems to support the latter process.<sup>89</sup>

A surface compound formation with chloride and bromide anions on copper under similar conditions is not found due to the higher solubility of the relevant compounds.



Fig. 17 In situ STM images of the 2D Cul films on (A) Cu(111) and (B) Cu(100). The direction of densely packed rows of iodide anions of the 2D Cul film is rotated by 7 degree and 44 degree with respect to the densely packed rows of the adsorbed iodide layer underneath (see text).



Fig. 18 In situ STM image of 3D Cul clusters on iodide precovered Cu(111) measured near *arrow* 3 in Fig. 15, image size 293 nm  $\times$  293 nm; (B) cross-section along the white line in (A).<sup>89</sup>

## **Metal Underpotential Deposition**

The process of electrodeposition of metals, galvanization and electroplating, is an important industrial process. Inasmuch as the amounts and structures of electrochemically deposited metals become smaller and smaller, as for instance for the on-chip wiring in modern mass-production of logic and memory devices, the phenomenon of "underpotential deposition (upd)" becomes more and more important. The equilibrium potential of deposition (reduction) and dissolution (oxidation) of a given metal on/from itself is described by the Nernst equation. If, however, the metal in question is electrochemically deposited (desorbed) on (from) an unlike metal surface, an additional chemical interaction between substrate and deposit comes into play and leads to deposition already before and desorption after the Nernst potential is reached.<sup>95</sup> This phenomenon of upd is largely confined to the deposition of one or two monolayers of the deposited metal, that is, to the spatial range of interactions between the unlike bonding partners.

This in turn is interesting because it enables the precise deposition of just one monolayer (or two) of deposit and not more. The in situ characterization of these upd adlayers has greatly benefited from the combined application of CV and EC-STM, which enable the identification of the adsorption/ desorption processes as well as the adsorbate structure, respectively, on the nanometer scale within the electrolyte. Here we present results for upd of cadmium on Cu(111) from a  $CdCl_2$  containing hydrochloric acid solution. Cadmium was chosen because the atomic radius of cadmium (161 pm) is significantly larger than that of copper (145 pm). As a consequence interesting superstructures are to be expected. Fig. 19 shows cyclic voltammograms of the Cu(111) sample in the 0.01 mM  $CdCl_2$  containing 10 mM HCl solution extending to different cathodic potentials. There is a clear distinction between the upd-regime (red trace) and the bulk deposition (opd-regime, blue trace) of cadmium. Note that the Cd upd-regime overlaps with the chloride adsorption regime on Cu(111) (shaded region).

Fig. 20 displays in situ STM images of the Cu(111) surface in (a) pure hydrochloric acid covered with a  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$  Cl layer, and in (b) the CdCl<sub>2</sub> containing solution after completion of the Cd upd layer (E = -950 mV vs. Hg/Hg<sub>2</sub>SO<sub>4</sub> in Fig. 19). The latter image clearly shows a new structure and the coexistence of two domains of a Moiré-type superstructure rotated by 11 degree with respect to each other. A zoom into one of these domains shows the surface atomic structure with high resolution (Fig. 20C). The modulated intensity of the spots (surface atoms) is characteristic for an incommensurate structure. Note, however, that the intensity distribution is not strictly periodic and the distribution of brighter atoms in different ensembles varies (compare the two encircled ensembles). This excludes an interpretation of the new structure by a simple commensurate  $(4 \times 4)$  superstructure as proposed by Ge and Gewirth.<sup>98</sup> Instead, like in the case of the Cl/Cu(111) system in Fig. 12, a careful Fourier analysis of high-resolution large-scale images of the Moiré superstructure enables the separation of different periodic contributions to this surface structure.<sup>96</sup> According to this analysis, the interatomic distance within the overlayer is a = 0.383 nm, and the overlayer as a whole is rotated by  $24.5 \pm 1^{\circ}$  with respect to the Cu(111) surface lattice. Moreover, the Moiré lattice is rotated by 2 degree with respect to the rows of the overlayer atoms, and the Moiré periodicity is 3.5a. Using this set of parameters, it is possible to simulate a hard-sphere model of the overlayer on the Cu(111) substrate. The resultant model, in which also the height of each overlayer atom at its position is relaxed to full contact with atoms of the Cu(111) surface underneath, is shown in Fig. 21. Even the height modulation (brightness) of the hard-spheres in Fig. 21A reproduces the intensity (brightness) of the experimental image (Fig. 21B) extremely well.

As mentioned before, specific chloride adsorption and upd of cadmium occur in the same potential regime (Fig. 19). The observation of the Cd upd signal in the CV as well as the occurrence of the new cadmium-induced surface structure seen in STM does not reveal whether chloride stays on the surface at all, and if yes underneath or on top of the cadmium layer. This problem was solved in the present case by ex situ XPS and ISS, a most surface-sensitive chemical analysis method, in a transfer chamber (see "UHV-EC transfer" section). These ISS measurements unambiguously showed that preadsorbed chloride and post-adsorbed cadmium



Fig. 19 Cyclic voltammograms of a Cu(111) electrode in 0.01 mM CdCl<sub>2</sub> containing 10 mM HCl solution with more and more negative potential limit. The red part corresponds to the upd-regime of cadmium-deposition/-desorption and overlaps with the potential regime of chloride adsorption (*shaded* region); the blue trace reflects the Cd bulk (opd) deposition/desorption (= stripping); *HER*, hydrogen evolution reaction.



**Fig. 20** In situ STM images of Cu(111) surface covered with (A) a  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$  Cl-layer; (B) two domains of a Cd + Cl coadsorption layer rotated by 11 degree with respect to each other; (C) zoom-in into one of the domains in panel (B). Note the difference in intensity (brightness) distribution within the two encircled dot-clusters, excluding the interpretation of this structure as a simple (4 × 4) superlattice.<sup>96</sup>



Fig. 21 (A) Hard-sphere model and (B) high-resolution in situ STM image of a Cd + Cl coadsorption layer on Cu(111) (see text).

exchange position and that the STM images shown in Figs. 20 and 21 actually represent a Cd–Cl bilayer with Cd in contact with the copper substrate and the chloride on top.<sup>96</sup>

## **Molecular Ordering**

The autonomous ordering and self-assembly of organic molecules on surfaces has become a promising route to produce ordered two-dimensional structures of specific functionality. Organic chemistry is able to synthesize the desired "building blocks," and surface physics makes methods available which permit the characterization of these structures on (even sub-) molecular level, in particular scanning probe techniques.

The preparation of such structures via vapor deposition of the molecules under vacuum conditions, however, may be limited by the thermal stability of the species. In particular, larger organic molecules may not be intact volatile. In this case, deposition of the molecules may only be possible from solution, either by spray techniques or directly from bulk solution, for instance, electrochemically in the form of ions from aqueous solution. This mode of deposition has the further advantage that the process of deposition as well as the 2D ordering on the surface may be studied as a function of an additional parameter, namely the electric potential of the sample electrode, obviously best by EC-STM.

Porphyrins are a class of organic molecules which are widely used to fabricate and study the 2D self-assembly on surfaces because they possess interesting electronic, sensoric, and catalytic properties. The basic core of these molecules, porphine, is shown in Fig. 22A. The replacement of the two inner H-atoms by metal atoms (e.g., Fe in heme or Mg in chlorophyll) as well as the attachment of ligands at various positions ( $\alpha$ ,  $\beta$ , meso) of the outer C-ring leads to the broad spectrum of functionalities of these molecules also for applications in solutions.

As an example of electrochemical deposition and self-assembly, we present the adsorption of *meso*-tetra(*N*-methyl-4-pyridyl)porphyrin cations (counter-anions: tosylate, **Fig. 22B**) on a Cu(100) surface in 5 mM H<sub>2</sub>SO<sub>4</sub>+1 mM KI+1 mM H<sub>2</sub>TMPyP solution. The adsorption strength of the anions in solution increases in the order tosylate < SO<sub>4</sub><sup>2-</sup> < I<sup>-</sup>; the strong adsorption of iodide displacing other anions has been discussed in "Chloride and iodide adsorption on Cu(111) section." Thus, the adsorption of the molecular H<sub>2</sub>TMPyP cations occurs on the iodide precovered surface. Moreover, the H<sub>2</sub>TMPyP molecules are redox active. **Fig. 23A** shows the cyclic voltammograms of a Cu(100) electrode in KI-containing (grey) and KI + H<sub>2</sub>TMPyP-containing sulfuric acid (black) solution, respectively. The addition of the porphyrin molecules to the electrolyte has three main effects: (1) the HER is shifted to drastically lower potentials, (2) the copper redeposition reaction (CRR) occurs also at more negative potentials, and (3) the two new current waves C1 and C2 are associated with two electroreduction steps of the molecules.<sup>99-101</sup> The retardation of HER and CRD is understandable in the presence of a molecular overlayer. EC-STM is able to show the structure of this overlayer as well as structural phase transitions of it as a consequence of the reduction of the molecules.

**Fig. 23B–E** displays large scale in situ STM images of the Cu(100) surface in the KI + H<sub>2</sub>TMPyP-containing solution registered on the electrode in the four indicated potential regimes I, II, III, and O in panel (A), respectively. According to the cyclic voltammogram, the four regimes correspond to (I) H<sub>2</sub>TMPyP<sup>4+</sup> on an adsorbed iodide layer, (II) reduced molecules on an adsorbed iodide layer, (III) reduced molecules on the iodide-free surface, and (O) adsorbed molecules in the regime of CuI compound formation (see "**Corrosive Surface Compound Formation**" section). All four images show clearly different structures. The stripes (of one of two possible orthogonal domains) of phase I on the terraces are parallel to the [011] surface direction, while the stripes of the different visible domains of phase II have a completely different orientation, namely  $\pm 26^{\circ}$  off the [011] direction. Phase III, seen on the surface after iodide desorption, is disordered, and phase O is characterized by more distant, noisy, and interrupted stripes. The insets in all four panels give a first impression of the structures on the molecular level. Zooming into the ordered phases I, II, and O discloses their fine structure and, thereby, very interesting properties.



Porphine

Meso-tetra(N-methyl-4-pyridyl)-porphyrin

**Fig. 22** Structure models of (A) a porphine molecule and (B) a *meso*-tetra(*N*-methyl-4-pyridyl)-porphyrin (H<sub>2</sub>TMPyP) cation with four tosylate counter-ions.


**Fig. 23** (A) Cyclic voltammogram of a Cu(111) surface in 5 mM  $H_2SO_4 + 1$  mM KI solution with (*black* trace) and without (*grey* trace) containing 1 mM  $H_2TMPyP$ ; scan rate 10 mV/s; A = onset of 2D Cul film formation, *CRD*, copper redeposition reaction; *C1*, *C2*, current peaks indicating two steps of  $H_2TMPyP$  reduction; *HER*, hydrogen reduction reaction; (B)–(E) four different structures (III, II, I, and O) are observed with in situ STM in the corresponding potential regimes marked in panel (A).



Fig. 24 High-resolution in situ STM images of the phases II, I, and O identified in Fig. 23, registered within the respective potential regimes marked in Fig. 23A. Phase III is disordered and not enlarged here (detailed discussion see text).

**Fig. 24A–C** shows high-resolution images of phases II, I, and O from left to right in the order of increasing potential. The molecules of phase I (panel (B)) are aligned in rows A, B along the [011], that is, the commensurate, direction of the underlayer of adsorbed iodide (**Fig. 25**), and within the rows, the molecules are slightly rotated with respect to this direction by (rows A) + 17 degree or (rows B) – 17 degree, respectively. These high-resolution images and structural details allow drawing some important conclusions about this adsorption system: (1) as expected, the individual molecules are lying flat on the surface, thereby optimizing their contact to the surface via their extended  $\pi$ -electron system. (2) The alignment of the molecular rows with the commensurate iodide direction, that is, the direction of the valleys (and hills) of the iodide adsorbate underneath hints to some "template" effect. (3) The rotation of the molecules within the rows minimizes steric hindrance between pyridyl ligands of neighboring molecules, and (4) obviously, the rotation can occur with equal probability by + 17 degree and – 17 degree resulting in two different unit cells of the molecular lattice as marked in panel (B), namely a (3 × 3) and *c*(3 × 6) structure with respect to the iodide layer underneath (**Fig. 25**), resulting however in the same molecular coverage of 0.055 ML or 3.39 × 10<sup>13</sup> molecules/cm<sup>2</sup>.<sup>102</sup>

A high-resolution STM image of phase II of reduced molecules (peak C1 in Fig. 23A) is shown in Fig. 24A. The molecules are also aligned in rows along the direction of the unit vector  $\vec{a}_{2}$ ; however, this direction is now off the [011] surface direction by 26 degree (Fig. 23C) excluding a simple commensurate structure in contrast to phase I. Within the rows, the molecules are no longer rotated with respect to the row direction, but are retorted sidewise, such that again a pyridyl ligand of one molecule points between two



**Fig. 25** Series of in situ STM images showing (A) a uniaxially compressed incommensurate  $c(p \times \sqrt{3})$ -I structure on Cu(111) as shown in **Fig. 13**; (B) the Cu(111) surface covered with  $c(p \times \sqrt{3})$ -I and H<sub>2</sub>TMPyP, "drastic" tunneling conditions in the upper part lead to removal of the organic molecules, which enables a direct correlation of the lattice of both the I-underlayer and the H<sub>2</sub>TMPyP-overlayer; (C) complete H<sub>2</sub>TMPyP overlayer on the I-precovered Cu(111) surface. The long white line from panel (A) to panel (C) emphasizes the same orientation of the commensurate direction of iodide anions and the molecular rows of the H<sub>2</sub>TMPyP overlayer; the unit cells of iodide- and H<sub>2</sub>TMPyP-layer indicate the structural coincidence of both layer (for details, see text).

pyridyl groups of the neighboring molecule, thereby reducing steric hindrance. The packing and higher electrostatic attraction at the more negative potential result in a molecular coverage of 0.069 ML or  $0.069 \times 10^{13}$  molecules/cm<sup>2</sup>, which is 24% higher than that of phase I.

Going to even more negative potential within regime III in Fig. 23A leads to desorption of iodide and the loss of molecular order (see inset in Fig. 23B). This underlines the importance of the iodide anion/H<sub>2</sub>TMPyP-cation double layer for the stability and order of the molecular layer.

Finally, starting with the well-ordered phase I in Fig. 24B and increasing the potential into the regime O in Fig. 23C leads again to structural changes within the  $H_2$ TMPyP layer as well as the appearance of new fuzzy bright features which in Fig. 24C (*arrows*) appear only next to every second row of molecules. Moreover, these features occur only between two aligned neighboring molecules of the same rotational orientation (AA, bib); there are no bright features between neighboring molecules with AB orientation.

We shortly mention here that the bright fuzzy features may be assigned to the formation of CuI surface compound. This is supported by (1) the electrode potential at which the formation of these features sets in (see CV in Fig. 23A), and (2) ex situ XPS measurements which indicate CuI compound formation.<sup>102</sup>

### The Tip as Tool

As expressed by Eq. (1), the tunneling current depends decisively on the width z of the tunneling gap and the LDOS at the tunneling position. In Fig. 12, we have made use of the latter dependence by varying the bias voltage which leads to different contributions of electrons tunneling into/out of different electronic states, belonging either to states of the substrate or to states of the adsorbate (chloride in Fig. 12). The superposition of the different contributions led to the determination of the absolute adsorption site. The same procedure, of course, may also be applied to adsorbed organic molecules. However, since the latter are adsorbed more weakly than high charge density anions like chloride, an alternative method is viable to determine their absolute adsorption position. This method exploits the z-dependence of the tunneling current and is demonstrated in Fig. 25. Fig. 25A shows the uniaxially incommensurate structure of adsorbed iodide on a Cu(100) surface. Fig. 25C shows the same surface covered with phase I(B) of H<sub>2</sub>TMPyP. If both images are taken immediately one after the other without changing the orientation of the substrate, it may immediately be concluded that the molecular rows in panel (C) run parallel to the [011], that is, the commensurate, direction of the iodide layer underneath. However, it is not possible to state that the molecules are adsorbed above wave valleys or wave crests, never mind to determine the exact relationship between the lattices of iodide underlayer and molecular overlayer due to possible drift between the two measurements in panels (A) and (C). This, however, can be achieved, by exploiting the z-dependence of  $I_{\rm T}$ , or vice versa by changing z by varying  $I_{\rm T}$ . Keeping  $I_{\rm T}$  constant and lowering  $U_{\rm B}$  or vice versa keeping  $U_{\rm B}$ constant and increasing  $I_{\rm T}$  means that the tip must come closer to the surface. Ultimately, this tip-surface approach can lead to a mechanical contact and, thereby, the removal of the organic molecules. This is demonstrated in panel (B) of Fig. 25 at potentials where the surface is covered by molecules. The upper part of the image is registered with "drastic" tunneling conditions, only the iodide structure is seen, and the molecules are brushed away. Increasing the tip-surface distance leaves the molecules unaffected on the surface as seen in the lower part of Fig. 25B. Now, either one of the two lattices, of the iodide or the molecular layer, can be extrapolated onto the other one, and the absolute adsorption position of the molecules (in Fig. 25B) with respect to the iodide lattice can be determined.

We mention here only briefly that the tip, appropriately polarized, can also be applied as an electrode to affect local electrochemistry on a surface. This has been exploited to electrodeposit small metal clusters on surfaces, or to etch structures into



**Fig. 26** (A) Illustration of the local electrochemical deposition of Co clusters from a gold tip onto a Au(111) electrode surface: (1) electrodeposition of Co from a  $Co^{2+}$  containing solution on the tip; (2) Co-covered tip; (3) dissolution of the Co from the tip; (4) imaging of the created Co cluster at shorter tip-surface distance. (B) STM image of two clusters (diameter at half-height  $15 \pm 1$  nm, height  $7.5 \pm 0.5$  nm), produced by a twofold application of the procedure illustrated in (A)).

a surface.<sup>15,103,104</sup> As an example, **Fig.** 26 shows the deposition of Co clusters on a Au(111) surface from a gold tip in an aqueous solution of 0.25 M Na<sub>2</sub>SO<sub>4</sub> + 1 mM CoSO<sub>4</sub>. As illustrated in **Fig.** 26A, at large tip-surface distance the tip is first polarized such that Co is deposited on the tip (I,II). Next, the polarization of the tip is changed to dissolve the Co again. Appropriate choice of the tip- and surface potential leads to deposition of Co clusters in the confined region between tip and surface, where the concentration of redissolving Co<sup>2+</sup> ions is highest. Finally, the tip-surface distance is lowered in order to image the resultant clusters (**Fig.** 26B).<sup>103</sup>

See also: Electrochemical Scanning Tunneling Microscopy; Exploring the Organic–Inorganic Interface With a Scanning Tunneling Microscope; Nonlocal Manipulation With the Scanning Tunneling Microscope.

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# **Electron Paramagnetic Resonance Spectroscopy at Surfaces**

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Nomenclature	e
Symbols	
$\mathcal{H}$	Hamilton operator
Ś	Vector operator of the electron spin
Í	Vector operator of the nuclear spin
$\overrightarrow{B}$	The external vector of the static magnetic field
8e	g-Factor of the electron; its value is approximately 2.002319
$\mu_{ m B}$	Bohr magneton
λ	Spin-orbit coupling constant
Δ	Energy splitting between SOMO and the LUMO of a superoxide radical
8	g-matrix often called the g-tensor
	Principal components of the g-matrix
<i>8</i> ⊥, <i>8</i>	Principal components of an axially symmetric g-matrix
<b>g</b> iso	Isotropic part of the g-matrix
<u>A</u>	Hyperfine interaction matrix
$A_{11}, A_{22}, A_{33}$	Principal components of the hyperfine interaction matrix
$A_{\perp}$ , $A_{  }$	Principal components of an axially symmetric hyperfine interaction matrix
a <sub>iso</sub>	Isotropic part of the hyperfine interaction matrix (due to Fermi contact interaction)
$T_1,T_2,T_3$	Dipolar components of the hyperfine interaction matrix.
Abbreviations a	nd Acronyms
CW	Continuous wave
DFT	Density functional theory
ENDOR	Electron nuclear double resonance
EPR	Electron norman constinues and a
	Electron paramagnetic resonance
ESEEM	Electron spin echo envelop modulation
ESEEM ESR	Electron spin echo envelop modulation Electron spin resonance
ESEEM ESR hfi	Electron spin echo envelop modulation Electron spin resonance Hyperfine interaction
ESEEM ESR hfi HYSCORE	Electron spin echo envelop modulation Electron spin resonance Hyperfine interaction Hyperfine sublevel correlation spectroscopy
ESEEM ESR hfi HYSCORE LUMO	Electron spin echo envelop modulation Electron spin resonance Hyperfine interaction Hyperfine sublevel correlation spectroscopy Lowest unoccupied molecular orbital
ESEEM ESR hfi HYSCORE LUMO SOMO	Electron spin echo envelop modulation Electron spin resonance Hyperfine interaction Hyperfine sublevel correlation spectroscopy Lowest unoccupied molecular orbital Singly occupied molecular orbital
ESEEM ESR hfi HYSCORE LUMO SOMO ML	Electron spin echo envelop modulation Electron spin resonance Hyperfine interaction Hyperfine sublevel correlation spectroscopy Lowest unoccupied molecular orbital Singly occupied molecular orbital Monolayer
ESEEM ESR hfi HYSCORE LUMO SOMO ML MO	Electron spin echo envelop modulation Electron spin resonance Hyperfine interaction Hyperfine sublevel correlation spectroscopy Lowest unoccupied molecular orbital Singly occupied molecular orbital Monolayer Molecular orbital
ESEEM ESR hfi HYSCORE LUMO SOMO ML MO NMR	Electron spin echo envelop modulation Electron spin resonance Hyperfine interaction Hyperfine sublevel correlation spectroscopy Lowest unoccupied molecular orbital Singly occupied molecular orbital Monolayer Molecular orbital Nuclear magnetic resonance
ESEEM ESR hfi HYSCORE LUMO SOMO ML MO NMR STM	Electron spin echo envelop modulation Electron spin resonance Hyperfine interaction Hyperfine sublevel correlation spectroscopy Lowest unoccupied molecular orbital Singly occupied molecular orbital Monolayer Molecular orbital Nuclear magnetic resonance Scanning tunneling microscopy
ESEEM ESR hfi HYSCORE LUMO SOMO ML MO NMR STM TE	Electron spin echo envelop modulation Electron spin resonance Hyperfine interaction Hyperfine sublevel correlation spectroscopy Lowest unoccupied molecular orbital Singly occupied molecular orbital Monolayer Molecular orbital Nuclear magnetic resonance Scanning tunneling microscopy Transverse electric

#### Introduction

Electron paramagnetic resonance (EPR) spectroscopy also known as electron spin resonance (ESR) spectroscopy has been used to characterize predominantly paramagnetic surface species for a long time. This technique offers detailed atomistic insights into the properties of the species, such as geometric and electronic structure or chemical environment. However, EPR spectroscopy is inherently restricted to species with a nonvanishing magnetic moment. Hence, the information will be mostly limited to a subset of the atoms on the surface, and it is typically necessary to combine EPR spectroscopy with other techniques to obtain a comprehensive understanding of the system at hand. In addition, microwave radiation has a significant penetration depth, even for adsorbing materials (e.g., metals). Hence, it is not inherently surface sensitive. Therefore, it cannot be assumed that an EPR signal is due to paramagnetic species located at the surface of the sample and additional efforts are needed to ensure the location of the species is the sample surface.

On the surface of solids, a variety of paramagnetic species may exist. Paramagnetic adsorbates such as molecular radicals (e.g., NO,  $O_2^-$  etc.) are one class of species, many of which result from reactions at the surface and are metastable entities. Another large class of paramagnetic species are transition metal ions (TMI). In particular for TMI, it is important to distinguish between isolated paramagnetic centers and systems with a short distance between paramagnetic TMIs such as binary compounds of such ions (e.g., CuO). The latter exhibit strong coupling between the paramagnetic centers. Depending on the distance, the coupling either can be of dipolar origin or may involve significant exchange contributions. Exchange-coupled systems will often show collective magnetism such as ferro-, antiferro- or ferrimagnetism, which has drastic consequences for the observed spectrum in an EPR experiment. An additional class of species—typically found in solids with a localized electronic structure—is paramagnetic lattice defects such as color centers. The nature of these sites crucially depends on the properties of the solid under consideration. In this introduction into EPR spectroscopy we will give examples for each class of species and try to emphasize the type of information being encoded in the spectra and how to retrieve the information.

Despite the fact that EPR spectroscopy has been used extensively to characterize paramagnetic surface species, it cannot be considered a standard tool in the field of surface characterization. Therefore, this chapter will try to acquaint the reader with the basic principles of EPR spectroscopy, possible applications, and, equally important, with its limitations. An example may be used to illustrate the latter point: consider a hydrogen atom, conceptually one of the simplest paramagnetic species. It has a <sup>2</sup>S ground state and hence shows an EPR spectrum. However, if the hydrogen atom is adsorbed on a metal surface (and this will also hold for metallic metal nanoparticles) an adsorbed H atom will not show any detectable EPR spectrum even if there is spin density on the hydrogen atom. The reason for the lack of an EPR signal is not due to a lack of transitions between spin states, but the dynamics of the spin system. On metals the coupling of the excited spin states to the electrons at the Fermi level reduces the lifetime of the state, such that the line is typically broadened below the detection limit. While dynamics is important for spectroscopy in general, this holds particularly for magnetic resonance spectroscopy. As the dynamics of the spin system is difficult to predict for an unknown system it is typically not straightforward to assume that all paramagnetic species will result in an EPR spectrum.

Historically, most of the information has been and still is obtained using continuous wave (CW) EPR spectroscopy operating at 10 GHz, which is also called X-band. Spectrometers of this kind are still by far the most abundant ones; however, the last decades have seen a significant diversification of experimental capabilities, namely, the commercial availability of spectrometers operating at different microwave frequencies as well as pulse spectrometers, which enable the use of more elaborate pulse techniques also outside of laboratories dedicated to instrumental developments in EPR spectroscopy.<sup>1,2</sup> Therefore, this chapter on EPR spectroscopy will focus on the analysis of CW EPR spectra being still the most common ones and typically the initial step of an EPR spectroscopic investigation. This discussion will be amended by examples on pulsed EPR techniques to illustrate how such methods are used to obtain valuable, additional information on paramagnetic species. The examples chosen in this chapter are mostly from paramagnetic species on oxide surfaces, but we have tried to put emphasize on the concepts, which should allow the reader to transfer them readily to other systems as well.

#### **Basic Experimental Considerations**

Prior to a discussion of EPR spectra, it is appropriate to spend some time on experimental aspects. The discussion will be restricted to basic considerations and will mainly focus on CW EPR spectroscopy. For more detailed information in particular with respect to pulsed spectroscopy the interested reader is referred to literature.<sup>3</sup>

CW EPR spectroscopy probes the properties of paramagnetic species by means of magnetic dipole transitions. As pointed out earlier, EPR spectroscopy is a microwave spectroscopy, typically done between 1 and 250 GHz even though setups at higher and lower microwave frequency exist. The choice of the operating frequency is readily associated with available technology. X-Band (10 GHz) spectrometers were developed because of the availability of monochromatic sources and the ability to provide the necessary magnetic field (about 0.35 T for a free electron, g = 2.0023) by means of an electromagnet. Higher frequencies increase spectral resolution and sensitivity. The reason is the dependence of magnetic field-induced splitting of the electron spin states, the so-called Zeeman interaction, on the magnetic field strength. As the energy difference between the states is in the microwave regime (at X-band this corresponds to a characteristic temperature of < 1 K), the population difference between the spin states, as described by the Boltzmann factor, will change significantly with increasing field. However, the required technology becomes increasingly

complex, e.g., spectrometers operating above 35 GHz (Q-band) require superconducting magnets to achieve the required magnetic fields. As of today commercial spectrometers are available up to 260 GHz, which illustrates the potential of experiments at higher fields.

Microwave radiation is composed of a magnetic and an electric field component. Unfortunately, the electric dipole excitations are often much stronger than the magnetic ones to be probed by EPR spectroscopy. In addition, the magnetic microwave field is typically rather weak. Therefore, most EPR experiments are done in resonator structures, which allow to enhance the magnetic field component as, e.g., characterized by the so-called quality factor and to spatially separate it from the electric one. Fig. 1 shows the field distribution exemplarily for a so-called TE<sub>102</sub> resonator a typical resonator used at X-Band. The resonator is a box with metallic walls whose dimensions are chosen to fit the wavelength of the microwave radiation. For X-band EPR spectroscopy radiation, the wavelength is about 3 cm, which translates into a length of the TE<sub>102</sub> resonator along the z-direction of about 4 cm.<sup>4</sup> It is seen from the field lines that the maxima of electric and magnetic field are shifted by quarter of a wavelength, which results in a maximum of the magnetic field in a plane in the center (along z) of the resonator being a nodal plane for the electric field. The sample is placed in this plane. It is important to remember that the "static" magnetic field has to be oriented perpendicular to the microwave magnetic field in the center plane is zero, it raises in both directions along z. In turn, with increasing size the sample will penetrate the electric field. In case of samples, which exhibit dielectric losses at the corresponding microwave frequency, this overlap with the electric field results in a dissipation of energy. Hence, the quality factor of the resonator i.e. the ability of the structure to store energy decreases.

Together with the filling factor and the conversion efficiency, the quality factor crucially determines the performance of an EPR experiment. For CW experiments the signal-to-noise ratio of an experiment is over a wide range proportional to the quality factor rendering it a very crucial parameter. In addition, a high filling factor increases the ability of the system to utilize the microwave radiation. This is seen from the definition of the filling factor as the integral of the microwave magnetic field over the sample volume divided by the integral of the magnetic over resonator volume.

A high-quality factor is obviously beneficial for the sensitivity of CW experiments; however, the situation is more complex in case of pulsed experiments. Pulsed experiments rely on a coherent excitation of the spins, which requires high field strength of the exciting radiation. With respect to this requirement a high-quality factor would be advantageous. However, two important aspects need to be considered, which render the use of a resonator with high-quality factor problematic. First, a high-quality factor will prolong the time required to dissipate the radiation in the resonator down to a level that allows for a detection of the signal. This time is usually called the dead time of the resonator, which becomes limiting if it is comparable to the relaxation times of the signal. In addition, a high-quality factor is associated with a small bandwidth of the resonator, which will limit the spectral width of an excitation pulse otherwise determined by the length of the pulse. Therefore, an ideal pulse resonator should exhibit a large bandwidth together with a large conversion efficiency (ratio between the incident microwave power and the resulting magnetic field at the position of the sample), which allows for a coherent excitation of a broad spectrum. A detailed discussion of these aspects goes beyond the scope of this chapter, and the interested reader is referred to the literature for a more comprehensive discussion.<sup>4</sup>



**Fig. 1** Mode pattern of a TE<sub>102</sub> resonator. Magnetic fields are indicated by dashed lines. Maxima of the magnetic field are found on the walls parallel to the *xy*-plane as well as in the center plane of the resonator along *z*. In these positions the electric field is zero. The static magnetic field is typically oriented along the *y*-direction within this framework and it has to be oriented perpendicular to the alternating one to induce magnetic dipole excitations.

The use of resonators implies the use of monochromatic radiation, which in turn means that the resonance condition has to be fulfilled by sweeping the external magnetic field. In contrast to pulse NMR spectroscopy, which allows to excite the entire spectrum by employing sufficiently short monochromatic pulses at a fixed magnetic field, the spectral width of most EPR spectra is too large to transfer this scheme directly to pulse EPR spectroscopy. Usually, in pulsed EPR spectroscopy only parts of the spectrum will be excited, even though considerable efforts are being made to enhance the available bandwidth of the setups. In practice, most pulse EPR experiments done today are based on echo detection schemes.

The amount of microwave radiation absorbed in a typical CW experiment is very small, which renders a sensitive detection scheme important. We will refrain from discussing the various aspects on the side of microwave technology but want to mention here that typical CW spectra are recorded using a so-called lock-in scheme. To this end the external magnetic field is modulated—often by means of a Helmholtz coil mounted on the side walls of the resonator (for the  $TE_{102}$  resonator on both walls in the xzplane)—with known frequency and phase, which allows a phase-sensitive detection of the corresponding Fourier component of the detector signal. Typically, modulation frequencies range from 1 to 100 kHz. The necessity to apply an alternating magnetic field to the sample imposes restrictions to the design of the resonators. In particular, the thickness of the metal walls used to build the resonators has to be chosen such that microwave radiation will stay inside the resonator, while the alternating magnetic field of the modulation field can still penetrate the walls. Even though it sounds like a pure technicality the use of a lock-in detection scheme has the important consequence that CW-EPR spectra are recorded as the first derivative of the absorption spectrum or more precisely the first derivative of the imaginary part of the complex high-frequency susceptibility by the field  $(d\chi'/dB)$  as a function of the magnetic field. This has considerable consequences for the appearance of the spectra in particular if spectra are composed of a superposition of lines. The number of spins being proportional to the area underneath the absorption spectrum may be determined from CW EPR spectra by double integration. This has to be done with particular care to avoid artifacts easily introduced by experimental imperfections such as a skewed baseline. Because of the direct relation of the EPR signal intensity with the susceptibility of paramagnetic samples, it should obey Curie's law, which predicts an inverse proportionality of the magnetic susceptibility and thus the EPR signal intensity with temperature. A simple and often used test for Curie behavior is to plot the EPR signal intensity multiplied by the sample temperature  $(I^*T)$  as a function of the temperature. For a paramagnetic sample with a constant number of spins this product should be constant and deviations can be used to draw conclusions on the magnetic properties of the sample. If the intensity change with temperature is reversible, the deviation from the expected Curie behavior may be due to nonparamagnetic species: ferro or superparamagnetic species give rise to signals in an EPR spectrum, too; however, their temperature-dependent intensity will not obey Curie's law. In case of paramagnetic species, temperature-dependent changes in the redox state may occur. In case of paramagnetic adsorbates desorption or reactions are typical channels for a loss or in case of TMI sometimes also for a gain in EPR signal intensity. The analysis of the temperature-dependent EPR signal intensity assumes that the experimental conditions will not induce additional changes in the measured spectrum. To this end, both instrumental effects such as a change in the quality factor of the resonator and effects of the spin system need to be taken into account. For the latter saturation effects may be one source of error because spin lattice relaxation time being the characteristic time constant of the system to decay back into the thermodynamic equilibrium ( $T_1$  time) is a function of temperature. Unfavorable relaxation properties may even be responsible for the difficulty to observe paramagnetic species at certain temperatures. Typical examples are some transition metal ions such as Co<sup>2+</sup> or Ni<sup>2+</sup>, which require very low temperature to be observed. As mentioned already in the introduction, the relaxation behavior of paramagnetic centers is a critical issue for EPR spectroscopy; however, a detailed discussion of this aspect goes beyond the scope of this introduction and the interested reader is referred to the literature on this topic.<sup>5–9</sup>

# **CW EPR Spectroscopy on Solid Surfaces**

#### Paramagnetic Species With $S = \frac{1}{2}$

To get acquainted with the language typically used in EPR spectroscopy we start the discussion using a free electron with a doublet spin ground state. Putting such a system in a magnetic field leads to a splitting of the two eigenstates of the spin with the energies  $E = m_s g_e \mu_B B_0$  ( $g_{er}$ , g-factor of the free electron  $g_e = 2.0023$ ;  $\mu_B$ , Bohrs magneton;  $m_{sr}$  eigenvalues of the  $S_z$  operator;  $B_0$ , static magnetic field along the *z*-axis) according to Zeeman interaction. The energy separation between the spin states raises linearly with increasing magnetic field as shown in Fig. 2. Irradiating the system with monochromatic radiation of frequency  $\nu$ , an absorption line will be observed if the energy separation between the states matches the energy of the radiation.

In case the paramagnetic species under consideration is anisotropic in space, the situation is more complicated. The reason is spin-orbit coupling. In a nonisotropic system this leads to a dependence of the resonance field on the orientation of the magnetic field with respect to the species under consideration. An ab initio description of spin-orbit coupling is a challenging task. Instead a phenomenological framework called the spin Hamiltonian is used to describe the system. The idea of this very successful approach is to describe the different quantum mechanical effects by means of proper Hamiltonians and introduce appropriate coupling constants to quantify the strength of the interaction. Within the framework of the spin Hamiltonian the complex problem of the spin-orbit interaction is parametrized by replacing the isotropic g-factor by a second rank tensor (in EPR spectroscopy one should better talk about coupling matrices). The spin Hamiltonian for the Zeeman interaction then reads:

$$\widehat{\mathcal{H}} = \mu_B \,\overline{\mathcal{S}} \, g \,\overline{\mathcal{B}} \tag{1}$$



**Fig. 2** Schematic energy diagram of the spin states (free electron) in a magnetic field. The red arrow symbolizes the energy of the microwave radiation. Absorption occurs if the spitting of the energy levels matches the energy of the radiation, which results in a resonance field ( $B_{res}$ ) as indicated.

where  $\vec{S}$  denotes the vector operator of the spin,  $\vec{B}$  is the vector of the "static" magnetic field,  $\mu_B$  is the Bohr's magneton, and  $\underline{g}$  is the interaction matrix of the anisotropic Zeeman interaction also called the g-tensor. The latter is a symmetric (3 × 3) matrix, which implies that it can be diagonalized. The components of the diagonal matrix are also called principal components of the corresponding interaction matrix, and it is important to note that these principal components span a well-defined Cartesian coordinate system within the local framework of the paramagnetic center. In case of an ordered system, which exhibits a single orientation of all the paramagnetic species with respect to the static magnetic field, this results in a single resonance. The top three spectra in Fig. 3 show this exemplarily for the magnetic field oriented along the principal components of the g-matrix. In a powdered material all orientations of the paramagnetic species with respect to the spectra of all orientations. The corresponding line shape is shown as the lower trace in Fig. 3.

The powder spectrum allows determining the position of the principal components straightforwardly as indicated by the vertical lines. While the determination of the principal component is fairly simple, the information about the orientation of the interaction matrix with respect to the species of interest is lost. In particular, the latter information is valuable to deduce the nature of the species at hand. To illustrate this, Au atoms will be used as an exploratory example. The electronic structure of Au atoms is characterized by an unpaired electron in the 6 s orbital leading to a <sup>2</sup>S ground state. In the particular example discussed here Au atoms are deposited on a single crystalline MgO(001) surface at 30 K to prevent diffusion of the atoms, which would lead to aggregate formation. The experiments were done under ultrahigh vacuum (UHV) conditions ( $p < 1 \cdot 10^{-10}$  mbar) to ensure that the results are not perturbed



Fig. 3 Simulated CW EPR spectra for a paramagnetic center exhibiting Zeeman interaction only. Top three spectra are spectra expected for an oriented ensemble of species, which exhibits only one orientation of the species with respect to the magnetic field. Spectra are simulations with the magnetic field along one principal axis of the g-matrix each. Bottom spectrum shows the expected powder spectrum, which assumes all orientations with equal probability.



**Fig. 4** (A) X-band EPR spectrum of 0.0025 ML Au on 20 ML MgO(001)/Mo(001) (T = 30 K), B||to surface; (B) resonance position as a function of the angle between the static magnetic field and the surface normal; back dots experimental points; red traces simulation using the magnetic parameters given in **Table 2**. (C) Low-temperature STM of Au atoms on an 8 ML MgO(001) film. (D) Expected EPR spectrum for Au atoms on MgO powder (properties as on the (001) surface).

by interaction with molecules from the gas phase. For the magnetic field being oriented parallel to the surface, Au atoms on MgO(001) show an EPR spectrum as presented in Fig. 4A.<sup>10</sup> Based on the simple consideration for the Zeeman interaction of a doublet spin state and an oriented system discussed earlier, a single line would be expected. In contrast, four nonequidistant lines are found. In general, it is not obvious that these four lines correspond to the same paramagnetic species. However, a closer look into the properties of Au atoms helps to rationalize the appearance of the spectrum. Au consists exclusively of the isotope <sup>197</sup>Au (100% natural abundance) having a nuclear spin of I = 3/2. The unpaired electron couples to the nuclear spin of the Au atom. The corresponding interaction is called hyperfine interaction (hfi). Therefore, it is expected that the Zeeman line splits into four peaks due to the interaction of the unpaired electron with Au nuclei, which can adopt four different nuclear spin states (2I + 1). A statistically picked Au atom within the ensemble will have a certain nuclear spin state and will contribute to one of the four lines observed in the spectrum. Because of the equipartition of the nuclear spin states even at 30 K, all four nuclear spin states are populated equally and thus the Boltzmann weight of each line is identical for an ensemble of spins. A double integration of the spectrum reveals that within experimental uncertainty the four lines have the same intensity, but do have quite different line width, which gives rise to the difference in signal amplitude.

Hyperfine interaction is an important quantity in EPR spectroscopy because it often allows deducing valuable information on the electronic structure as well as on the environment of the paramagnetic center under consideration. A gold atom bound to a surface is an anisotropic system, in contrast to the atom in the gas phase. The same argument leading to an anisotropic Zeeman interaction holds for the hyperfine interaction. The spin Hamiltonian describing Zeeman and hyperfine interaction thus reads. The nuclear Zeeman interaction has been omitted because it does not change the appearance of the EPR spectrum:

$$\widehat{\mathcal{H}} = \mu_{B} \overrightarrow{S} g \overrightarrow{B} + \overrightarrow{S} \underline{A} \overrightarrow{I}$$
<sup>(2)</sup>

where in addition to Eq. (1)  $\vec{I}$  denotes the vector operator of the nuclear spin and <u>A</u> describes the interaction matrix of the anisotropic hyperfine interaction.

Angle-dependent experiments shown in **Fig. 4B** reveal a significant dependence of the resonance positions on the orientation of the magnetic field as expected in case of an anisotropic interaction of the electron spin with both the magnetic field and the nuclear spin of the Au atoms. In general, symmetry is a powerful tool to predict the properties of the coupling matrices. **Table 1** summarizes the relationship between g- and A-matrix components and their relative orientation with the point group symmetry of a paramagnetic site.<sup>11</sup> As seen from the low-temperature STM image in **Fig. 4**C the Au atoms are located predominately on the terraces of the MgO(001) surface. This information is not sufficient to infer the adsorption site. A more detailed analysis of the STM images reveals that the large majority of Au atoms on thick MgO(001) surfaces occupy the same adsorption site, but it is impossible to deduce the site from the STM images.<sup>12</sup> The basal plane of the rock salt structure looks like a chessboard with alternating oxygen and magnesium ions and offers several high-symmetry adsorption sites. From the EPR results some conclusions can already be drawn. The first conclusion is that one of the principal components is aligned with the surface normal and the other two are oriented in the surface plane, because both are extrema in the angular-dependent spectra. This is perfectly in line with respect to the surface normal.<sup>13,14</sup> In addition, **Table 1** suggests that all adsorption sites with a local symmetry lower than  $C_{3V}$  should exhibit a so-called orthorhombic tensor with three different tensor components. Typical examples would be bridge sites on the (001) surface. To this end it is important to note that in case of a static magnetic field the fourfold symmetry of the surface is lifted and the structurally equivalent bridge

Symmetry of EPR parameters	Relationship between g- and A-matrix elements	Relationship between the axis of the coupling matrices	Point group symmetry of the system
Isotropic	$g_{11} = g_{22} = g_{33}$ $A_{11} = A_{22} = A_{22}$	All axis coincident	0, 0 <sub>h</sub> , T, T <sub>d</sub> , T <sub>h</sub>
Axial	$g_{11} = g_{22} \neq g_{33}$ $A_{11} = A_{22} \neq A_{33}$	All axis coincident	$D_{\infty h}, C_{\infty v}, D_{6h}, D_6, C_{6v}, D_{4h}, D_4, C_{4v}, D_{3h}, D_{3d}, D_3, C_{3v}, D_{2d}$
Rhomic	$g_{11} \neq g_{22} \neq g_{33}$ $A_{11} \neq A_{22} \neq A_{33}$	All axis coincident	$C_{2v}, D_2, D_{2h}$
Axial, degenerate axes noncollinear	$g_{11} = g_{22} \neq g_{33}$ $A_{11} = A_{22} \neq A_{33}$	$g_{zz}$ collinear with $A_{zz}$	$C_3,\ C_{3h},\ C_4,\ C_{4h},\ S_4,\ C_6,\ C_{6h},\ S_6$
Monoclinic	$g_{11} \neq g_{22} \neq g_{33}$ $A_{11} \neq A_{22} \neq A_{33}$	One axis of $g$ and $A$ collinear	$C_2,\ C_{2h},\ C_S$
Triclinic	$g_{11} \neq g_{22} \neq g_{33} \\ A_{11} \neq A_{22} \neq A_{33}$	All axis non coincident	C <sub>1</sub> , C <sub>i</sub>

#### Table 1 Correlation of point group symmetry and symmetry properties of EPR parameters

sites become magnetically inequivalent. This should result in a splitting of the resonances for the orientation of the magnetic field in the surface plane.

For systems with rather large hyperfine interaction such as Au atoms discussed here, it is necessary to solve the eigenvalue problem associated with the Hamiltonian (2). Algorithms to solve this problem are, e.g., implemented in the freely available suite of Matlab routines called "EasySpin," which is a very powerful toolbox to simulate EPR spectra.<sup>15</sup> Fits of the angular-dependent EPR spectra were made, and the results are shown as red traces in Fig. 4B. To simulate the resonance positions a single axially symmetric, collinear g- and hfi-matrices were assumed. Hence, two of the principal components are identical, and the nondegenerate value is typically referred to as the parallel, while the other is called perpendicular component. The principal components of the g- and the A-matrix extracted from the fits are shown in Table 2. The EPR spectra observed here report on Au atoms adsorbed on terraces of the MgO(001) islands, while the STM image (Fig. 4C) taken at 4 K on single crystalline MgO(001) surface reveals Au atoms adsorbed on step edges or corner sites as well. The absence of these species in the EPR spectra is due to their low abundance.

The observed differences of the signal amplitude for the four lines are due to small differences in the hyperfine coupling constants within the ensemble. The interested reader is referred to the literature for details.<sup>10</sup>

The situation on a single crystalline surface is of course different to a disordered substrate typically found for most samples. Assuming the same adsorption behavior, the EPR spectrum of such a powder material is considerably different because the sample contains all orientations with equal probability, which were investigated separately in the single crystal case. **Fig.** 4D shows a simulation of the expected line shape neglecting the dependence of the hyperfine coupling constant on the adsorption sites. It is seen that each of the hyperfine manifolds does now show a spectrum governed by the g-anisotropy, where the low-field maximum corresponds to  $g_{\perp}$  and the high-field minimum to  $g_{||}$  as indicated in **Fig.** 4D. In this particular case the situation is rather simple because the hyperfine interaction is almost isotropic and large. Thus, the effect of the g-matrix anisotropy on the individual hyperfine lines is clearly visible. It is obvious that the spectrum interpretation of a powder sample with anisotropic g- and hfi-matrix, which overlap spectrally, can be involved. A unique determination of the corresponding principal components requires sufficient spectral resolution, which is not always available in particular if several species with overlapping spectral features are present. To this end, spectra taken at different microwave frequencies, which changes the Zeeman interaction, but leaves the hyperfine interaction constant, are very helpful. For a complex EPR spectrum some experience is required to deduce an appropriate spin Hamiltonian together with the matrix elements of the coupling matrices from a given line shape.

#### Physical Interpretation of g- and Hyperfine-Matrix Components

One of the core results of the spectral analysis was the determination of the characteristic coupling parameters, namely, the anisotropic hyperfine and the Zeeman interactions. A very important question remains: What additional insight can be obtained from the values of the g- and A-matrices? A detailed quantitative discussion of this aspect is in general rather involved and requires high-level calculations to describe the subtle interactions correctly. Significant progress in this respect has been made in recent years by

Table 2	g- and A-matrix components for Au atoms on MgO <sup>10</sup>	
$g_{\perp}$		2.0652
$g_{  }$		1.9904
A		1402 MHz
		1410 MHz

computational approaches mostly based on DFT methodologies, which are now capable to calculate g- and A-matrix components with sufficient precision for meaningful comparisons (e.g., Refs.<sup>16–22</sup>). The progress in this field has advanced the understanding of paramagnetic centers tremendously. A discussion of the theory goes beyond the scope of this chapter. However, valuable insight can often be achieved based on a qualitative or semiquantitative discussion of the expected electronic structure of the site under consideration, e.g., an analysis of the crystal field of a transition metal ion.

Information on the electronic properties of the system at hand is encoded in both the g- and the A-matrix. Conceptually, it is perhaps easier to start with the discussion of the hyperfine interaction. As mentioned earlier, it is described by a symmetric  $(3 \times 3)$  matrix, which can thus be diagonalized. This diagonal matrix has a trace, but it is possible to decompose the matrix into two parts: an isotropic, scalar part ( $a_{iso}$ ) and an anisotropic dipolar part ( $\underline{T}$ ), which is a traceless (3 × 3) matrix. Mathematically this can be written as follows:

$$\underline{A} = \begin{pmatrix} A_x & 0 & 0 \\ 0 & A_y & 0 \\ 0 & 0 & A_z \end{pmatrix} = a_{iso} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \begin{pmatrix} T_1 & 0 & 0 \\ 0 & T_2 & 0 \\ 0 & 0 & T_3 \end{pmatrix}$$
(3)

The reason for this decomposition is that these two parts of the hyperfine interaction can be associated with different physical effects. The isotropic hyperfine coupling constant is also known as the Fermi contact term and is a direct measure of the electron spin density at the nucleus. For Au atoms on MgO a large isotropic hyperfine coupling constant is expected because the spin density is predominately of s character (unpaired electron in the 6 s orbital) and should thus have an appreciable density at the nucleus. It is interesting to note that the isotropic hyperfine coupling constant of the adsorbed Au atoms is decreased by more than 50 % as compared to the value measured for Au atoms in a rare gas matrix.<sup>23</sup> What is the reason for the reduced s-electron spin density on the MgO surface? On the one hand the spin density itself could be reduced, e.g., by partial charging of the Au atoms on the surface. On the other hand, it is possible that the s character of the spin density is reduced. These two effects cannot easily be disentangled based on the experimental results alone. However, theoretical calculations can help to answer this question. Proper density functional calculations revealed that the charge transfer between the Au atoms and the MgO surface is small, which renders a reduced spin density an unlikely explanation. The spin density as shown in Fig. 5A, however, is no longer spherical as expected for s orbitals but is polarized away from the surface as a result of the Pauli repulsion due to the interaction with the oxygen anions of the surface. In a simple orbital picture this polarization implies that the corresponding wave function contains components with higher angular momentum (p or d orbitals), which reduce the s contribution and thus the isotropic hyperfine interaction. From an energetic point of view this means that the Au 6 s orbital is destabilized due to the Pauli repulsion with the lattice oxygen ions of the MgO. This effect is not restricted to coinage metals on MgO but has been seen before, e.g., for alkali metals on MgO or coinage metals on alkali chloride surfaces.<sup>24-26</sup>

Hyperfine interaction extends also beyond the atom or atoms where the spin density is mainly localized. The hyperfine interaction found on more distant atoms is often called super hyperfine (shf) interaction. To exemplify the kind of information, which can be accessed, Fig. 5B shows the largest EPR line of Au atoms. For the black spectrum MgO was grown (see Fig. 4A) with conventional oxygen, whereas the green spectrum was measured after growing the MgO(001) surface with <sup>17</sup>O<sub>2</sub> (I = 5/2; 90% enrichment).<sup>10</sup> The single line splits into six lines and a small signal at the original position. The latter is due to Au atoms interacting only with <sup>16</sup>O in the film. The observed intensity is about 10% of the original signal, which is expected based on the enrichment of the oxygen source. The sextet of lines observed in the spectrum is readily understood by coupling to one <sup>17</sup>O nucleus of the MgO lattice. Given an isotopic enrichment of 90%, coupling of the Au atom to a single oxygen ion allows to disregard all adsorption sites, which have more than one equivalent oxygen neighbor such as the Mg cation site. The analysis of the angular-dependent measurements resulted in collinear axial coupling matrices, which suggest a local symmetry higher than C<sub>3V</sub>. In combination with the fact that the atoms couple to one oxygen atom only, it is possible to deduce that the atoms have to be bound on-top of the oxygen ions on the MgO(001) lattice, which is perfectly consistent with theoretical predictions.<sup>27,28</sup>



**Fig. 5** (A) Calculated spin density of Au atoms adsorbed on oxygen ions of a MgO(001) surface. Adapted from Yulikov, M.; Sterrer, M.; Heyde, M.; Rust, H. P.; Risse, T.; Freund, H.-J.; Pacchioni, G.; Scagnelli, A. Binding of Single Gold Atoms on Thin MgO(001) *Films. Phys. Rev. Lett.* **2006**, *96*, 146804. (B) EPR signal of the most intense line from **Fig. 4**A (*black trace*) and spectrum found after growth of a <sup>17</sup>O enriched MgO(001) film (*green trace*).

Apart from hyperfine interaction the g-matrix also contains valuable information. The extraction of this information is intimately linked to the electronic structure of the system at hand. For transition metal ions, which are a prominent class of paramagnetic centers in catalytic systems, but also molecular radicals crystal field theory forms the basis of the qualitative and semiquantitative discussions. The various situations found for transition metal ions have been investigated early on, and there are excellent books and reviews summarizing their properties (e.g., Refs. <sup>11,29,30</sup>). Here the information encoded in the g-matrix components will be exemplified using  $O_2^-$  radicals on MgO(001). Adsorption of molecular oxygen at 30 K on a 4 ML thick MgO(001) film grown on a Mo(001) single crystal leads to the spontaneous formation of  $O_2^-$  radicals, characterized by the angular-dependent EPR spectra shown in Fig. 6A.<sup>31</sup> At this point we will not go through the analysis of the angle-dependent spectra in detail. The discussion would be identical to the one on Au atoms earlier. The result of the analysis of the presented spectra together with spectra taken at a different azimuthal orientation of the (001) surface with respect to the magnetic field (not shown) reveals an orientation of principal components of the g-matrix to be along the surface normal and two [110] equivalent directions within the (001) surface. This orientation dependence proves that the radical adsorbs on the terraces of the MgO(001) islands and aligns with [110] equivalent directions (see Fig. 6B), which is in perfect agreement with theoretical predictions for the adsorption site.<sup>32,33</sup> More important for the present discussion are the values of the g-matrix elements in particular the gzz component (the component parallel to molecular axis) compiled in Table 3. For this discussion  $O_2^-$  radicals on the MgO thin films are compared to  $O_2^-$  centers on powder samples. The radicals do not form spontaneously on the stoichiometric surface of MgO powder, but extra electrons are required as introduced, e.g., by alkali metal atom doping.<sup>34–37</sup> A detailed analysis of the powder data in comparison with theoretical calculations revealed that the gzz-component of the matrix strongly depends on the adsorption site. In particular, radicals adsorbed on morphological defects such as edges or corners show a significant reduction of the gzz-component as compared to the regular terraces site (Table 3). This reduction can be understood considering the following expression, which is a first-order approximation for the  $g_{zz}$ component of such a 13-electron radical<sup>38</sup>:

 $g_{zz} = g_e + 2[\lambda^2/(\lambda^2 + \Delta^2)]^{1/2}$ 

Here,  $\lambda$  is the spin–orbit coupling constant and  $\Delta$  is the energy difference between the singly and the doubly occupied  $\pi^*$  orbitals schematically shown in Fig. 6C. This equation emphasizes that the origin for the deviation of the *g*-matrix components from the free electron values is due to spin–orbit interaction. The reduction of the  $g_{zz}$ -component with a reduction of the local coordination of the adsorption site on an ionic crystal is directly associated with an increase of the local electric field at the adsorption site. An increased electric field leads to increased splitting between the  $\pi^*$  orbitals of the  $O_2^-$  radical ( $\Delta$ ). Therefore, the  $g_{zz}$ -component will be found closer to the g-value of the free electron, which is the explanation for the experimental observation made on powders. However, an important question remains: What is the reason for the reduced  $g_{zz}$ -values measured for  $O_2^-$  radicals on terraces of the thin film as compared to terrace sites on the MgO powders? The explanation is intimately related to the question of the stability of the  $O_2^$ radicals on the thin MgO film. Theory predicts that the electron transfer from the metal substrate through the MgO film onto the oxygen molecule is stabilized by a so-called polaronic distortion of the MgO lattice, an effect considered important not only for the adsorption of molecules but also for metal adsorbates, which become charged upon adsorption in the oxide surface such as Au.<sup>32,33,38</sup> If the adsorbed  $O_2^-$  radical is bound in between 2 Mg cations along the [110] direction it is stabilized by a polaronic distortion of the lattice as indicated in Fig. 6D: the Mg cations are pulled out of their regular lattice positions. This lattice distortion increases the electric field encountered by the oxygen molecule on the surface and thus reduces of the  $g_{zz}$  component of the



**Fig. 6** (A) Angle-dependent EPR spectra of  $O_2^-$  radicals spontaneously formed on 4 ML thick stoichiometric MgO(001) film.  $\theta$  is the angle between the surface normal and the magnetic field. (B) Schematics of the experimental geometry. (C) Schematic MO diagram of an  $O_2^-$  radical. (D) Binding geometry as calculated theoretically.

		g <sub>xx</sub>	g <sub>yy</sub>	g <sub>zz</sub>
MgO/Mo(001) exp. <sup>31</sup>	Terrace	2.002	2.012	2.072
MgO powders exp. <sup>39</sup>	Terrace	2.002	2.008	2.091
MgO powders exp. <sup>40</sup>	Edge	2.002	2.008	2.077

 Table 3
 Measured g-matrix components for 02<sup>-</sup>-radicals adsorbed on the surface of thin Mg0(001)/Mo(001) films and Mg0 powders

g-matrix. This example illustrates the type of information encoded in the *g*-matrix components nicely. It should be emphasized that a discussion of the experimental results very often requires support from theoretical calculations. This support is not only valuable but often indispensable for an understanding of the experimental results as it allows to correlate the values of the *g*- and hfi matrices with the geometric and electronic structure of a system.

#### Impact of Rotational Dynamics on CW EPR Spectra

The paramagnetic species discussed earlier were considered static entities and given the temperature of 30 K, at which the spectra were measured, this assumption is justified. However, paramagnetic surface species may also be present, e.g., on small nanoparticles forming a stable colloidal dispersion. In such a system the orientation of the paramagnetic center with respect to the static magnetic field is no longer constant. However, the important question whether or not this matters for the EPR spectrum of these species is a matter of time scales. To this end there is no definite answer. The time scale depends on the actual experiment. For CW-EPR spectroscopy at X-band (10 GHz) the rigid limit assumption is valid if the rotational correlation time is longer than about 100 ns. The effect of rotational motion may be illustrated using the EPR spectrum of vanadyl(IV) species characterized by a spin of ½ and nuclear spin of the vanadium of I = 7/2. Fig. 7A shows the EPR spectrum of a frozen solution of vanadyl(IV)acetylacetonate  $(c = 5*10^{-4} \text{ mol L}^{-1})$  in toluene at 77 K.<sup>41</sup> The spectrum is in line with expectations for a spin  $\frac{1}{2}$  species with an anisotropic hyperfine as well as an anisotropic Zeeman interaction. Similar line shapes are also found for VO<sup>2+</sup> species on solid surfaces such as titania particles loaded with vanadium. As discussed earlier the line shape is due to a superposition of lines arising from centers, which have a different orientation of the local framework with respect to the magnetic field for the different nuclear spin state manifolds. This picture implies that the orientation of the species is stationary on the characteristic time scale of the EPR spectroscopy. In case the orientation changes on the time scale of the experiment the resonance condition and hence the appearance of the spectrum will change as well. To illustrate the effect, it is easiest to consider the extreme of fast reorientation dynamics on the time scale of the EPR experiment. In such a case the anisotropy of the matrices can no longer be probed by the experiment, and the resulting spectrum is determined by the isotropic g-value as well as the isotropic hyperfine interaction constant ( $a_{iso}$ ), which can be calculated from the matrices as the mean values of the principle components (e.g.,  $g_{iso} = 1/3 (g_{11} + g_{22} + g_{33}))$ ). For the vanadyl species one expects an eight-line spectrum centered at  $g_{iso}$  with a splitting of  $a_{iso}$  between the lines within the so-called high-field approximation. Fig. 4B shows the spectrum of the same sample measured at 236 K.<sup>41</sup> Qualitatively, the spectrum is in line with the expectations. However, the linewidth and thus the amplitude of the lines are different for the different nuclear spin states. Depending on the rotational correlation time the reason for the different linewidth may be due to residual anisotropy of the g- and hfi-matrix, but even more importantly anisotropic relaxation effects contribute to this as well. While the two extreme cases can be treated rather simply, the region of slow motion in which most of the motional averaging of the matrix anisotropy occurs is rather difficult to treat theoretically. One framework based on a stochastic Liouville equation (SLE), which can address rotational motions within diffusion models, has been developed by Freed and coworker.<sup>42,43</sup> In essence, the signal will undergo drastic changes in the line shape between the rigid and the fast rotational limit. This affects both the line position and the line width for the different manifolds. Applying the SLE framework to simulate the effect of rotational diffusion to the vanadyl system discussed here indicates that changes in line shape occur for rotational correlation times smaller than 10 ns while a spectrum as shown in Fig. 7B corresponds to a rotational correlation time of about 0.1 ns.

While paramagnetic centers in bulk solids and low-molecular-weight molecules in solution are easily categorized into the rigid or the fast rotational limit, respectively, a back of the envelope calculation using Stokes–Einstein equation reveals that objects of



Fig. 7 (A) CW EPR spectrum of vanadyl(IV) acetylacetonate in frozen toluene solution at 77 K. (B) Same sample measured at 236 K. Adapted from Wilson, R.; Kivelson, D. ESR Linewidths in Solution. I. Experiments on Anisotropic and Spin—Rotational Effects. *J. Chem. Phys.* **1966**, *44*, 154.

a few nanometers in diameter will have rotational correlation times in the slow motion regime of CW EPR at X-band at room temperature. Paramagnetic centers present on the surface of such nanoparticles will thus exhibit rotational correlation times, which impact the line shape of CW EPR spectra. The same argument holds if the paramagnetic center rotates with respect to the surface.<sup>44,45</sup> With respect to the spectral analysis one should note that, in case of dynamic effects being present, a determination of the characteristic magnetic interaction parameters requires particular care and a spectrum taken at a certain temperature may only give apparent magnetic parameters. This issue should be kept in mind when comparing magnetic parameters with literature values in case the paramagnetic species may exhibit rotational dynamics.

# Pulsed Spectroscopic Techniques: Hyperfine Interactions as an Introductory Example

It was already shown that hyperfine interaction is an important source of information in EPR spectroscopy. In the spectra discussed earlier lines were split due to hyperfine interaction, which allows to extract the values of the principal components directly from the CW EPR spectra. However, this is not always straightforward. For solid powders, which are usually much more complex materials than the ideal case discussed earlier, the assignment is more difficult. The problem is often caused by a lack in spectral resolution either due to overlapping lines or due to splittings, which are smaller than the line width of the CW EPR signal. Additional information on such systems is obtained using pulse spectroscopic techniques. Coarsely, pulse techniques addressing interaction to adjacent nuclei are subdivided into experiments relying on nuclear modulation effects and double resonance experiments called electron nuclear double resonance (ENDOR). The former experiments go back to experiments made in the 1960s, which showed that the decay of primary electron spin echoes is modulated with frequencies corresponding to nuclear frequencies as well as their differences and sums.<sup>46,47</sup> The term ESEEM (electron spin echo envelop modulation) was coined for these experiments. ENDOR was first demonstrated by Mims in 1965 and Davies added a second important variant of it in 1974.<sup>48,49</sup> Both techniques have their advantages, but it goes beyond the scope of this chapter to discuss them in detail here. The interested reader is referred to literature.<sup>3,50,51</sup>

In the following we will discuss two examples using ESSEM or advanced variants of it. There are several aspects both on the experimental and on the analysis side of ESEEM experiments, which need to be considered and the interested reader is referred to the appropriate literature (e.g., Refs. 52,53). The effect should be exemplified with TiO<sub>2</sub> nanoparticles, which play an important role in a variety of technical applications. Photocatalytic processes are one of them, and elucidating the fate of the primary electron hole pair, which may separate after the photoexcitation event, is crucial for an understanding of these processes. In TiO<sub>2</sub> both the "electrons" and the "holes" are associated with paramagnetic states. At this point we will focus on a very special question, namely, the environment of the hole and the electron center created subsequent to the photoexcitation. From CW-EPR spectra it is readily inferred that the hole centers are associated with oxygen-based radicals, namely, O<sup>-</sup> centers, which give rise to characteristic EPR signals spectrally well separated from the EPR signals of the electron centers. At least part of the electrons generated by such processes get trapped by titanium ions and reduce them to Ti<sup>3+</sup> centers, which are EPR active d<sup>1</sup> ions. These centers are observed at higher magnetic fields (lower g-values) than the hole centers. Apart from the g-anisotropy the CW-EPR spectra do not reveal any additional splitting, which could be associated with the coupling to other nuclei. A 2-pulse ESEEM experiment schematically shown in the inset of Fig. 8A was measured at 7 K by setting the magnetic field to an absorption line of the  $O^-$  centers and the Ti<sup>3+</sup> centers, respectively. The Fourier transform of the delay time  $\tau$ -dependent echo intensities reveals a signal at 14.9 MHz for the hole centers but no signal for the corresponding electron centers.<sup>54</sup> The signal is very close to the nuclear Larmor frequency of hydrogen at the field strength used. This proves the oxygen-centered radical to be located in the vicinity of protons (OH groups) typically located on the surface of the nanoparticles. However, the hyperfine coupling is weak, which can be used to argue that the paramagnetic centers have a certain distance from the protons they are coupled with. In contrast, the electron-related signal located on titanium sites does not show any indications for proton coupling. Hence, these centers have a significantly larger distance to the surface OH groups rendering them to be bulk species.

In case of a single weakly coupled nucleus the analysis of the ESEEM traces is straightforward; however, in case of more than one coupled nucleus and different coupling constants the analysis can become rather intricate and one would like to enhance the spectral information content. A well-established strategy in this respect is the use of two-dimensional spectroscopy, which aims at dispersing overlapping effects along second time axis. In the realm of hyperfine interaction, one tries to correlate the different hyperfine levels present in such an ESEEM experiment and thus allow to simplify the analysis of the ESEEM experiment. The corresponding experiment first performed by Höfer et al. is called HYSCORE (hyperfine sublevel correlation spectroscopy) and improves the initial 2D-ESEEM experiments proposed by Merks and de Beer.<sup>55,56</sup> To illustrate the ability of this approach, potassium atoms adsorbed to MgO surfaces will be considered. Fig. 8B shows a HYSCORE spectrum taken at 10 K for potassium atoms adsorbed on high-quality <sup>17</sup>O-enriched (enrichment approx. 10%) MgO powder.<sup>24</sup> The CW spectrum shows a clear coupling of the potassium atom to one oxygen atom as we have seen it in case of the Au atoms. A close look at the HYSCORE spectrum reveals at least three oxygen atoms couple to the potassium atom. Two of these interactions are found in the (-,+) quadrant of the spectrum shown on the left as pairs of cross peaks located at (-5.8, 1.7) and (-1.7, 5.8) MHz, and at (-4.2, 1.1) and (-1.1, 4.2) MHz. These two sites show a rather large hyperfine interaction, a condition for which the two cross-peaks should be separated by approximately twice the nuclear Zeeman frequency  $(\nu_0)$ . A third signal is found in the (+,+) quadrant located at approximately the nuclear Zeeman frequency. While this indicates that the coupling to the latter oxygen ions is small, one should note that the signal is elongated perpendicular to the diagonal of the quadrant (width about 1.2 MHz), which indicates that a sizable hyperfine coupling exists



**Fig. 8** (A) ESEEM spectra observed after 355 nm excitation of  $TiO_2$  nanoparticles measured at a resonant field of trapped holes (*red*) and trapped electrons (*black*) (T = 7 K). Adapted from Dimitrijevic, N. M.; Saponjic, Z. V.; Rabatic, B. M.; Poluektov, O. G.; Rajh, T. Effect of size and shape of nanocrystalline  $TiO_2$  on photogenerated charges. An EPR study. *J. Phys. Chem. C* **2007**, *111*, 14597. Copyright 2007 American Chemical Society. (B) HYSCORE spectrum of K atoms deposited on <sup>17</sup>O enriched MgO powder at 10 K. Adapted from Chiesa, M.; Giamello, E.; Di Valentin, C.; Pacchioni, G.; Sojka, Z.; Van Doorslaer, S. Nature of the Chemical Bond between Metal Atoms and Oxide Surfaces: New Evidences from Spin Density Studies of K Atoms on Alkaline Earth Oxides. J. Am. Chem. Soc. **2005**, *127*, 16935. Copyright 2005 American Chemical Society.

even for these oxygen sites. The question is now: Which adsorption site would give the observed coupling pattern? In principle several possibilities exist. Again, theoretical calculations are important to identify the adsorption site. The role of the calculations is not only to provide values for the hyperfine interaction matrices but also to compare the stability of the sites. Combining the experimental results with theoretical calculations, it is possible to deduce that the adsorption site of the potassium atoms on the MgO surface is a so-called reverse corner site.<sup>24</sup> These two examples may serve as introductory examples to illustrate that pulse EPR techniques allow to address aspects, which cannot be accessed by CW EPR spectroscopy. The additional information accessible by pulsed EPR spectroscopy is not restricted to hyperfine interaction. A simple question concerns, e.g., the spin state of a paramagnetic surface center. While the answer to this question is sometimes simple especially in case one knows the nature of the species, it is in general impossible to tell from a CW EPR spectrum. To this end, pulsed EPR spectroscopy offers a possibility based on the fact, that the nutation frequency of the spins depends on the spin state of the spectrum.<sup>57</sup> Such an approach was successfully used to classify the spin state of different resonances observed for a MgO sample used for the oxidative coupling of methane, which exhibits a complex EPR spectrum.<sup>58</sup> The examples given here are far from exhaustive but are meant to illustrate the possibilities of pulsed spectroscopy. It should be noted that most of the pulsed techniques require cryogenic temperatures, which limits their applicability in case the investigations require ambient or elevated temperature.

# Conclusion

Within this chapter we have illustrated what kind of information can be gathered from g- and hfi-matrices typically determined by CW-EPR spectra. We have restricted the discussion to spin  $S = \frac{1}{2}$  species, which implies that zero field splitting can be neglected. Understanding EPR spectra of species with  $S > \frac{1}{2}$  is in general considerable more complex than the  $S = \frac{1}{2}$  systems discussed here. A comprehensive discussion would go far beyond the scope of an introduction in to EPR spectroscopy, and the interested reader is referred to excellent textbooks on this subject.<sup>11,29</sup> The examples discussed in this chapter use rather simple model systems to illustrate the type of information encoded in the g- and the hfi-matrices. While hyperfine interaction can be used to derive information on geometric and electronic structure it is most valuable to characterize the chemical environment around a paramagnetic center. The values of the g-matrix are altered by spin–orbit interaction. While this is rather difficult to assess directly, we have shown how crystal field theory provides means to derive at least a qualitative picture for the expected effects. At this point it should be emphasized once more that a detailed understanding of the systems greatly benefits from a close interplay between experiments and theory. Finally, we have presented two brief examples to show that pulsed EPR techniques are able to provide additional

information, which go beyond conventional CW EPR spectroscopy. Even though the two examples discussed above focus on the environment of the paramagnetic center the additional information is not restricted to these questions. With respect to experimental conditions it has to be kept in mind that pulse spectroscopic experiments are mostly done at low temperature, which renders experiments at ambient or elevated temperatures difficult.

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# **Ellipsometry in Passive Films**

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# **Passive Films and Ellipsometry**

When metals are exposed to oxidative condition in atmosphere and aqueous solution, oxide and/or hydroxide layers are spontaneously formed and some of them act as a barrier against corrosion. On iron, cobalt, nickel, chromium, etc., very thin oxide films invisible to the naked eyes are formed to protect the substrate metals. The thin oxide films working as corrosion barrier are called passive layers, and the state protected by the thin oxide is called passivity.

In Fig. 1, the potential-current relationship of pure ion is shown, which is one of the typical passive metals.<sup>1</sup> The current density (CD) in Fig. 1 was taken after constant potential polarization at individual potentials for 1 h in phosphate and borate solutions at various pH values. Under the active state in the lowest potential region, iron dissolves from bare surface as ferrous ion (Fe<sup>2+</sup>). With increasing potential in the active state region, the CD initially increases and then sharply decreases to reach the passivity or passive state. The CD decreases by 3–4 decades in acidic solution from the active state to the passive state. In the passive state, one supposed the presence of the thin passive oxide in the early 1900s. Freundlich et al.<sup>2</sup> and Tronsdat and Borgmann<sup>3</sup> first found a thin oxide film on passivated metal surface by an optical reflection method using polarized light (i.e., ellipsometry). The ellipsometry detects the change of elliptical shape of the polarized light occurring by reflection at the solid surface and enables us to distinguish the surface film sub nm thick. Because one uses in ellipsometry visible polarized light that can penetrate in aqueous solution, in situ detection of the passive oxide films on metals in aqueous solution is possible.



**Fig. 1** Quasi-stationary potential–CD curve of pure iron electrode in phosphate solution at pH 1.85 ( $_{\odot}$ ), 3.02 ( $\bigtriangledown$ ), and 4.35 ( $_{\Box}$ ), and in borate solution at pH 7.45 ( $_{\bigtriangleup}$ ), 8.42 ( $\blacktriangle$ ), 9.37 ( $\blacksquare$ ), and 11.50 ( $\bullet$ ).

In this article, brief theory of reflection of polarized light and ellipsometry is introduced and further applications of ellipsometry to the passivity studies are presented.

# **Reflection of Polarized Light**

The optical reflection method has been often used to study passive oxide film on metal electrode, the state of which was stably controlled by electrochemistry in aqueous electrolyte solution. For in situ measurement, it is desirable to analyze the surface without change of the oxidation state and the environment. Further, water is transparent for visible light, and the optical reflection of visible light is useful to detect the surface film in the aqueous solution. Here, the basic theory of light reflection on the solid surface is introduced.

A schematic model of light reflection of a plane-polarized light on a solid surface is shown in Fig. 2 in which the light is described as a sine wave of electric field vector. By the reflection, the wave of the plane-polarized light undergoes amplitude decrease and phase retardation. As shown in Fig. 2B, the changes in the amplitude decrease and phase retardation are enhanced with oxide film formation. This change of the wave from the incidence to the reflection can be described by the following reflection coefficient (r).

$$r = |r|\exp(j\Delta) \tag{1}$$

where |r| is an amplitude ratio of the incidence to reflection lights,  $\Delta$  is phase retardation between the incidence and reflection lights, and *j* is an imaginary unit,  $j^2 = -1$ . The reflection coefficients are changed with propagating planes on which the wave is vibrated. At first, we define the incidence plane in which the incidence and reflected light beams are included. The incidence plane is placed in normal direction to the reflection plane of the solid surface, as illustrated in Fig. 3. We define in the reflection two basic planepolarized lights: parallel polarized (p-polarized) light and perpendicular polarized (s-polarized) light. (The origin of "s" is a German word of "senkrecht" for the meaning of perpendicular.) The waves of p-polarized and s-polarized light propagate on the plane placed parallel and perpendicular to the incidence plane, respectively. The reflection coefficients,  $r_p$  and  $r_s$ , can be written for pand s-polarized lights, respectively.

$$r_p = |r_p| \exp(j\Delta_p) \tag{2}$$

$$r_s = |r_s| \exp(j\Delta_s) \tag{3}$$

The individual reflection coefficients are described by Snell's law for light refraction, Fresnel's equations for light reflection, and Drüde's equation for multiple reflections in an interfacial layer as a function of complex refractive indices of solid phase, environmental phase, and interfacial layer, and thickness of the layer. The complex refractive index is written for light-absorbing *i*-phase.

$$N_i = n_i - k_i j \tag{4}$$



**Fig. 2** (A) Reflection of plane-polarized light at solid/liquid interface. (B) Reflection at the interface in which the solid was covered by a thin surface layer. The electromagnetic wave of light exhibits amplitude decrease and phase retardation by reflection, and the amplitude decrease and the phase retardation are changed with the growing surface layer.



Fig. 3 Change from plane-polarized light of incidence to elliptically polarized light of reflection. The incidence plane is defined as a plane including incidence and reflection light beam and normal to the reflection solid surface. The incidence plane-polarized light consists of p-polarized light with a vibration plane parallel to the incidence plane and s-polarized light with a vibration plane perpendicular to the incidence plane.

where  $n_i$  is a refractive index and  $k_i$  an extinction index (or absorption index). The electric field vector E of propagated light into the absorbing phase is described as a function of distance,  $x_i$ 

$$E = |E|\exp(-j2\pi N_i x/\lambda)$$
  
= |E|exp(-2\pi k\_i x/\lambda)exp(-j2\pi n\_i x/\lambda) (5)

where  $\lambda$  is the wavelength of light. Eq. (5) indicates that the amplitude of the vector attenuates with the penetration distance, that is, the light intensity gradually decreases with increase of the distance from the interface in the light-absorbing phase.

In Fig. 3, we consider the incidence light consisting of p- and s-plane polarized lights and no phase retardation between the two polarized lights. Addition of vectors of the two waves of p- and s-polarized lights orthogonal to each other makes a plane-polarized light wave with an azimuthal angle,  $\theta$ , relative to the incidence plane.

$$\theta = \arctan\left(|E_s|/|E_p|\right) \tag{6}$$

where  $|E_s|$  and  $|E_p|$  are amplitudes of waves of s- and p-polarized lights, respectively. Because the reflection coefficients of the two plane-polarized light waves are different from each other as described later, the two polarized light waves undergo amplitude decrease and phase retardation different from each other in the reflection. The phase difference between the two plane-polarized lights indicates that the addition of vectors of the two waves exhibits an elliptical shape as the Lissajous figure and the shape changes with the amplitude ratio and phase difference between the two plane-polarized light waves.

### **Reflection Coefficient**

When light beam is incident from one phase (*i*-phase) to another phase (*j*-phase), it is refracted and a relationship between the incidence angle ( $\phi_i$ ) and refractive angle ( $\phi_i$ ) is written according to the Snell's law.

$$N_i \sin \phi_i = N_j \sin \phi_j \tag{7}$$

where  $N_i$  and  $N_j$  are complex refractive indices of *i*- and *j*-phases, respectively. The reflection coefficients at the interface between *i*- and *j*-phases for p- and s-polarized lights are written by the following Fresnel's equations,

$$r_{p,ij} = \frac{N_j \cos\phi_i - N_i \cos\phi_j}{N_j \cos\phi_i + N_i \cos\phi_j} \tag{8}$$

$$r_{s,ij} = \frac{N_i \cos\phi_i - N_j \cos\phi_j}{N_i \cos\phi_i + N_i \cos\phi_i}$$
(9)

In next, when the interfacial layer (phase 2) is formed between the environmental phase (phase 1) and solid substrate (phase 3), the reflection coefficients are written as the following Drüde's equation, in which the multiple reflection is considered in the layer, for both the p- and s-polarized lights.

$$r_{123} = \frac{r_{12} + r_{23}\exp(-j2\pi D)}{1 + r_{12}r_{23}\exp(-j2\pi D)}$$
(10)

$$D = \frac{2n_2(\cos\phi_2)d}{\lambda} \tag{11}$$

where  $r_{12}$  and  $r_{23}$  are reflection coefficients at the interfaces between the environmental and the surface layers and between the surface layer and solid substrate, respectively.  $r_{12}$  and  $r_{23}$  in Eq. (10) are given by Eq. (8) for p-polarized light and by Eq. (9) for s-polarized light, using the complex refractive indices  $N_1$ ,  $N_2$ , and  $N_3$  of the three phases. d and  $\lambda$  in Eq. (11) are thickness of the layer and wavelength of light used, respectively, and  $\phi_2$  is a refractive angle of the layer calculated from Eq. (7).

The simulation of multilayer systems can be performed by an application of reflection coefficients of Fresnel's and Drüde's equations. For example, when one considers a bilayer system with  $N_{2(in)}$  and thickness  $d_{in}$  for the inner layer and  $N_{2(out)}$  and  $d_{out}$  for the outer layer, the reflection coefficient can be described for both the p- and s-polarized lights.

$$r = \frac{r_{12(\text{in})2(\text{out})} + r_{2(\text{out})3} \exp\left(-j2\pi D_{2(\text{out})}\right)}{1 + r_{12(\text{in})2(\text{out})} + r_{2(\text{out})3} \exp\left(-j2\pi D_{2(\text{out})}\right)}$$
(12)

$$D_{2(\text{out})} = \frac{2n_{2(\text{out})} \left(\cos\phi_{2(\text{out})}\right) d_{(\text{out})}}{\lambda}$$
(13)

In Eqs. (12) and (13),  $\phi_{2(\text{out})}$  and  $r_{2(\text{out})3}$  are refractive index of the outer layer and the Fresnel's equation at the outer layer (2(out)-phase)/environment (3-phase) interface, respectively, and  $r_{12(\text{in})2(\text{out})}$  is the reflection coefficient at the outer layer/inner layer (2(in)-phase) interface with considering the multiple reflection in the inner layer.

$$r_{12(\text{in})2(\text{out})} = \frac{r_{12(\text{in})} + r_{12(\text{in})}r_{2(\text{in})2(\text{out})}\exp\left(-j2\pi D_{2(\text{in})}\right)}{r_{12(\text{in})} + r_{12(\text{in})}r_{2(\text{in})2(\text{out})}\exp\left(-j2\pi D_{2(\text{in})}\right)}$$
(14)

$$D_{2(\mathrm{in})} = \frac{2n_{2(\mathrm{in})} \left(\cos\phi_{2(\mathrm{in})}\right) d_{(\mathrm{in})}}{\lambda} \tag{15}$$

where  $\phi_{2(in)}$  is the refractive index of the inner layer and  $r_{12(in)}$  and  $r_{2(in)2(out)}$  are the reflection coefficients written by the Fresnel's equations at the substrate (1-phase)/inner layer (2(in)-phase) interface and at the inner layer/outer layer interface, respectively.

When one solves the relationship between p- and s-polarized lights, the reflection coefficients of p- and s-polarized lights are different with each other for two-phase and three-phase systems. We consider that a plane-polarized light wave with propagating plane inclined at the angle *P* from the incidence plane is incident on the solid surface. The plane-polarized light can be divided into p- and s-polarized lights.

$$E_p^{\prime} = E \cos P = |E| \cos P \exp j(2\pi N_1 x/\lambda)$$
(16)

$$E_{s}^{l} = E \sin P = |E| \sin P \exp j(2\pi N_{1} x/\lambda)$$
(17)

where *E* is the electric field vector of the incident plane-polarized light wave, and  $E_p^i$  and  $E_s^i$  are the vector of the incident p- and spolarized light waves, respectively. There is no phase difference between the incident p- and s-polarized lights. After the reflection on the solid surface, the electric field vector changes to

$$E_p^r = r_p E \cos P = \left| r_p E \right| \cos P \exp j \left[ (2\pi N_1 x/\lambda) + \Delta_p \right]$$
(18)

$$E_s^r = r_s E \sin P = |r_s E| \sin P \exp j[(2\pi N_1 x/\lambda) + \Delta_s]$$
<sup>(19)</sup>

where  $E_p^{\ i}$  and  $E_s^{\ i}$  are the electric field vectors of the reflected p- and s-polarized light waves, respectively, and  $r_p$  and  $r_s$  are reflection coefficients of p- and s-polarized lights described in Eqs. (8)–(15), respectively. When the vectors orthogonal to each other exhibit different phases, the loci resulting from the addition of the two vectors show an elliptic shape which changes with a ratio of amplitudes ( $|r_p E| \cos P/|r_s E| \sin P$ ) and a phase difference ( $\Delta_p - \Delta_s$ ).

#### Ellipsometry and Differential Reflectance

In ellipsometry, one measures the change of the elliptic shape between incidence and reflection polarized lights accompanied by the reflection on a solid surface. The change of the elliptical shape can be defined by a ratio  $\rho$  of reflection coefficients,  $r_p$  to  $r_s$ .

$$\rho = r_p/r_s = \left( \left| r_p \right| / \left| r_s \right| \right) \exp j(\Delta_p - \Delta_s) = \tan \Psi \exp j\Delta$$
<sup>(20)</sup>

where  $\tan \Psi$  is the relative amplitude ratio and  $\Delta$  the relative phase retardation and both parameters of  $\tan \Psi$  and  $\Delta$  are measured by an ellipsometer. Theoretically, the parameters can be simulated as a function of complex refractive indices  $(N_1, N_2, and N_3)$ , layer thickness (d), and incidence angle  $(\phi_1)$  by Eqs. (7)–(11) for a simple monolayer system. When the multilayer structure is assumed, the parameters of complex refractive index  $(N_i)$  and thickness  $(d_i)$  of individual layers are added for the simulation.

Another method to measure the optical property including thickness of the surface oxide is differential reflectance by which reflectance change from the bare surface ( $R_{0,s \text{ or } p}$ ) to the surface covered by the growing oxide film ( $R(f)_{p \text{ or } s}$ ) is measured by using p- and s-plane-polarized lights.

$$\left(\frac{\Delta R}{R_0}\right)_p = \frac{R(f)_p - R_{0,p}}{R_{0,p}}$$
(21)

$$\left(\frac{\Delta R}{R_0}\right)_s = \frac{R(f)_s - R_{0,s}}{R_{0,s}} \tag{22}$$

Because the reflectance in Eqs. (21) and (22) is the second power of the amplitude of the reflection coefficients in Eqs. (8)–(15), they can be also simulated as a function of  $N_1$ ,  $N_2$ ,  $N_3$ , d, and  $\phi_1$  for the monolayer system.

An issue in the measurement of the surface layer using ellipsometry or differential reflectance emerges in the case that the surface oxide exhibits light-absorbing property, because three unknown parameters even in the simple monolayer system must be simulated from the two measured parameters of tan  $\Psi$  and  $\Delta$  in ellipsometry, and  $(\Delta R/R_0)_p$  and  $(\Delta R/R_0)_s$  in differential reflectance. Among the parameters of the monolayer system, it is possible to measure  $N_1$  (complex refractive index of the environment) other optical experiments or refer it from the data book, and  $N_3$  (complex refractive index of the substrate metal) can be calculated by the ellipsometric data measured for the film-free surface. The angle of incidence ( $\phi_1$ ) is determined from the apparatus condition. Finally, the unknown parameters to be simulated are real ( $n_2$ ) and imaginary parts ( $k_2$ ) of the complex refractive index of the surface layer ( $N_2$ ), and its thickness (d). Because it is impossible to simulate the three unknowns from the two measurable parameters, combination of the ellipsometry with the differential reflectance has been planned, in which the three unknowns have been simulated from the three measurable parameters. Such measurement technique is called three-parameter (3-P) ellipsometry,<sup>4, 5</sup> in which tan  $\Psi$  and  $\Delta$  have been measured together with a differential reflectance ( $\Delta R/R_0$ ).

#### **Apparatus**

Apparatuses of ellipsometry (i.e., ellipsometer) are divided into two types: one is the classical null method ellipsometer and the other photometric ellipsometer,<sup>6</sup> and both types can be purchased from several optic makers. The recent automated ellipsometers commercially available are almost the photometric type.<sup>6, 7</sup>

One of the photometric type ellipsometers is a rotating-analyzer ellipsometer with an optical arrangement of optical sourcepolarizer (P)-reflection surface (S)-analyzer (A). In the ellipsometer, the intensity of the reflected light detected by a photomultiplier or a semiconductor photo cell is measured as a function of azimuth A of the rotating analyzer, as shown in Fig. 4.

$$R = R_0 [1 + \alpha \cos 2A + \beta \sin 2A]$$
<sup>(23)</sup>

where  $R_0$  is an average reflectance. The values of tan  $\Psi$  and  $\Delta$  are calculated from  $\alpha$  and  $\beta$  by the following equation.<sup>6</sup>

$$\tan\psi\exp j\Delta = \tan P \frac{1+\alpha}{\beta\pm j(1-\alpha^2-\beta^2)}$$
(24)

where *P* is a polarizer azimuth fixed. In the ellipsometer with a phase compensator that is located at the front or back of the reflection surface, the calculation equation of tan  $\Psi$  and  $\Delta$  changes to the slightly more complicated formula.<sup>6, 7</sup>

The photometric ellipsometer has a merit that the average reflectance,  $R_0$ , can be evaluated simultaneously with tan  $\Psi$  and  $\Delta$ , as shown in Fig. 4. When one measures the reflectance change of the surface covered by growing oxide film relative to the reflectance of the bare surface, together with the changes of tan $\Psi$  and  $\Delta$ , the apparatus can be used as a 3-P ellipsometer. For the measurement of the reflectance change, long-term stability of the light source and the apparatus must be assured.



**Fig. 4** Intensity change of reflected elliptical-polarized light as a function of azimuth (*A*) of rotating analyzer in an ellipsometer with the optical arrangement of polarizer (P)-reflection surface (S)-analyzer (A).

# Thickness of the Passive Oxide Film Under Quasi-stationary State

When the passive oxide film is formed by potentiostatic control for 1 h or longer, it is held in stationary or quasi-stationary state in which the CD and thickness remain constant. Fig. 5 shows a result of 3-P ellipsometry applied to the passive oxide film on iron under in situ condition in pH 8.4 borate buffer solution. The measurement was carried out after 1 h oxidation at individual potentials. The data at -0.76 V versus Ag/AgCl/saturated KCl (SSC) correspond to those of the surface reduced at constant cathodic current of 10  $\mu$ A cm<sup>-2</sup>. The reduced surface was assumed to be a bare surface without any oxide layers. With increasing potential,  $\Psi$  and  $\Delta$  change to decreasing angle and  $\Delta R/R_0$  changes to decreasing value, where  $\Delta R/R_0$  is the average of  $(\Delta R/R_0)_R$  and  $(\Delta R/R_0)_S$ .

Fig. 6A and B shows thickness and complex refractive index of the oxide layer simulated from the three parameters in Fig. 5, respectively. Before the simulation, the complex refractive index of the substrate iron was calculated from date of  $\Psi$  and  $\Delta$  measured by reduction at -0.76 V. The refractive index (real part) of the oxide layer is scattered from 2.55 to 2.8 and the average is about 2.7, and extinction index (imaginary parts) increases with increase of potential in the initial potential region and becomes constant at about 0.53 in potentials higher than 0.3 V. The film thickness increases from 1.8 nm at -0.14 V to 4.5 nm at 1.16 V at a rate of 2.0 nm V<sup>-1</sup>. In the passive region, CD taken after 1 h oxidation at constant potential is almost constant at about 0.05  $\mu$ A cm<sup>-2</sup> as plotted in Fig. 6A. The linear growth of the thickness and constant CD in the passive region indicates that electric field in the oxide inducing the ion migration is constant, not depending on the potentials applied. The linear relation of thickness with potential has been interpreted by a high-electric-field ion migration model proposed by Cabrera and Mott.<sup>8</sup>

The thickness of passive oxide films on nickel,<sup>9-11</sup> cobalt,<sup>12, 13</sup> chromium,<sup>14</sup> SUS304 stainless steel,<sup>15</sup> and titanium<sup>16, 17</sup> under the quasi-stationary state has been reported by Ohtsuka et al. and Seo et al. The passive oxide on iron and titanium thickened linearly with potential, and however, for the oxide films on nickel and SUS304 stainless steel, whose thickness is thinner than 2 nm, the relation of their thickness with potential was not represented in a simple function. The behavior may be related with a composition



**Fig. 5** Change of ellipsometric parameters of the passive oxide film on iron. (A) Change in  $\Delta$  and  $\Psi$  with potential. (B) Change in reflectance ( $\Delta R/R_0$ ) with potential. The iron was passivated in pH 8.4 borate buffer solution by potentiostatic oxidation in which each constant potential was held for 1 h. The ellipsometric measurement was carried out at angle of incidence of  $\phi_1 = 60^\circ$  with a light of wavelength at  $\lambda = 460$  nm.



**Fig. 6** Thickness (*d*) and complex refractive index ( $N_2 = n_2 - jk_2$ ) of passive oxide film on iron as a function of potential. They were calculated from the date of  $\Psi$ ,  $\Delta$ , and  $\Delta R/R_0$  plotted in **Fig. 5**.

change with potential: Chromium ratio in the passive oxide on stainless steel was presented to change with potential and oxidation time,<sup>18</sup> and on nickel, the nonstoichiometry of x in  $Ni_{1-x}O$  in the passive oxide was suggested to change with potential.<sup>11</sup>

# **Transient Change in Thickness of Passive Oxide Films**

In situ ellipsometry is very useful when it is applied to study transient change in thickness of the passive oxide film.

Ohtsuka et al. studied the influence of ferrous ions on formation of the passive oxide on iron in pH 8.4 borate solution by ellipsometry.<sup>19</sup> In Fig. 7A, the transient of  $\Psi$  versus  $\varDelta$  loci of the growing passive oxide in the solution containing ferrous ion at concentration of 0, 0.25, and 0.5 mM is shown. With the initial 20-s oxidation at 0.80 V versus Ag/AgCl/saturated KCl (SSC), the loci move from the initial bare surface to the lower and left direction. When the solution contains ferrous ions, the loci change to the upper and left direction after the initial 20 s. The change of  $\Psi$  versus  $\varDelta$  loci was then simulated by a model of the growing oxide film with two layers, and the simulation is represented in Fig. 7B. From the simulation, it was proposed that the inner layer with a complex refractive index of  $N_{in}=2.3-j0.5$  grows to a thickness of about 4.5 nm during the initial 20 s, and then, the outer layer with  $N_{out}=1.8-j0.1$  gradually grows to thickness larger than 10 nm.

From the simulation, the change in thickness with the oxidation time is calculated and the results are given in Fig. 8. When no ferrous ions are contained, the passive oxide grows to 4.5 nm at the initial 20 s and its thickness almost remains constant after 20 s. When the ferrous ion is contained in the solution, the outer layer growth is added and the growth rate is a linear function of time and the concentration of ferrous ions. The thickness reached 25 nm in the oxidation time of 900 s at the concentration of ferrous ions at 0.5 mM. It was proposed that the outer layer was formed by an anodic deposition of ferrous ions to hydrate ferric oxyhydroxide

$$Fe^{2+} + 3H_2O \rightarrow FeOOHH_2O + 3H^+ + e^-$$
(25)

and the growth rate of the outer deposited layer was assumed to be controlled by diffusion rate of ferrous ion in the solution.

The results indicate that the thickness of the anodic passive oxide is much dependent on the concentration of ferrous ion in the solution. When one oxidizes the iron electrode in a neutral solution by a potential sweep, the ferrous ion is dissolved in the initial



**Fig. 7** (A)  $\Psi$  versus  $\varDelta$  loci of growing passive oxide film on iron at 0.80 V versus Ag/AgCl/sat. KCl in pH 8.4 borate solution containing Fe<sup>2+</sup> at concentration of 0, 0.25, and 0.5 mM. (B) Simulation loci of bilayer structure of passive oxide film. The inner layer growth was drawn with complex refractive index  $N_{inner} = 2.3 - j0.50$  (at 0.5 mM Fe<sup>2+</sup>) and  $N_{inner} = 2.3 - j0.38$  (at 0.25 mM Fe<sup>2+</sup>) and the outer layer growth with  $N_{out} = 1.8 - j0.96$  (at 0.5 mM Fe<sup>2+</sup>).



Fig. 8 Change in thickness of the passive oxide film on iron at 0.80 V in pH 8.4 borate solution containing ferrous ion at concentration of 0. 0.25, and 0.5 mM. The thickness was calculated from the simulation described in Fig. 7.

active region and the amount of dissolved ferrous ion is increased with the slower sweep rate or the longer period in which the iron electrode stays in the active region. When the potential reaches the passive region, ferrous ion is deposited as the ferric hydroxide in the outer layer.<sup>20, 21</sup> Because the thickness of the oxyhydroxide layer is proportional to the amount of ferrous ion in the electrolyte, the thickness of the outer layer increases with the smaller sweep rate. Though the anodic behavior of passive iron in neutral solution has been investigated by many researchers, the results have not necessarily been identical. The difference may be originated in the ferrous ion concentration that has changed with experimental conditions.

The growth mechanism has been pursued from a transient change in thickness of the passive oxide. Fig. 9A shows changes of CD and thickness of the passive oxide on Fe-Nd-B permanent magnet at potential of 0.5 and 1.5 V versus reversible hydrogen electrode at the same solution (RHE) in pH 8.4 borate solution.<sup>22</sup> The passive oxide rapidly formed in the initial 10 s and then gradually increased to 3.1 nm at 0.5 V and 6.3 nm at 1.5 V in 1 h. The passive oxide film on the magnet alloy consisted of about 75 mol% Fe oxide or hydroxide.<sup>21</sup> After Mott and Cabrera, the ion migration rate (*i*<sub>m</sub>) under high electric field is described as the following.<sup>8</sup>

$$i_m = i_0 \exp(zaF/RT)(\Delta E/d) \tag{26}$$

where  $\Delta E$  and d are the potential drop in the oxide layer and thickness of the oxide layer, respectively, and thus  $\Delta E/d$  represents an average electric field in the oxide layer. a is a half jump distance or activation distance for ion migration in the oxide layer,  $i_0$  is a migration CD at zero field, and z is valence of the migrating ion. If converting Eq. (26) to logarithmic form,

$$\log(i) = \log(i_0) + (zaF/2.303RT)(\Delta E/d)$$
(27)

The plot of log(*i*) versus 1/d at constant potential (i.e., constant  $\Delta E$ ) exhibits a linear relation. The plot is shown in Fig. 9B in which the linear relation is seen in CD smaller than  $10^{-4}$  A cm<sup>-2</sup> and the slope of the linear portion is increased with increase in potential. From a ratio of the slope in the linear portion to the potential, the half jump distance can be estimated as the following.

$$d(\text{slope})/d\Delta E = zaF/(2.303\text{RT})$$
(28)

$$slope = d\log(i)/d(d^{-1})$$
<sup>(29)</sup>

The half jump distance and the potential at which the potential drop in the oxide film is zero ( $\Delta E = 0$ ) were estimated to be 0.35 nm with assumption of z=3 and -0.68 V versus RHE, respectively, from the linear relation between the slope and potential. The  $i_0$  value was estimated to be  $3.5 \times 10^{-8}$  A cm<sup>-2</sup> from the converged point.

The growth of passive oxide film on titanium during the anodic potential sweep was measured by the in situ 3-P ellipsometry, and the dependence of properties of the oxide film on the sweep rate of potential increase was discussed.<sup>17</sup>

Fig. 10 shows CD-potential curves of titanium electrode in 0.1 M sulfuric acid solution during the potential sweep from 0.26 to 4.26 V versus RHE, following a potentiostatic oxidation at 0.26 V for 1000 s.<sup>17</sup> In Fig. 10, the sweep rates were changed from 2 to 500 mV s<sup>-1</sup>. The increase of CD is observed just after the start of the potential sweep, followed by a plateau on which the CD gradually decreases. In the plateau stage, the CD is almost proportional to the sweep rate and assumed to correspond to the oxide-film growth CD. When the sweep rate is smaller than 20 mV s<sup>-1</sup>, the increase of the CD is observed at potentials higher than 3 V, due to overlapping of the CD of oxygen evolution reaction on the film-growth CD. The oxide growth during the sweep oxidation was monitored by the 3-P ellipsometry with 632.8 nm wavelength light at an incidence angle of 60.0°. The results are given in Fig. 11, in which the  $\Psi$  versus  $\Delta$  loci are plotted during the oxide growth to 3.05 V at various sweep rates.<sup>13</sup> With the growth of the oxide film,  $\Delta$  decreases from 128.31° and  $\Psi$  increases from 32.54°. The initial values correspond to the values of surface covered by the oxide formed at 0.26 V for 1000 s. The open circle in Fig. 11 ( $\Psi$  = 32.45° and  $\Delta$  = 130.68°) indicates the values measured by



**Fig. 9** (A) Change in thickness (*d*) of the passive oxide and CD in logarithmic scale (log *i*) of Fe-Nd-B alloy at 0.5 and 1.5 V versus RHE in pH 8.4 borate solution. (B) Plot of logarithm of CD (log *i*) versus reciprocal of thickness ( $d^{-1}$ ) of the passive oxide on Fe-Nd-B alloy at 0.5, 0.7, 0.9, 1.1, 1.3, 1.5, and 1.7 V versus RHE in pH 8.4 borate solution.



**Fig. 10** CD in logarithmic scale of titanium against potential at anodic potential sweep at various sweep rates from 2 to 500 mV s<sup>-1</sup> in 0.1 M sulfuric acid solution. The potential sweep was followed by potentiostatic oxidation at 0.24 V versus RHE for 1000 s.



**Fig. 11**  $\Psi$  versus  $\varDelta$  plot of growing passive oxide film on titanium during the potential sweep from 0.24 to 3.05 V at various sweep rates from 2 to 500 mV s<sup>-1</sup> in 0.1 M sulfuric acid solution.

the initial reduction at -0.54 V for 600 s by whose procedure it was assumed that the nearly bare surface emerged. In Fig. 11, the  $\Psi$  versus  $\Delta$  loci change with the sweep rate. When the sweep rate is larger, the loci exhibit the steeper slope. The different loci indicate that the complex refractive index of the growing oxide film is not constant, but changes with the sweep rate. In Fig. 12, the refractive index,  $n_2$ , and thickness, d, of the oxide film taken at 3.05 V during the potential sweep are plotted as a function of the sweep rate. For the simulation of  $n_2$  and d as well as  $k_2$  (extinction index of complex refractive index,  $N_2 = n_2 - jk_2$ ), the changes of  $\Psi$ ,  $\Delta$ , and  $\Delta R$ /



Fig. 12 Refractive index of the growing passive oxide and thickness of the oxide taken at 3.05 V on titanium in 0.1 M sulfuric acid solution as a function of potential sweep rate.

R<sub>0</sub>, in which the  $\Delta R/R_0$  data are not given here, were used. The  $k_2$  values simulated are almost zero, indicating that the oxide films are transparent for the light at 632.8 nm wavelength used. The  $n_2$  value decreases with increase in sweep rate from  $n_2 = 2.24$  at 2 mV s<sup>-1</sup> to 2.61 at 500 mV s<sup>-1</sup>, whereas the thickness is increased by 1.57 times with the sweep rate from 4.92 nm at 2 mV s<sup>-1</sup> to 7.71 nm at 500 mV s<sup>-1</sup>. The changes of  $n_2$  and d with the sweep rate were discussed in the aging of the passive oxide<sup>23</sup> as the following way. The oxide formation is assumed to start with the formation of hydrated oxide, TiO<sub>2</sub>·xH<sub>2</sub>O or oxyhydroxide compound of TiO<sub>2-x</sub>(OH)<sub>2x</sub>.

$$Ti + (2 + x)H_2O \rightarrow TiO_{2-x}(OH)_{2x} + 4H^+ + 4e^-$$
 (30)

The starting material of hydrated oxide gradually changes to the dehydrated TiO<sub>2</sub>, that is, hydration number of x is decreased.

$$\text{TiO}_{2-x}(\text{OH})_{2x} \rightarrow \text{TiO}_{2-x'}(\text{OH})_{2x'} + (x-x')\text{H}_2\text{O}(x > x')$$
 (31)

Since the refractive index of the oxide is usually decreased with its density and the density is decreased with increase in x, the smaller refractive index of the oxide film formed at the higher sweep rate indicates that the film is composed of the more hydrated oxide with larger number of x. The more hydrated oxide film may become thicker with the higher sweep rate. From the above discussion, the following mechanism can be inferred. When the sweep rate is relatively large, the dehydration process does not overtake the growth of the hydrated oxide,<sup>23</sup> and thus, the oxide film remains hydrated and maintains the larger thickness. Conversely, when the sweep rate is relatively small, the film may be approaching the dehydrated oxide.

# Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) has been applied to characterization of the surface film with light-absorbing property. The spectral range of incident light of SE is expanded from infrared to near-ultraviolet light.<sup>24</sup>

In SE, one measured at individual wavelengths of  $\lambda_i$  the values of  $\Psi_i$  and  $\Delta_l$ , from which the complex refractive indices of the film at individual wavelengths were simulated with the thickness. If the surface film is light-absorbing property, the number of the unknown parameters is larger than that of the measurable parameters ( $\Psi_i$  and  $\Delta_i$ ), and thus, the simulation to obtain one set of unique solution is possibly arbitrary. Since, in many cases, the complex refractive index of the substrate is unknown, the number of the unknowns further increases and the simulation may be more complicated. The number of unknown properties can be reduced by describing the complex refractive index with dispersion equations and the Kramers–Kronig relation between  $n_i$  and  $k_i$ . Several simulation techniques have been introduced by Hilfiker et al.<sup>25</sup> and McGahan et al.<sup>26</sup>

For application of SE in a wide spectroscopic range to the electrode surface, suitable windows on the optical–electrochemical cell are required for incidence and reflection lights. For passivity study, the spectroscopic property of the passive oxide films was presented on iron,<sup>27–31</sup> nickel,<sup>30, 32</sup> and titanium<sup>30</sup> by using SE.

Fig. 13 indicates one of the results measured by SE, in which spectra of  $n_2$  and  $k_2$  of the titanium passive oxides formed at 6.74 and 9.74 V versus RHE in pH 8.4 borate solution.<sup>30</sup> The values of  $k_2$  are close to zero in the light of wavelengths longer than 390 nm



Fig. 13 Refractive and extinction indices of anodic oxide films on titanium at 6.74 and 9.74 V versus RHE in pH 8.4 borate solution as a function of wavelength of light.

and sharply increases in the shorter wavelength region. The absorption edge at 390 nm wavelength corresponds to a photon energy of 3.2 eV that may represent a band gap energy of the passive oxide. For the passive oxide film, anatase type of  $TiO_2$  was identified by Raman spectroscopy<sup>33</sup> and the band gap energy is almost in agreement with that of anatase  $TiO_2$ .

#### Microscopic Measurement by Ellipsometry

It was assumed in the above sections that the surface and oxide films were uniform and homogeneous. The practical metallic materials such as steel, titanium alloy, and copper alloy are, however, made up of polycrystalline in which individual crystallites have different crystallographic orientations from each other. The passive oxide films formed on the metals are influenced by the surface inhomogeneity and do not have homogeneous properties. The ellipsometry has been applied to survey on the microscopic heterogeneity of passive oxide films by combining with optical microscope.

Fig. 14 shows the schematic view of ellipso-microscopy<sup>35</sup> in which the measurement was performed on the basis of manual nullmethod ellipsometry<sup>6</sup> with an optical arrangement of polarizer (P)-phase compensator (C)-reflection sample surface (S)-analyzer (A). The light from the individual positions on the reflection surface was focused on the 3-M pixel CMOS camera, and the surface was imaged on the camera. In the null method, C is fixed at the azimuth of  $-45^{\circ}$  and one seeks extinction state of reflected light intensity on the CMOS camera by manually controlling the azimuths of P and A. If the heterogeneity of the surface oxide in thickness and optical property emerges, the extinction state is not kept on the whole surface, and the image on places having different thickness and optical property deviates from the extinction state, slightly brightening. The place with the larger deviation exhibits the more brightness. From microscopic view in brightness, the microscopic heterogeneity of the passive oxide can be discussed.

Fig. 15 shows an example of the ellipso-microscopy measurement.<sup>35</sup> When polycrystalline titanium was dynamically polarized in anodic direction at a sweep rate of 5 mV s<sup>-1</sup> in 0.05 M H<sub>2</sub>SO<sub>4</sub>, anodic oxide film formed on the titanium, accompanied by the evolution of oxygen gas. The ellipso-microscopic image becomes brighter as the potential increases, and the average intensity of the image increases with increase in potential, indicating that the oxide film thickened as the potential increases. Moreover, a patch pattern in the image also becomes clearer as the potential increases. Fig. 16 shows an inverse pole figure of the intensity in the ellipso-microscopic image at 4 V shown in Fig. 15E. The intensity in Fig. 16 was normalized by the highest intensity in Fig. 15E in which crystallographic orientation of the individual places in the substrate titanium was measured by electron backscatter diffraction (EBSD) patterning. If the intensity increase is assumed to correspond to increase of the film thickness, the place with the lower intensity is inferred to be covered with a thinner oxide film. From Fig. 16, it is seen that the grain of the (0001) plane is covered with a thinner film than other grains. This result is in good agreement with the results in previous studies in which the close-packed plane of (0001) is covered with a thinner film, whereas the lower density atomic planes of (XXX0) with thicker films.<sup>34, 36</sup>

Ellipso-microscopy is effective for imaging heterogeneous oxide film during not only formation but also degradation. Fig. 17 shows a current transient during dynamic polarization of titanium in  $0.05 \text{ M H}_2\text{SO}_4$  containing 1.5 M KBr in which Br<sup>-</sup> ion attacks the titanium oxide and induces the breakdown of passivity on titanium.<sup>35</sup> Immediately before a catastrophically large current flow indicating the initiation of passivity breakdown at 1081.4 s (5.37 V), a slight current increase was detected from 1081.0 s, as shown in Fig. 17A. Simultaneously, a dark spot in the ellipso-microscopic image appeared as shown in Fig. 17E and the area of the dark spot increased with time. The dark spot initially appearing is due to thinning or change of the oxide, though that observed at the stage later than 1081.4 s might originate from a gas bubble adhering to the surface and simultaneously a large current flow was



**Fig. 14** Schematic diagram of the setup of ellipso-microscopy.<sup>34</sup> (A) specimen, (B) counter electrode, (C) reference electrode, (D) electrolyte solution, (E) laser, (F) beam splitter, (G) light intensity monitor, (H) depolarizer, (I) polarizer, P, (J) compensator, C, (K) analyzer, A, (L) CMOS camera, (M) macro-lens for ellipso-microscopy, (N) CMOS camera for specimen observation, (O) macro-lens for specimen observation, (P) potentiostat and function generator, (Q) PC.



**Fig. 15** (A) Anodic current and average intensity of an ellipso-microscopic image as a function of potential during dynamic polarization of titanium in 0.05 M  $H_2SO_4$  solution. Ellipso-microscopic images (B) at the initial null condition and at potentials of (C) 2, (D) 3, (E) 4, (F) 5, (G) 6, (H) 7, and (I) 8 V versus SSC. The potential was swept in the positive direction at 5 mV s<sup>-1</sup>.



Fig. 16 Contour map of light intensity in the ellipso-microscopic image for the oxide film formed at 4 V (Fig. 6E) drawn on an inversed pole figure. The light intensity at each spot in the image was normalized by the largest intensity and marked with a cross in the map. The crystallographic orientations of individual crystallites were determined by EBSD patterning.



**Fig. 17** (A) Time variations of current and area of the dark spot spreading in the ellipso-microscopic image during dynamic polarization in the positive direction of titanium with a sweep rate of 5 mV s<sup>-1</sup> in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution containing 1.5 M KBr. Ellipso-microscopic images of the titanium surface at the time of (B) 1080.5, (C) 1081.0, (D) 1081.03, (E) 1081.07, (F) 1081.1, (G) 1081.13, (H) 1081.17, (I) 1081.2, (J) 1081.23, (K) 1081.27, (L) 1081.37, and (M) 1081.40 s. The spot area was estimated after binominal image-filtering.

observed. From the results, it was found that the ellipso-microscopy with enough rapid response enables us to assign the initiation place where local breakdown of the film is started. In a separated Auger electron spectroscopy measurement of the specimen surface, the small amount of Br was detected on the dark spot surface before the catastrophically large current flowed. It was suggested that the locally absorbed Br<sup>-</sup> ion caused thinning or breakdown of the oxide film and electron transferred through the locally thin oxide film, evolving Br<sub>2</sub> or O<sub>2</sub> gas, and finally, the depassivation was induced.

#### Summary

Ellipsometry is sensitive to thin film several nm thick and applicable as an in situ observation method of passive film in electrochemical system. Its combination with electrochemistry enables us to examine mechanism and kinetics for the formation of oxide films on metals. The application of electrochemical ellipsometry possibly makes properties of passive film and phenomena concerned with passivity clear.

For the passive oxide with light-absorbing property, three-parameter (3-P) ellipsometry is very available, because the three unknown parameters of the refractive index, extinction index, and thickness of the oxide film can be simulated by the three measurable parameters without any assumption. The photometric ellipsometer can be converted relatively easily to the 3-P ellipsometer. The passive oxides have been investigated by the 3-P ellipsometry not only under the quasi-stationary state, but also during the nonstationary transient growth.

Combination of ellipsometry with optical microscopy enables us to pursuit the heterogeneous property of the passive oxide and the localized attack of the passivated metal.

Various types of ellipsometer such as 3-P and spectroscopic ellipsometer are available at the present from the many optical devise makers, but some suitable planning such as construction of optical–electrochemical cell and selection of optical windows may be required for their application to the electrochemical passivity investigation. Further, suitable simulation programs may be necessary for the investigation.

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# **Experimental Methods in Interfacial and Surface Chemistry**

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An understanding of chemical processes at surfaces and interfaces ultimately requires a detailed knowledge of the involved species, their chemical potential (determined by pressure or concentration and temperature) and all their interactions within very few atomic/molecular layers on either side of the respective interface.<sup>1</sup> The number of atoms within these few layers is of the order of  $10^{15}$  cm<sup>-2</sup> equivalent to  $10^{-9}$  mol cm<sup>-2</sup> and thus, very small relative to the comparatively infinite number of atoms/molecules in the bulk of the adjacent 3D phases. As a consequence, suitable experimental methods for the investigation of surface-confined properties and processes need to fulfill two conditions: (a) they need to be very *sensitive*, that is sensitive to  $\leq 10^{15}$  atoms/molecules depending on the detected surface area, and (b) they need to be *surface/interface specific*, that is they must discriminate between signals coming from the few layers at the immediate interface and those coming from the adjoining bulk phases.

In principle, there are three possibilities to distinguish a surface/interface specific signal from a bulk related signal: (i) the signal arises from a species which exists *only* at the surface/interface, (ii) the probe itself is only sensitive to very few surface/interface near-atomic/molecular layers (and 'blind' for the rest of the sample), and (iii) grazing excitation/detection geometry limits the penetration depth of the probing process.

Figure 1 illustrates typical surface experiments: The sample is excited by an electron-, photon-, atom- or ion-beam, investigated with a scanning probe, simply heated or, in electrochemistry, an electric potential is applied, etc.

Likewise, the signal emitted from the surface can be an electron-, photon-, atom- or ion-beam, a physical effect registered by the tip of a scanning probe, a flux of desorbing atoms/molecules, or in electrochemistry, for instance the flow of a current. Depending on the combination of the various excitation methods on the one hand and the detected quantity on the other hand, also as a function of energy, momentum, polarization, etc., a huge number of surface analytical techniques has been developed over the past four decades, in order to answer specific surface and interface related chemical and physical questions.

An important qualification of the various possible methods, however, is in place though. This has to do with the interaction strength of the various possible probes with matter. Electron-, atom-, and ion-beams, depending on their energy, interact rather strongly with condensed matter. As a consequence these particle beams have only a very limited *mean free path length* in solids, liquids, or high pressure gases; they reach the site of excitation and vice versa the detector undisturbed only through a very thin layer of these condensed phases. For instance, **Figure 2** shows the mean free path length of electrons in metals; it depends on the kinetic energy  $E_{kin}$  of the exciting (or emitted) electron beam between 50 and 1000 eV of the order of only 1–2 nm. Thus, techniques based on electrons, atoms, or ions can essentially only be applied to bare surfaces in vacuum and are per se highly *surface-specific*.<sup>2–4</sup> Conversely, these techniques are of very limited use to study 'buried interfaces' between two condensed phases, for example, solid/electrolyte interfaces.

Instead, photons penetrate condensed phases over much longer distances and are therefore less surface-specific, but enable to reach buried interfaces, in order to provide spectroscopic information from, for example, the surface of a catalyst in contact with a high-pressure gas or from an electrode immersed in an electrolyte. Taking advantage of polarized light, a consequence of the so-called 'surface selection rule'<sup>3</sup> is that only p-polarized light is sensitive to species which are *adsorbed* at a surface/interface (see Figure 6).

The basis of scanning probes is to bring a very fine, preferably mono-atomic, tip very close to the surface to be studied, and to measure, while scanning across the surface, for example, the tunneling current, the mechanical or magnetic interaction force, the heat conductivity, etc. across the gap between surface and tip.<sup>5,6</sup> For very small tip-surface distances of say 1 nm these probes may provide 'microscopic maps' of these physical quantities across the surface with up to atomic/submolecular resolution even



Figure 1 Representation of typical surface/interface analytical methods (see text).



Figure 2 Mean free path length of electrons in metals as a function of their kinetic energy.<sup>2,3</sup>

at solid/liquid interfaces. As an example, Figure 3 shows a scanning tunneling microscopy (STM) image of a Cu(111) single crystal electrode surface covered with a monolayer of porphyrin molecules; this image has been registered *in solution*.

Finally, the temperature of an adsorbate covered surface can just be raised linearly and the desorbing atoms/molecules be detected with a mass spectrometer. Likewise, the potential of an electrode in solution can be increased/decreased until cations/ anions desorb from the electrode, indicated by a concomitant current in a current vs. potential curve.<sup>7</sup>

Table 1 gives a selection of a few standard methods applied in surface/interface studies in ultrahigh vacuum, gas atmosphere, orliquids. A rather exhaustive list of surface/interface methods can be found in Wandelt.<sup>3</sup>

The detection of chemical species which are already known to exist only at the surface or at the interface, that is adsorbates, does not require methods which discriminate between bulk and surface/interface signals. Given sufficient sensitivity, signals from these adsorbates provide immediate information about, for example, their surface concentration, their bonding interaction with the substrate and, as a consequence thereof, their intra-molecular, that is chemical, alteration due to adsorption. For instance, **Figure 4** exhibits thermal desorption spectra of carbon monoxide desorbing from a  $Cu_3Pt(111)$  surface in vacuum. The adsorbate-specific desorption temperature is a rough measure of the bond strength between the respective adsorbate and the surface. Obviously CO is bound more weakly on  $Cu_3Pt(111)$  than on a pure Pt(111) surface. Similarly, **Figure 5** shows a typical cyclic voltammogram<sup>7</sup> of a Cu(111) single crystal electrode in hydrochloric acid solution. Between the hydrogen evolution reaction (HER) at negative (cathodic) potentials and the copper dissolution reaction (CDR) at positive (anodic) potentials, the two extra peaks indicate the adsorption and desorption of chloride anions at this electrode surface.<sup>7</sup>

Infrared spectroscopy, though per se not a surface-specific method provides such information from adsorbed molecules confined to solid/vacuum or solid/gas as well as solid/electrolyte interfaces. Figure 6 displays the IR-spectrum of cyanide ( $CN^-$ ) adsorbed on a Pt(111) electrode surface in hydrochloric acid solution. Only the spectrum excited with p-polarized light is sensitive to the *adsorbed* cyanide anions ('surface selection rule').<sup>3</sup>



Figure 3 Scanning tunneling microscopy (STM) image of adsorbed and self-assembled porphyrin molecules on a Cu(111) electrode surface in solution.<sup>8</sup>





**Figure 4** Thermal desorption spectroscopy of carbon monoxide (CO) from a  $Cu_3Pt(111)$  alloy surface in ultrahigh vacuum. CO adsorbed at 50 K desorbs from a physisorbed state, from Cu-sites and from Pt-sites at the surface (upper trace). With increasing CO population of the Pt-sites CO desorbs at lower temperature (lower traces). Compared to CO adsorbed on a pure Pt(111) surfaces CO on Pt-sites in the alloy surface desorbs at  $\sim 100$  K lower temperature.<sup>9</sup>



Figure 5 Cyclic voltammogram of a Cu(100) single crystal electrode in hydrochloric acid solution; HER = hydrogen evolution reaction, CDR = copper dissolution reaction.


Figure 6 Infrared spectra (IR) of cyanide anions adsorbed on a Pt(111) single crystal electrode *in solution*; due to the 'surface selection rule' only polarized light is sensitive to the *adsorbed* species.

In those cases where the relevant species exists both at the surface *and* in the bulk of the sample the method of choice must be surface specific, if only the *surface* concentration of this species is to be determined. For instance, due to segregation the concentration of one constituent of an alloy may be enriched at the very surface compared to the bulk. As an example, **Figure** 7 shows the Auger-electron spectrum of a Pt<sub>3</sub>Ti(111) surface (a). Exposure to increasing doses of oxygen (b and c) not only leads to the appearance and increase of the oxygen signal at 503 eV but also to an enrichment of titanium at the surface. Vice versa, it may be interesting to know whether a contaminant is confined to the surface (due to unwanted adsorption) or whether it exists throughout the whole sample bulk. In both cases two methods are needed, one which is as surface specific as possible and another one which probes the bulk concentrations, like ion scattering spectroscopy (ISS) and X-ray absorption spectroscopy (XAS), respectively. Ideal are methods whose 'information depth' is tunable. Considering the energy dependence of the *mean free path length* of electrons in condensed



**Figure 7** Auger electron spectra (AES) of (a) a clean  $Pt_3Ti(111)$  surface, (b) the oxidized surface obtained after exposure to  $9 \mid 0_2$  (p( $0_2$ ) =  $10^{-8}$  mbar) at 1000 K, and (c) the oxidized surface obtained after exposure to  $180 \mid 0_2$  (p( $0_2$ ) =  $10^{-7}$  mbar) at 1000 K. Note the increase not only of the oxygen signal but also of the titanium signal.<sup>10</sup>



**Figure 8** Schematic illustration of the penetration/escape depth  $d_i$ , that is the 'information depth,' of photon beams as a function of the angle of incidence  $\Theta_i$ .

phases (see Figure 2), X-ray photoelectron spectroscopy (XPS) using synchrotron radiation would be the method of choice. By varying the energy  $h\nu$  of the incident photon beam also the kinetic energy  $E_{kin}$  of emitted photoelectrons of given binding energy  $E_b$  varies according to

$$E_{\rm kin} = h\nu - E_{\rm b} \tag{1}$$

and thereby, their mean free path length in the sample material. In this way it is literally possible to monitor indepth concentration profiles perpendicular to the surface *without* surface erosion.

Finally, the surface- vs. bulk-sensitivity of a per se non-surface specific method can be varied by changing the angle of incidence of the exciting or emitted beam. For instance, despite their long penetration length through solid matter *grazing incident* X-rays ( $<1^{\circ}$  with respect to the surface) capture only a very thin surface-near layer (Figure 8). This technique can be used, for example, in the form of grazing incidence X-ray absorption spectroscopy (GIXAS) in order to determine the composition of ultrathin surface films or in the form of grazing incidence X-ray diffraction (GIXRD) in order to investigate their 2D crystallographic structure.

Systematic development and application of surface analytical methods as described above and listed in Table 1 since the 1960s has led to the fundamental insight: Surfaces and interfaces are a new, 2D state of matter, with specific physical and chemical properties different from those of the adjoining 3D phases.

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# Field Ion and Field Desorption Microscopy: Surface Chemistry Applications

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### **Overview**

The field ion microscope (FIM) was the first device to image individual atoms on the solid surfaces.<sup>1,2</sup> The image in the FIM is created by ions of an imaging gas (mainly noble gas such as He or Ne) field-ionized over the protruding surface atoms of a sharp tip used as a specimen. The imaging ions are accelerated by an applied field of  $3-5 \text{ V} \text{ Å}^{-1}$  necessary for field ionization of imaging gas and form a projection image on a phosphor screen. Applying an electric field sufficient for the field desorption of adsorbed atoms or even for field evaporation of the surface atoms of the specimen, the field ions of such species can also be utilized for imaging in a field desorption mode (field desorption microscopy (FDM)). In the last 50 years, the FIM and related atom probe (AP) FIM<sup>3</sup> had a significant impact mainly on materials research and on studies of the behavior of individual atoms on metal surfaces. This development and achievements are comprehensively illustrated in the existing literature (e.g., Refs. [3–9] and references therein). This module is therefore rather focused on the recent surface chemistry applications, such as in situ imaging of catalytic reactions (since the 1990s). These novel applications have significantly contributed to the revival of the FIM-based techniques and to developing of new versions, such as lithium field desorption microscopy (Li-FDM), which is in detail described in the present contribution.

## **Principles of FIM Operation**

The FIM is in its principle a point projection microscope that achieves its extraordinary magnification by the radial projection of individual surface sites using beams of imaging gas ions. In a typical FIM, a cryogenically cooled specimen of the shape of a sharp tip (Figure 1(a)) with a radius of curvature in the submicrometer range is positioned a few centimeters away from an image intensifier (usually a microchannel plate/phosphor screen assembly). The tip, usually prepared by electrochemical polishing (see the details and recipes in Ref. [9]), is exposed to a high electric field (few V/Å; the tip is positively charged) in the presence of an imaging gas at  $10^{-5}$ – $10^{-3}$  mbar. In such a high field, the atoms or molecules of the imaging gas (usually He, Ne, or reactive gases like oxygen) become polarized and are attracted to the specimen surface where they accommodate at cryogenic temperatures, losing their kinetic energy in a thermal accommodation process.<sup>9,10</sup> The accommodated gas atoms follow the local field gradient across the surface, arrive at the local field maxima above the prominent surface atoms, and become, in the case of the usually used He or Ne as imaging gas, field-adsorbed on protruding surface atoms. The following accommodated gas atoms become steadied over those field-adsorbed species, where the local field maxima exist.<sup>11–14</sup> Such 'second-layer' atoms energetically fully accommodated on top of the field-physisorbed gas atoms are then field-ionized by electron tunneling through the field-adsorbed atoms into the specimen.<sup>9</sup> A collision-induced exchange process between the field-adsorbed and 'arriving' accommodated gas atoms is also possible close prior to the field ionization event.<sup>14</sup>

At the instance of field ionization, the gas atoms are localized near the critical distance  $z_{crit}$  (Figure 1(c)) to the specimen surface. This distance is necessary to allow lifting the atom's valence electron level over the Fermi level of the specimen by the applied field: tunneling at smaller than  $z_{crit}$  distances is not possible since it would mean tunneling into occupied states below the Fermi level (Figure 1(c)).

Due to ion formation at  $z_{crit}$ , away from the tip surface, the gas ions get not the full energy corresponding to the potential of the tip but an amount lower by a so-called energy deficit, a term closely related to the field ion appearance energy (FIAE; see the details in Ref. [13–15]).



**Figure 1** Principles of the FIM. (a) Geometry of the point projection. The surface of the specimen apex is projected on a screen by imaging particles with a magnification  $M \approx R/r$ . The imaging particles are electrons (in FEM), imaging gas ions (in FIM), or Li<sup>+</sup> ions (in Li-FDM). The tip apex is shown as a spherical fcc ball model. The inset illustrates the mechanism of the ion formation in FIM: Imaging gas ions are generated over the protruding surface atoms covered by field-adsorbed gas atoms; field-ionized atoms are replaced by highly mobile accommodated gas atoms (see text). (b) Ne<sup>+</sup> field ion image of a [111]-oriented Rh field emitter tip. (c) Potential energy diagram for field ionization over a metal surface. Based on Figure 1 in Suchorski, Y.; Drachsel, W. In: *Surface and Thin Film Analysis*; Friedbacher, G.; Bubbert, H.; Wiley-VCH: Weinheim, 2011.

The imaging gas ions formed at (or beyond)  $z_{crit}$  are accelerated in the applied field projecting the positions of surface atoms on a screen and creating thus a field ion image (Figure 1(b)). An extremely high degree of the spatial localization of the imaging gas atoms at the instant of field ionization provides atomic resolution in the FIM images. The essential role for the atomic resolution in FIM plays the field-adsorbed layer of the imaging gas atoms as illustrated for Ne gas atoms ionized over a Rh tip in Figure 2 (from Ref. [12]). Increasing the temperature of the tip or enhancing the field over the best image field, the field-adsorbed layer is depleted, and the following features are observed for noble imaging gas atoms such as Ne or He: (i) The field ion image becomes blurred, (ii) the field ionization rate at the probed surface sites decreases drastically, (iii) the value of the FIAE (for details, see Refs. [13–15]) derived from the field ion retardation curves decreases and becomes equal to the ionization energy of the free gas atom, and (iv) the full width at half maximum of the field ion energy distribution increases significantly.

A wide range of conducting samples can be studied by FIM: metals including alloys, semiconductors, and even oxides.<sup>4–9</sup> This basic projection principle holds also for the field emission microscopy (FEM) where the emitted *electrons* create a projection image of the tip surface.<sup>16</sup> The distinguishing feature of the projection microscopies such as FIM and FEM is the parallel imaging, that is, all the surface atoms provide the information (via ions or electrons) simultaneously, in contrary to, for example, scanning tunneling microscopy (STM) where the collecting of the information occurs sequentially, via scanning from one surface atom to another. Therefore, the FIM and FEM allow in situ imaging of dynamic surface processes on the nanometer or even subnanometer scale with a time resolution limited mainly by the frame exposure time of the applied camera, which is, even in the case of the newest CCDs, orders of magnitude above the limitations caused by gas supply at pressures of  $10^{-5}-10^{-4}$  mbar.<sup>17,18</sup>

The natural limit of the FIM applicability is the field evaporation process (i.e., field desorption of the specimen lattice atoms) in which the surface atoms of the specimen are field-ionized and removed from the surface. This process is used for controlled fine shaping and cleaning the tip<sup>9</sup>; it can however lead to the destruction of the specimen when the imaging field is equal or higher than the onset of field evaporation of the particular sample. The values of the evaporation field strength are listed in the literature<sup>4,9</sup>; for the details of the field desorption and field ionization processes, we address the reader to the literature.<sup>4,9,15,19</sup>

Since the 1990s, the FIM operation with reactive imaging gases, such as  $O_2$ , CO, and  $N_2$ , becomes popular, especially for in situ imaging of catalytic reactions.<sup>20–22</sup> Such imaging occurs mainly by field desorption of the adsorbed gas molecules, which are replaced by a diffusion supply from the tip shank where the mobile gas molecules are adsorbed.<sup>23–25</sup> Thus, an FIM operating



**Figure 2** Field-adsorbed Ne atoms in localized field ionization. (a) Ne field ion image of a [111]-oriented Rh emitter at 79 K and at 35 V nm<sup>-1</sup> (field-adsorbed Ne layer is present). The area encircled in white represents the probe hole; (b) the locally measured Ne<sup>+</sup> retardation curve  $N(\delta)$  and the differentiated curve,  $dN/d\delta$ ; (c) the same as in (a), but at 107 K (field-adsorbed Ne layer is depleted); (d) corresponding Ne<sup>+</sup> retardation curve  $N(\delta)$  and the differentiated curve,  $dN/d\delta$ . One observes the following: (i) The field ion image becomes blurred, (ii) the field ionization rate decreases drastically, (iii) the value of field ion appearance energy derived from the field ion retardation curves decreases and becomes equal to the ionization energy of the free gas atom, and (iv) the full width at half maximum of the field ion energy distribution increases significantly (from 1.45 to 2.08 V). Adapted from Schmidt, W. A.; Suchorski, Y.; Block, J. H. *Surf. Sci.* **1994**, *301*, 52.

with a reactive imaging gas is basically a field desorption microscope. An example of such FIM imaging with  $O_2^+$  ions is shown in Figure 3, where the initial stages of the oxidation of the Rh surface are visualized in situ.<sup>26</sup>

Such studies provide a unique possibility to reveal the effect of high electric field in order of few volts per angstrom on the surface oxidation<sup>26</sup> and generally allow to study the interaction of gas molecules such as, for example, nitrogen with the solid state surface in high electric fields.<sup>27</sup>

# **Basics of the Field Desorption Microcopy**

As already mentioned in the preceding text, the limit of the FIM applicability is the field evaporation process. However, the fieldevaporated ions field-emitted directly from the surface can also be utilized to obtain images of the specimen surface. When the *preadsorbed* atoms are field-removed, the effect is called *field desorption*,<sup>28</sup> and in the case when the *substrate* atoms are fieldremoved, *field evaporation*.<sup>9</sup> In both possible cases, namely, when ionized specimen atoms are used as imaging species or when the adsorbed metal atoms are exploited, the corresponding technique is called FDM.<sup>29</sup> While in the first case, the imaging process is rather instable because of the evaporation of the specimen during visualization<sup>30</sup>; in the second one, especially when using Li<sup>+</sup> ions supplied by diffusion from the specimen shank, stable images comparable with those obtained by FIM can be obtained.<sup>31</sup>

The corresponding device, lithium field desorption microscope (Li-FDM) developed by Medvedev and Suchorski in the 1990s, <sup>32</sup> is based on the principle that surface sites can be visualized by radial projection of the Li<sup>+</sup> ions field-desorbed from these sites themselves. Desorbed Li atoms are continuously replaced by surface diffusion from the long-lasting multilayer Li deposit on the shank of the tip (**Figure 4**). When the diffusion supply along the surface is sufficient (desorption rate does not exceed the diffusion supply), the surface can be imaged in a continuous imaging mode. However, in case the diffusion supply does not provide a sufficient number of Li atoms in the desorption zone, the pulsed mode can be used: the image is then created by Li<sup>+</sup> ions desorbed by periodic high-voltage pulses. Between the pulses, sufficient Li coverage is collected on the imaged surface via surface diffusion.

Since the surface diffusion is a field-dependent process, the rate of the diffusion supply can be adjusted by a high-field bias, when a constant field is applied that is sufficient for an accelerated surface diffusion of Li, but not sufficient for field desorption (the field



**Figure 3** FIM imaging with reactive imaging gases: (a)  $O_2^+$  field ion image of the initial stage of the oxygen interaction with Rh at 375 K. (b–e)  $O_2^+$  field ion micrographs showing the sequential stages of the interaction of oxygen at  $5.2 \times 10^{-5}$  mbar in the presence of an external field of 15 V nm<sup>-1</sup>; (f)  $O_2^+$  field ion micrograph showing the result of reduction of the oxidized surface by CO in the presence of an external field of 15 V nm<sup>-1</sup>. Reproduced from Medvedev, V. K.; Suchorski, Y.; Voss, C.; Visart de Bocarmé, T.; Bär, T.; Kruse, N. *Langmuir* **1998**, *14*, 6151.

desorption occurs then by additionally applied field pulses). Thus, varying the temperature and the applied field values, the relation between the diffusion supply and desorption rate can be adjusted to obtain the optimal image intensity.

The initial development of Li-FDM was concerned with the imaging of different clean and adsorbate-covered metal surfaces, investigations of the mechanisms of Li-FDM image formation,<sup>31,32</sup> and visualization of dynamic reaction–diffusion processes.<sup>33</sup> As a result, the Li-FDM is capable of operating in the presence of CO and oxygen (up to  $10^{-3}$  mbar) and of imaging at these conditions the dynamic processes on metal surfaces with a time resolution of 0.01 s. Figure 5 shows an example of such visualization for the [110]-oriented Pt tip.



**Figure 4** Lithium field desorption microscope: principle of the image formation in Li-FDM. Li atoms diffuse from the multilayer deposit on the shank of the tip toward the apex. Li<sup>+</sup> ions field-desorbed from the apex on the tip create a projection image on the screen.



**Figure 5** Surface of the [110]-oriented Pt tip as imaged by field-desorbed Li<sup>+</sup> ions. (a) Ne FIM image, 78 K, 10380 V (35 V nm<sup>-1</sup>); (b) crystallographic map; (c) Li-FDM image of the same surface as in (a), 446 K,  $V_{const}$ =1145 V (3.8 V nm<sup>-1</sup>),  $V_{pulse}$ =1600 V (5.4 V nm<sup>-1</sup>), f=9260 Hz; (d) the same as in (c) but the surface is CO-covered, 417 K,  $V_{const}$ =969 V (3.8 V nm<sup>-1</sup>),  $V_{pulse}$ =3000 V (5.1 V nm<sup>-1</sup>), f=333 Hz; (e) the same as in (c) but the surface is oxygen-covered, 417 K,  $V_{const}$ =5000 V (8.4 V nm<sup>-1</sup>),  $V_{pulse}$ =3000 V (5.1 V nm<sup>-1</sup>), f=540 Hz; (f) the same as in (e) but imaged with  $V_{const}$ =2541 V (4.3 V nm<sup>-1</sup>),  $V_{pulse}$ =5000 V (8.4 V nm), f=54 Hz. Based on Medvedev, V. K.; Suchorski, Y.; Block, J. H. *Appl. Surf. Sci.* **1994**, *76*/77, 136.

Since in the temperature range of 400–450 K, lithium can be desorbed from the Pt surface by an applied field less than 1 V Å<sup>-1</sup>; other adsorbed layers, such as oxygen or CO, remain intact during the Li-FDM operation, that is, they can be imaged by Li<sup>+</sup> ions (**Figure 5(c)–5(f)**). During the pulsed mode of imaging, surface diffusion of Li occurs between the pulses (only those regions are imaged, where Li diffusion provides a sufficient Li coverage); thus, the extent of the imaged region can be adjusted by varying the frequency and duration of the field pulses (compare **Figure 5(e)** and **5(f)**). Many of the catalytic reactions, such as CO oxidation reaction, occur via Langmuir–Hinshelwood mechanism, that is, the reacting species are adsorbed on the surface prior to and during the reaction. Therefore, the reaction process can be directly imaged in situ by Li-FDM (for examples of such application, see Chapter "Surface Chemistry").

#### **Surface Science Applications**

### Surface Physics and Material Science

As already mentioned, until the 1990s, the most important applications of FIM took place in materials science, especially in metallurgy, where the segregation of impurities, grain boundary segregation, decomposition of alloys, role of lattice defects, and other surface effects were studied on an atomic scale.<sup>5–9</sup> Simultaneously, a significant contribution to the surface physics has been accomplished by FIM, especially in studying the diffusion processes and behavior of individual atoms on metal surfaces<sup>7,8,34</sup> long before as such studies became routine for STM.<sup>35,36</sup> The first evidences of a substrate-mediated indirect interaction of adatoms were obtained by FIM for Re adatoms on W(110),<sup>37</sup> as well as for W–Pd and Re–Pd and Re–Pd atom pairs on W(110).<sup>37,38</sup> A compilation of this early development including the dipole–dipole and elastically mediated non-oscillatory interactions is given in a comprehensive review.<sup>39</sup> The first experiments on a directional walk of adsorbed atoms in an externally applied field gradient<sup>40</sup>

and on field desorption of single adatoms by a voltage pulse<sup>41</sup> were direct predecessors of the atom manipulation in STM.<sup>42</sup> However, since the 1990s, with the progressing domination of the STM-based techniques, the FIM contribution to the surface physics became less meaningful, but at the same time, a revival of the FIM in surface chemistry began, initiated by the first in situ observations of a catalytic surface reaction on a nanoscale in Block's group in Berlin.<sup>20,21</sup> An important role in this development played an increasing understanding of the importance of the *parallel imaging principle* (which distinguishes the FIM from, e.g., STM with its sequentially scanning imaging mechanism) for such real-time observations. This advantage was convincingly demonstrated by the use of the photoemission electron microscope for the real-time surface chemistry studies on the macroscopic (~ $\mu$ m) scale. Various spatial–temporal phenomena as target patterns, island formations, spirals, standing waves, etc. were observed and are summarized in reviews<sup>43,44</sup> and in the Nobel Prize Lecture by G. Ertl.<sup>45</sup>

### Surface Chemistry

In the early 1990s, it was demonstrated that such spatiotemporal phenomena occurring on the catalytically active metal surfaces can be also imaged in situ by FIM with a nanometer resolution using platinum metal tip specimens, which served as models for the catalytically active precious metal particles. Similarly to a catalytic particle of comparable dimensions, the apex of a field emitter tip exhibits a heterogeneous surface formed by differently oriented nanofacets (compare Figure 6(a) and 6(b)).

However, in contrast to a catalyst particle, the tip surface can be prepared reproducibly by field evaporation and subsequently characterized with atomic resolution by imaging in the FIM (Figure 6(c)). Such a well-defined sample can be used to catalyze a surface reaction, and the process can be followed by FIM in real time. Another benefit of the FIM-based methods is the possibility to study the structural changes on an atomic scale caused by molecular adsorption or by the catalyzed reaction itself. Reconstruction phenomena on nanofacets, which are hardly accessible by other analytical techniques, are well observable in FIM<sup>26</sup>; observations of the reaction-induced morphological changes are summarized in the present contribution later.

The breakthrough in the FIM visualization of catalytic reactions was achieved by using reactive gases such as oxygen as imaging gas, instead of traditionally used noble gases such as, for example, neon. Figure 7 shows an example of such an in situ visualization, where CO oxidation on a Rh tip is imaged by  $O_2^+$  ions.<sup>46</sup> Such imaging allows deep insights into the microscopic mechanisms of the processes occurring during the reaction; for example, the coarsening of the surface (Figure 7(b)) indicates the formation of RhO<sub>x</sub> granules during the kinetic transition from an inactive (CO-covered) to the catalytically active (oxygen-covered) Rh surface, an effect that was not observed at that time on the macroscopic single-crystal surfaces.

The size of the formed granules depends on the tip temperature: a decrease in the tip temperature leads to a rather fast decrease in the granule size (Figure 7(c) and 7(d)). In turn, the transition from the oxygen- to the CO-covered Rh surface, which starts near the centers of the {111} and {100} planes, is accompanied with the disappearing of the RhO<sub>x</sub> granules (Figure 7(e) and 7(f)). Using FIM, important questions concerning the surface reactions could be answered: (i) the role of the applied electric field on the reaction mechanism,<sup>47</sup> (ii) the influence of the structural heterogeneity of the field emitter tip surface (dynamic coupling effects between the individual planes),<sup>48</sup> (iii) the role of fluctuations on reaction kinetics and possible fluctuation-induced deviations from the behavior predicted by macroscopic (mean-field) rate laws.<sup>49,50</sup>

To prove experimentally the effect of the imaging electrostatic field, the unique feature of FIM was used, namely, the possibility to switch quickly from the FIM imaging by  $O_2^+$  ions (applied field ~ 12 V nm<sup>-1</sup>) to the imaging with field-emitted electrons (FEM; applied field ~ 4 V nm<sup>-1</sup>) just by reversing the applied voltage polarity.

Since additional FEM measurements performed with pulsed high-voltage supply with a varying duty cycle factor showed no influence of the duration of the pulses on the catalytic CO oxidation,<sup>47</sup> the FEM results can be interpreted as quasi *field-free*. By polarity switching, such quasi *field-free* (FEM) results can be directly compared with the *high-field* (FIM) data.

In FIM the different ionization probabilities for oxygen (used as imaging gas) over the oxygen- and CO-covered surface<sup>51</sup> and in FEM the local work function variations create the image contrast. This allows to identify the catalytically active state and to observe the transitions from the catalytically *active state* (oxygen-covered surface) to the *inactive state* (CO-covered surface) when the reaction parameters (e.g., *T*,  $p_{CO}$ , and  $p_{O_2}$ ) are varied. The parameter values at which the oxygen layer is replaced by the CO layer or vice versa are called *kinetic transition* points and can be plotted in a chart in the *T*,  $p_{CO}$ , and  $p_{O_2}$  parameter spaces. Such a plot, illustrating the



Figure 6 (a) Ball model of the apex of a spherical fcc tip; (b) metal aggregate on an oxide substrate; (c) field ion image of the [111]-oriented Rh field emitter tip. Reproduced from Suchorski, Y.; Drachsel, W. *Top. Catal.* **2007**, *46*, 201.



**Figure 7** Field ion imaging with  $O_2^+$  ions. (a–f)  $O_2^+$  images of the CO oxidation reaction on a [111]-oriented Rh tip; (a–d) transition from the COto the oxygen-covered surface. (a) The initial stage, 350 K; (b) beginning of the transition, coarsening of the surface, 410 K; (c) further granulation of the surface due to RhO<sub>x</sub> formation, 483 K; (d) after fast drop of temperature from 483 to 370 K; (e), (f) the sequential stages of a reverse process. Reproduced from Medvedev, V. K.; Suchorski, Y.; Block, J. H. *Appl. Surf. Sci.* **1995**, *87/88*, 159.

transitions between the steady states of high reactivity and low reactivity, is called reactive *kinetic phase diagram*, due to the formal similarities between the nonequilibrium kinetic transitions occurring in the reaction and equilibrium phase transitions (for details, see Ref. [52] and references therein). Because of a certain asymmetry in the CO and oxygen adsorption (in contrary to CO, the oxygen molecule needs two adsorption places for dissociative adsorption) reactions, *hysteresis* can be observed; a transition from the active (oxygen-covered surface) state to the inactive (CO-covered surface) state occurs (at constant  $p_{O_2}$ ) at higher CO pressure than that that is necessary for the reverse transition. Within the hysteresis loop, the system exhibits *bistability*, that is, it can be in an active or inactive state at the same parameter values depending on the prehistory.<sup>43-45,47,52</sup>

Figure 8(a) shows the kinetic phase diagrams obtained with both FIM and FEM for the same Pt tip and the same oxygen partial pressure  $4 \times 10^{-4}$  torr. The phase diagram obtained by FIM appeared as shifted significantly to lower  $p_{CO}$  values in comparison with



**Figure 8** C0 oxidation on a [111]-oriented Pt tip. (a) Kinetic phase diagrams for C0 oxidation on a Pt tip determined with FEM ( $F_0 = 4 \text{ V nm}^{-1}$ ) and FIM ( $F_0 = 12 \text{ V nm}^{-1}$ ). The shaded areas mark oscillation ranges. Below their crossing point (marked by red arrow), the boundary lines for instabilities enclose a region of bistability. The open circles are Pt(110) single-crystal data indicating the oscillation range; the bistability range of reaction on Pt(110) at T=349 K is indicated by filled circles. The insert shows the geometry of the [111]-oriented Pt tip used in our experiments (clean Pt surface imaged at 78 K with FIM using Ne as imaging gas,  $F_0=35 \text{ V nm}^{-1}$ ); the central (111) and one of three {110} planes are indicated. (b) Oscillatory behavior of C0 oxidation on the Pt tip apex. Upper curve: Total FEM image intensity; lower curve: local FEM intensity of the (110) plane. T=398 K,  $p_{C0}=6.2 \times 10^{-6}$  torr, and  $p_{0_2}=4.3 \times 10^{-4}$  torr. Adapted from Suchorski, Y.; Imbihl, R.; Medvedev, V. K. *Surf. Sci.* **1998**, *401*, 392.

the field-free one. The physical reason for this effect was revealed by the energy analysis of  $CO^+$  and  $O_2^+$  ions<sup>24,25</sup> and relies on the differing field effect on the binding energy of adsorbed CO and oxygen.<sup>53</sup>

Under certain conditions, the CO oxidation reaction may exhibit self-sustained *oscillations*, that is, the oscillating reaction rate (CO<sub>2</sub> production), is observed at constant reaction parameters (T,  $p_{CO}$ , and  $p_{O_2}$ ), as was detected on the single-crystal surfaces.<sup>43–45</sup> Figure 8(b) illustrates the local and 'global' oscillatory behaviors of the CO oxidation on the nanosized Pt tip shown in the inset of Figure 8(a).<sup>47</sup> Although such a tip contains differently oriented facets, the whole tip area undergoes synchronous transitions from a CO-covered surface to an oxygen-covered surface and vice versa (compare variation of the local and total image intensity in Figure 8(b)), an effect that is not observed for different orientations on macroscopic samples. The parameter range at which the reaction oscillates is also indicated in the phase diagram, which exhibits a cross-like shape with a *crossing point* (called also often *bifurcation point*) where the bistable behavior of the system changes to the oscillating one.

The comparison of FEM measurements with data for catalytic CO oxidation on a macroscopic Pt(110) surface reveals the role of the structural heterogeneity of the field emitter tip surface: the single-crystal studies by Eiswirth et al. (open circles in Figure 8(a),<sup>54</sup>) and Moldenhauer (filled circles<sup>55</sup>) suggest the position for the crossing point in the reaction phase diagram, which is significantly shifted in respect to the FEM results. These differences can be directly attributed to the size of the system and to dynamic coupling effects of the {110} facets with neighboring orientations.

The CO oxidation reaction is especially suitable for FEM/FIM studies since the difference in the work function of the CO and oxygen layers adsorbed on platinum group metals is big enough to provide a sufficient contrast on both FEM and FIM imaging modes. Of course, CO oxidation is not a sole reaction that can be studied in FIM. Other reactions like H<sub>2</sub> oxidation<sup>48,56,57</sup> and NO reduction with H<sub>2</sub><sup>58–60</sup> were also studied using FIM/FEM, often in combination with AP techniques to get an insight into the chemical composition of the surface and intermediate species. Mostly, the Pt, Rh, and Pd tips were used as specimens in these studies due to the importance of these metals in automotive exhaust converters. In studies of NO reduction with hydrogen on Pd, the FIM imaging was often combined with local chemical probing, that is, the structural transformations of the Pd specimen were correlated with the direct local information on the surface composition.<sup>58–60</sup> FIM brightness analysis provided data about the hysteresis behavior, and a corresponding kinetic phase diagram consisting of the NO-covered steady state, hysteresis region, and H<sub>2</sub>-covered steady state in the temperature region 450–575 K could be determined.<sup>60</sup> Local chemical probing suggests that processes in the subsurface region play a significant role, for example, the exchange of the hydrogen atoms between the adsorbed layer and palladium bulk and Pd surface oxidation (PdO<sub>2</sub><sup>+</sup> ions were detected).<sup>60</sup> On the NO side of the reaction, N<sub>2</sub>O<sup>+</sup> ions were observed, suggesting the presence of N<sub>2</sub>O<sub>ad</sub> species on the surface. The detection of small amounts of (NO)<sub>2</sub><sup>+</sup>, in turn, indicates that the appearance of N<sub>2</sub>O is caused mainly by the formation of (NO)<sub>2</sub> dimers and their dissociation toward N<sub>2</sub>O and O<sub>ad</sub>,<sup>61</sup> similarly as it was observed earlier for Au tips.<sup>62</sup>

An important process that accompanies often the surface reactions is the change of the oxidation state and of the morphology of the sample. Here, FIM allows again a direct in situ observation, whereas a direct comparison of the local behavior of crystallographically differently oriented facets is possible (Figure 9).<sup>26</sup>

In particular, the stepped regions between the low-index poles appear to be most susceptible to oxidation. This is different from the behavior of the central Rh(111) plane and of the  $\{001\}$  peripheral planes, which seem to be rather reluctant to oxidation. Quite interestingly, the  $\{011\}$  planes seem to undergo slower oxidation than the  $\{113\}$  planes. Following the results of previous field-free measurements, both planes are not expected to be reconstructed at 375 K. For the quantitative evaluation, the local FIM intensity for



**Figure 9** FIM monitoring of the Rh surface oxidation. (a)  $O_2^+$  field ion image of the initial stage of the oxygen interaction with Rh at 375 K. (b–d)  $O_2^+$  FIM video frames showing the sequential stages of the surface oxidation of Rh at  $5.2 \times 10^{-5}$  mbar of oxygen in the presence of an external field of 15 V nm<sup>-1</sup>; (e) corresponding local image intensity for (111), (001), (011), (113), and (012) planes as a function of the oxidation time. Based on Medvedev, V. K.; Suchorski, Y.; Voss, C.; Visart de Bocarmé, T.; Bär, T.; Kruse, N., *Langmuir* **1998**, *14*, 6151.

different facets was extracted from the corresponding video sequence.<sup>26</sup> As is clearly visible in Figure 9(b), after a considerable time delay, a steep increase of local FIM brightness, related to the  $RhO_x$  formation, occurs.

The time dependence of the local image brightness, shown in Figure 9(b), demonstrates the high activity of the stepped planes {113} and {012} toward the surface oxidation. In contrast, the low-index planes are much less active, while (011) presents an intermediate case. Assuming pseudo-first-order reaction kinetics, the rate constants can be estimated from the initial slopes of the curves shown in Figure 9(b). The values of  $1.7 \text{ s}^{-1}$  at 350 K and  $2.3-2.4 \text{ s}^{-1}$  at 375 K for both (113) and (012) planes, respectively, were found in the range of  $5-17 \text{ kJ mol}^{-1}$ .

### Fluctuation-induced effects

Nanofacets on the specimen apex can serve as an excellent model of nanosized systems where a significant influence of fluctuations is potentially expected. Such expectations are based on the  $1/N^{1/2}$  (*N* being the number of fluctuating particles, e.g., reacting molecules) scaling of the relative amplitude of fluctuations. The number of the reacting particles on a nanofacet varies in the  $10^2-10^3$  range; thus, one may observe deviations from the behavior predicted by macroscopic rate laws, such as, for example, fluctuation-induced transitions in a bistable system.<sup>63</sup> The 'parallel' imaging principle of the FIM makes this technique naturally suitable for monitoring fluctuations: the process proceeding on the different surface regions can be analyzed simultaneously, and the time resolution is limited mainly by the features of the used video technique. The processing of the corresponding video frames allows to study the dynamic processes within the ROIs (regions of interest in digitized video frames, which correspond to the selected surface regions of few nm<sup>2</sup>) arbitrarily located on the surface.<sup>64</sup>

Figure 10 shows exemplarily the local time series recorded for a small  $2 \times 2 \text{ nm}^2$  area in the vicinity of the (110) facet of a Pt tip. The small-amplitude fluctuations caused mainly by CO diffusion and characterized by a Gaussian probability distribution were observed in the *monostable* range on the inactive branch of the reaction. This is illustrated by the time series *a* (Figure 10(a)) and a corresponding probability distribution (Figure 10(b)). Similar time series but with somewhat higher magnitude of fluctuations was also observed in the monostable range on the active branch (curve *b* in Figure 10(a)). Unexpectedly, in the bistable range



**Figure 10** Fluctuation-induced transitions in catalytic CO oxidation on a Pt field emitter tip. (a) Time series of the local  $(2 \times 2 \text{ nm}^2)$  FEM brightness and (b) corresponding probability distributions (right-hand side). The inset shows an FEM image with a marked rectangular area where the local FEM brightness was analyzed; (c) break of the spatial correlation of the first atomic step (marked by an arrow) confining the individual (112) facet. The letters refer to different reaction conditions, and the distance zero refers to the edge of the facet; (d) increase in the average amplitude of the local FEM brightness fluctuations on a Pt(112) facet at approaching the critical point given by the crossing point of the two boundary lines of the bistability range. Adapted from Suchorski, Y.; Beben, J.; Imbihl, R.; James, E. W.; Liu, D.-J.; Evans, J. W. *Phys. Rev. B* **2001**, *63*, 165417.

of the reaction, the probability distribution becomes broad and asymmetrical and turns even into a bimodal probability distribution (curves c and d in Figure 10(a) and corresponding distributions in Figure 9(b)). The bimodal distribution d in Figure 10(b) evidences the fluctuation-induced transitions between the two possible states in the bistability region.<sup>49</sup>

Another unexpected result was the absence of the synchronization between the fluctuations on the neighboring facets.<sup>50</sup> This is unexpected because the tip is known to behave as one synchronized dynamic system during kinetic transitions from the active state to inactive state (marked by lines in the cross-shaped diagrams in Figure 8); the spatial coupling occurs apparently due to the fast CO diffusion.

More detailed studies using the Haar wavelet analysis detected that such fluctuation-induced transitions occur spatially correlated over the flat facet surface (the mentioned region in the vicinity of Pt(110) was identified as a small (331) facet)<sup>65</sup> and are confined by the first atomic step due to the disturbed diffusional coupling over the stepped surface. We note that this effect cannot be predicted within the mean-field theory. The Monte Carlo simulations naturally incorporating the stochastic nature of the modeled processes can, in turn, predict such an effect provided that the modeled system is sufficiently small and in close proximity to a bifurcation (critical) point where bistability vanishes and fluctuations diverge.<sup>66</sup>

The lack of synchronization in respect to fluctuations between the various orientations can be understood if one takes into account that differently oriented facets may own different intrinsic kinetic reaction diagrams at the same external p, T parameters. The stepped regions around the individual facets disturb the diffusive coupling via CO so much that it is not sufficient to synchronize the fluctuations on different facets. **Figure 10(c)** illustrates this by showing the break in the spatial correlation of the fluctuation at the position of the first atomic step confining the individual facet. In turn, within the individual facet, the reaction-induced fluctuations are generally well correlated.  ${}^{50,65,66}$ 

In addition, the degree of the spatial coherence increases at approaching the critical point (crossing point in the phase diagram in Figure 10(d)) simultaneously with the amplitude of fluctuations (Figure 10(d)).<sup>66</sup> Similar behavior is well known for the equilibrium systems where the correlation length diverges (in an infinite system). In our case, the correlation length seems to be simply limited by the size of the facets.

The noise-induced transitions in the CO oxidation detected first on the Pt nanotips<sup>49</sup> allowed to explain the vanishing bistability during CO oxidation on a Pd model catalyst consisting of small Pd particles.<sup>67</sup> For the model system consisting of particles of  $\sim$  500 nm size, a pronounced bistability is observed that vanishes when the particle size becomes smaller than 6 nm (approximately the size of an individual facet of the field emitter tip). The fluctuation-induced transitions, which occur in an unsynchronized way, lead to the apparent disappearance of the bistability as is reflected in the total (averaged) CO<sub>2</sub> rate for many particles, measured in Ref. [67].

Another promising FIM application that exploits the fluctuation effects is monitoring the surface diffusion by a 'virtual probehole' technique. The idea that the local image brightness fluctuations in the recorded FIM video images can provide the surface diffusion parameters is based on Onsager's hypothesis about the applicability of macroscopic diffusion laws to the microscopic density fluctuations<sup>68</sup> and on the finding that such brightness fluctuations reflect microscopic concentration deviations in an apparently homogeneous adsorbed layer and can thus be analyzed via the density fluctuation method, proposed by Kleint and Gomer.<sup>69,70</sup> The 'parallel' imaging principle of FIM allows the simultaneous analysis of processes on many chosen surface regions of only a few square nanometer size using the video-FIM and digitally created 'virtual probe holes.' In contrast, in the 'real probe-hole' measurements, the emission from just one or two regions (in a 'two-probe-hole' experiment<sup>71</sup>) can be experimentally registered. Particularly promising is the use of the field-desorbed Li<sup>+</sup> ions in such an application (see section 'Li-FDM Applications').<sup>72</sup>

# **Li-FDM Applications**

In most of the applications of the FDM, the parallel imaging principle (the same advantage as in the FIM) is exploited: the fast dynamic processes and the spatial correlation of the events occurring simultaneously on spatially separated regions of the sample can be monitored. In the case of the Li-FDM, an additional important advantage becomes relevant: an exceptionally low value of the applied field that is necessary to desorb Li atoms from most of the solid surfaces. Even at cryogenic temperatures, this value hardly exceeds  $1 \text{ V Å}^{-1}$ , that is, it is at least by factor 3.5 lower than the best imaging field for Ne<sup>+</sup> ions. This allows using of the Li<sup>+</sup> ions for the imaging of the field-sensitive processes, such as surface reactions.

It was, for example, possible to image by  $Li^+$  ions a sole reaction front in the CO oxidation on a [111]-oriented Rh tip and the propagation of this front during the extension of the oxygen-covered surface and CO-covered surface. The illustration of such imaging is presented in Figure 11 where different reaction states and reaction front shapes are imaged.<sup>73</sup>

It is also possible to adjust the applied field to a value that is sufficient for the field desorption of Li from the CO-covered surface, but is not sufficient to remove Li from the oxygen-covered surface (due to the higher binding energy of Li in the Li/O coadsorption system). This allows to create unique situations where an alkali promoter is added only to one reactant (oxygen) in the catalytic CO oxidation and to observe in situ the result of such spatially separated reaction promotion. Since the surface density of Li adatoms in the imaged area (reaction zone) can be adjusted by the field- and temperature-dependent surface diffusion of Li from the shank of the tip, the degree of the local alkali-induced modification of the surface can be controlled in a reproducible way.

Using the coadsorption of Li, even a reaction mode can be induced, which does not exist in a Li-free case, namely, oscillating CO oxidation on Rh.<sup>33</sup> The prerequisites necessary for the oscillating behavior of the isothermal CO oxidation reaction on



**Figure 11** Visualization of the CO oxidation reaction on a [111]-oriented Rh tip by Li<sup>+</sup> ions; (a) crystallographic map; (b) steady state at 417 K,  $p_{CO} = 1.5 \times 10^{-5}$  torr,  $p_{O_2} = 7.5 \times 10^{-5}$  torr,  $F_{const} = 0.85$  V Å<sup>-1</sup>,  $F_{pulse} = 0.70$  V Å<sup>-1</sup>, f = 526 Hz; (c-e) the extension of the oxygen-covered surface caused by reducing of the CO pressure from  $1.5 \times 10^{-5}$  torr to  $1.3 \times 10^{-5}$  torr; (f) the initial stage of a reverse process. Reproduced from Medvedev, V. K.; Suchorski, Y.; Block, J. H. *Vacuum* **1995**, *46*, 563.

catalyst surfaces are (i) the existence of a bistability region in the phase diagram of the CO/Oad-Pt(Pd) adsorption system and (ii) involvement of a feedback mechanism. In the present case of the Li-induced oscillations, the reversible formation of surface oxide serves as a feedback mechanism (Figure 12).<sup>33</sup> In the experiment, the reaction front imaged by  $Li^+$  ions is observed as a line created by irregular bright spots in Figure 12(b) and 12(c). The contour of the front is indicated in Figure 12(d); note that both the  $Li^+$  image in Figure 12(b) and 12(c) and the Ne<sup>+</sup> image of the same surface in Figure 12(d) are point projections with the same geometric magnification. The reaction front marks the spatial separation between the CO-covered surface and the area covered with oxygen (and Li). Such separation is a consequence of the increased rate of oxygen adsorption on the alkali-precovered surface.

The exposure of Rh to oxygen in high-field conditions leads to morphological changes of the Rh surface (see Figure 9), increasing its roughness due to  $RhO_x$  formation. The field desorption of Li is extremely sensitive to surface roughness because of the strong influence of this effect on the local field. Thus, the variation of the surface roughness modulates the field desorption of Li. Increased local field due to the  $RhO_x$  formation leads to the avalanche-like field desorption of Li from the roughened surface. This causes a sudden motion of the border between the oxygen- (and Li-) covered part of the tip and the rest of the surface (compare Figure 12(b) and 12(c)). The progressive reversal of the oxygen-caused roughness by CO should lead in turn to the gradual motion of the Li desorption borderline (reaction front) toward the top of the tip. Under certain conditions, this process begins to oscillate, as is in fact observed in the experiment (Figure 12(a)).

The individual steps of the oscillating mechanism are shown in Figure 13(a)-13(d), where the particular processes, such as the storage of oxygen via Li-accelerated oxidation of Rh (Figure 13(a)), Li desorption due to the roughness-enhanced local field (Figure 13(b)), and subsequent reduction of the stored oxygen (Figure 13(c)), are depicted. The drawings in Figure 13(a) and 13(b) correspond to the micrographs in Figure 12(b) and 12(c), respectively.

The use of Li as an imaging medium has allowed also for the first direct evidence of the surface reconstruction as a feedback mechanism in the oscillating reactions on the nanometer-sized Pt facets.<sup>74</sup> Despite the tacit assumption that the 'macro'-oscillating reaction kinetics, including the reconstruction-driven feedback mechanism, should also be valid for the nanometer-sized facets of 'real catalyst' Pt particles, no experimental evidence has been provided until 2006 (a kind of a 'material gap' problem). It means it



Figure 12 Li-mediated oscillations in CO oxidation on a [100]-oriented Rh tip: (a) time dependence of the reaction front propagation. The current position of the front is measured from the center of the apex (100) plane along the [001] zone line; (b), (c) Li-FDM images of the maximum (b) and minimum (c) extent of the reaction–diffusion front; (d) Ne-F1M image of the [100]-oriented Rh tip at 78 K. Part of the zone in which the oscillating motion of the reaction–diffusion front was observed is marked. Reproduced from Medvedev, V.; Suchorski, Y.; Block, J. *Appl. Surf. Sci.* **1996**, *94/95*, 200.

could not be excluded that oscillations on a nanosized small metal particle with its differently oriented facets, which are confined by stepped regions, might also be induced by reaction-diffusion processes coupled in a complex manner.<sup>48</sup>

The extreme sensitivity of Li to the atomic structure of the surface was exploited to prove the feedback mechanism of oscillations on Pt(110) nanofacets of a Pt tip.<sup>74</sup> In Figure 14(a), the time dependence of the local Li<sup>+</sup> image brightness within an ROI placed in a (110) region during the oscillating CO oxidation is shown. During the self-sustained oscillations in the reaction, the Li-FDM image switches periodically, with a period of ~120 s, between a circular-pattern (Figure 14(b)) and a cross-shaped pattern (Figure 14(c)).

The surface reconstruction of the Pt(110) facets from the  $(1 \times 1)$  to  $(1 \times 2)$  structure provides, due to the different corrugations of the reconstructed and unreconstructed surfaces, different local field enhancements 'felt' by adsorbed Li atoms. When the externally applied field is adjusted to the value, which is just sufficient for the field desorption of Li from the oxygen-covered  $(1 \times 2)$  surface (Figure 14(b)), the desorption of Li from the CO-covered much smoother  $(1 \times 1)$  surface does not take place (Figure 14(c)), since the local field is not sufficient (corrugation-caused field enhancement is too low<sup>13</sup>) for the desorption of Li. This is evidence for two different structures of the same (110) facet caused by different CO coverages. The switching between the  $(1 \times 1)$  and  $(1 \times 2)$ structures modifies the sticking coefficient for oxygen on the nanometer-sized Pt(110) facets, thus providing the same feedback mechanism as is known for the macroscopic single-crystal surfaces.<sup>45</sup>

As already mentioned in the preceding text, the analysis of intensity fluctuations in the Li-FDM images can be used for the study of the surface diffusion of Li. This may shed light on an important, but often overlooked, factor in catalysis, namely, the mobility of the catalytic (alkali) promoter itself. The first successful attempt to measure in situ the diffusivity of an alkali coadsorbate in a catalytic reaction was undertaken in 2007 by the use of the fluctuation method described in Ref. [64] and applied to Li in CO oxidation on Pt.<sup>72</sup> Figure 15 shows the Li-FDM images taken at similar conditions as in Figure 14 and the corresponding locally measured intensity series. With the corresponding calibration, the intensity fluctuations can be related to the fluctuations of the number of Li adatoms  $N_{Li}$  in the probed area.

The corresponding autocorrelation function (Figure 15(c)) is related to the diffusion coefficient, which can be obtained from the comparison of the experimental and theoretical autocorrelation functions.<sup>64,75,76</sup> The results shown in Figure 15(c) demonstrate the differences in the diffusivity of Li on the CO-covered Pt(111) surface along and across the atomic steps and indicate a 'slowing' effect of the coadsorbed CO on the Li diffusion.

The lithium field desorption microscope can also be operated by making use of a supply mechanism in which Li diffuses as a species intercalated in the region between a Rh metal and a surface carbon layer created by the graphitizing of a Rh tip.<sup>77</sup> Figure 16



Figure 13 Mechanism of the Li-mediated oscillations. (a) Initial state: Oxygen is being stored in a 'reservoir'; (b) growth of oxide granules resulting in increased roughness of the Rh surface; (c) avalanche-like Li field desorption and consequent removal of the oxygen layer; (d) final state: oscillatory cycle may start again. Reproduced from Medvedev, V.; Suchorski, Y.; Block, J. *Appl. Surf. Sci.* **1996**, *94/95*, 200.

shows a [111]-oriented Rh tip that was field-evaporated (Figure 16(a)) and annealed in UHV at 1000 K in a subsequent step. During this step, carbon segregated to the surface producing a graphite-like overlayer structure in which further field evaporation created occasionally two circular windows that could be imaged by either  $\text{Li}^+$  (Figure 16(b)) or  $O_2^+$  (Figure 16(c)) ions. Bright rings in Figure 16(b) appear as a result of Li<sup>+</sup> desorption at the border between the clean Rh and the surrounding graphite-like overlayer. Obviously, Li is continuously supplied from the shank reservoir to the tip apex. This evidences the mobile Li atoms to be intercalated between the Rh surface and the graphite-like layer.

Such mode of imaging allows to study quantitatively the diffusivity of the intercalated Li layer using, for example, a pulsed mode of imaging and adjusting the pulse frequency to the diffusion rate, as it was demonstrated in Ref. [46]. Additionally, the formation of subsurface oxygen within the circular windows was detected by comparison of the  $O_2^+$  FIM image intensity for the CO- and oxygen-covered surfaces.<sup>77</sup>

### **Probe-Hole Ion Analysis**

Using a small probe hole in the screen, which corresponds to a microscopically small area of surface, ions emitted locally from this area can be analyzed. Since the early attempts pioneered by Ingram and Gomer in the 1950s,<sup>78,79</sup> such analyses provided basic contributions to the field ion mass spectrometry (FIMS) and to the local field ion energy analysis. FIMS was used mostly to study the gaseous compounds ionized by a strong electric field at surfaces; the main contributions were made by Beckey,<sup>80</sup> Block,<sup>81</sup> and few other groups. A version of this technique, pulsed field desorption mass spectrometry, which combines a FIM



**Figure 14** The oscillating CO oxidation reaction on Pt nanofacets monitored with field-desorbed Li<sup>+</sup> ions at 490 K,  $p_{CO} = 1.8 \times 10^{-5}$  mbar,  $p_{0_2} = 2 \times 10^{-4}$  mbar. (a) Local intensity of the Li-FDM image in the (110) region versus time; (b) Li-FDM image of the oxygen-covered apex of the [100]-oriented Pt tip. The dotted circles indicate the (110) regions; (c) the same for the CO-covered surface. The (110) regions remain dark (no field desorption of Li from those regions under these conditions). Reproduced from Suchorski, Y.; Drachsel, W.; Gorodetskii, V. V.; Medvedev, V. K.; Weiss, H. *Surf. Sci.* **2006**, *600*, 1579.

with the time-of-flight analysis of surface species, field-desorbed as ions, offers a unique method to study the reaction intermediates or products, which can be sampled far below the temperatures that would normally be required for their unassisted thermal desorption.<sup>82,83</sup>

Progress in methods for measurements of energy distributions of field ions has led to the development of the field ion appearance energy spectroscopy (FIAES<sup>13–15</sup>). The main strength of the FIAES is the ability to obtain locally the binding energy of adsorbed (or field-adsorbed) atoms or molecules on chosen surface sites by the direct measuring of appearance energy of corresponding field



**Figure 15** Li<sup>+</sup> intensity fluctuations in the CO oxidation on a [100]-oriented Pt tip (at the same conditions as in **Figure 13**). (a) In the inactive (CO-covered) state, fluctuations of the image originate from Li diffusion. The ROI in the position 1 (the square-shaped window is placed across the circular atomic step line confining the (111) facet) allows to monitor the diffusion across the atomic steps, which confine the (111) facet, the ROI in position 2 (the same window but rotated perpendicularly to position 1) along the steps, correspondingly. An example of a locally measured time series and a corresponding (Gaussian-like) amplitude distribution is shown in the succeeding text; (b) in the active (oxygen-covered) state, fluctuations of the image are caused by the reaction itself. The corresponding local time series exhibits a bimodal (non-Gaussian) distribution; (c) autocorrelation functions that demonstrate the differences in the diffusivity of Li on the CO-covered Pt(111) surface along (**a**) and across (**b**) the atomic steps. The diffusion coefficients ( $D=8 \times 10^{-13}$  and  $2 \times 10^{-13}$  cm<sup>2</sup> s<sup>-1</sup>) are derived from the theoretical autocorrelation functions fitting the experimental data. Based on Suchorski, Y.; Beben, J.; Frac, A.; Medvedev, V.; Weiss, H. *Surf. Interface Anal.* **2007**, *39*, 1061.



**Figure 16** Li layer intercalated between the Rh and the surface carbon layer. (a) Ne<sup>+</sup> FIM image of a [111]-oriented Rh tip ( $F \approx 35$  V nm<sup>-1</sup>, T=78 K; note that field evaporation does not remove surface carbon quantitatively); (b) Li<sup>+</sup> FDM image (F=9.5 V nm<sup>-1</sup>, T=407 K) of the section indicated by the square in (a) after the Rh tip was heated to ~1000 K to produce a graphite-like overlayer. Two circle-like windows of the clean surface contain Rh(100) (top) and Rh(123) (bottom) planes; see white circles in (a); (c) the same as in (b) but imaged with  $O_2^+$  ions at 78 K, F=12.2 V nm<sup>-1</sup>; (d) scheme of the mechanism leading to the formation of bright ring patterns in (b). Li supply is provided by interlayer diffusion of the intercalated Li layer. Based on Medvedev, V. K.; Suchorski, Y.; Visart de Bocarme, T.; Bär, T.; Kruse, N. *Ultramicroscopy* 1999, *79*, 239.

ions.<sup>84</sup> This has allowed, for example, measurements of the local electric fields above the individual surface atoms from the binding energies of the field-adsorbed noble gas atoms<sup>13,14</sup> and of the binding energies of CO and O<sub>2</sub> molecules on various metal surfaces.<sup>22–25</sup>

The probe-hole analysis of field ions allows also the chemical identification of single surface atoms by the atom probe field ion microscope (APFIM), developed by Müller et al.<sup>3,85</sup> Since that time, this technique, commonly called AP, has evolved to a 3-D atom probe tomography (APT), which allows 3-D reconstructions of the sample on an atomic scale and is not dependent on the probe-hole analysis anymore. Due to a wide use of these commercially available techniques, an abundance of reviews and monographs dedicated to various versions of AP and 3-D APT is available,<sup>4–7,86–89</sup> including the descriptions of the recently developed local electrode atom probe (LEAP<sup>R</sup>).<sup>86,88,89</sup> A combination of the LEAP<sup>R</sup> design with laser pulsing provides state-of-the-art due to its high mass resolution and high data collection rate the wide field of possible applications.

## **Summary and Future Perspective**

In exploring solid surfaces, two aspects are usually dominating: (i) imaging, if possible with atomic resolution, and (ii) laterally resolved chemical identification of surface species. The field ion microscope (FIM) equipped with the AP was historically the first technique able to handle both aspects on an atomic scale. FIM and AP and their 'descendants' such as 3-D-AP and LEAP are widely applied since the 1960s in materials science, particularly in the study of metallurgical problems. Apart from this, FIM has stimulated the development of other atomic resolution microscopies, especially STM. Before the STM techniques accrued from adolescence (i.e., before the 1990s), FIM has contributed significantly to such important developments as the study of surface diffusion of single atoms and of small atomic clusters by direct observation of particle displacements. The random walk of individual atoms and their movement under a driving force produced by, for example, a field gradient or by atomic interactions could be comprehensively studied in FIM. Later on, the FIM observations of the atomic random walk provided the finding that the interaction potential between two adatoms may exhibit both repulsive and attractive regions. This was the first observation of the indirect adatom–adatom interaction, which is discussed intensively until now.

Since the 1990s, the experimental efforts of several FIM groups became focused on using the FIM-based techniques to study catalytic reactions and other dynamic phenomena on the surface of field emitter tips used as models of catalytic particles. The FIM/FEM techniques are exploited in such studies as a flow reactor with a controlled supply of the gas reactants that react on the surface of the catalytically active specimen. Using the digital video technique, the breakthrough was achieved in the sense that the reaction fronts, self-sustaining oscillations, and other evidences of the spatially temporal self-organization, known for the macroscopic flat surfaces, became visible in situ for the first time on the nanometer scale. Mainly, not only the CO oxidation reaction but also other reactions like  $H_2$  oxidation and NO reduction with  $H_2$  on Pt, Rh, and Pd surfaces (which are relevant in the sense of automotive catalytic converters) were visualized, and kinetic phase diagrams for the nanosized samples were published. Effects, which are basically not observable on the macroscopic surfaces, such as fluctuation-induced kinetic transitions or size-dependent phase diagrams were detected and described. Corresponding reviews<sup>17,18,90,91</sup> were published recently, where also the role of the size effects, applied electric field, and reaction-induced fluctuations are analyzed.

Despite the snowballing development of the STM-based studies, the niche for the FIM application is still sufficiently big due to the possibility of parallel imaging, which is inherent to the FIM functional principle. Especially such in situ studies of the dynamic processes, where a direct comparison of the individual behavior of atoms or molecules on crystallographically different facets of the same specimen (i.e., in the exact same conditions) is desired, are suitable for the FIM. FIM is also a native technique to study the field effects and especially to understand the field-induced chemistry: in the fields of the order of volt per angstrom, chemical effects come into play, because certain electronic orbitals get field-modified to such a degree that the chemical characteristics of an atom or molecule become altered, for example, by establishing new bonding orbitals.<sup>92</sup> Still, a lot can be done by FIM in this direction, especially for nonmetallic systems.

Distinguishing atoms of different chemical natures in a nondestructive way, for example, just from imaging, remains a great challenge in FIM. Already in the early days of FIM, such attempts were undertaken for binary alloys.<sup>93</sup> Today, the improved calculation possibilities may provide a much better basis for such identification, as was shown in the STM studies of ordered alloys<sup>94</sup> where different chemical species provide differing STM image intensities. A breakthrough in such identification would allow to characterize the surface composition just by visual counting the number of atoms of the particular species. Alternatively, as proposed already in 1993,<sup>95</sup> the FIAES of the noble gases from the individual surface sites may reveal the 3-D distribution of the local field above individual atoms and thus provide the insights into the local electron density distribution. This could open the way to a nondestructive AP.

Promising fields of possible FIM applications are nanotubes and nanowires. Whereas both nanotubes (e.g., CNTs) and nanowires (e.g., ZnO<sup>96</sup>) are often used as electron emission sources, difficulties caused by low evaporation fields hinder up to now the wide application of FIM to such nanostructures. Cooling down to 4 K or using mixtures of imaging gases might circumvent these problems; thus, one may expect a breakthrough in the near future. A very promising future application of field ionization over the carbon nanotubes seems to be the use of the planar array of CNTs as a high-efficiency detector for the neutral supersonic helium beams.<sup>97</sup> The need for such a compact high-sensitivity detector results from the perspective of a helium atom microscope (de Broglie microscope) with nm resolution, where the supersonic helium beams would be used as surface probes.<sup>98</sup> However, a lot of difficulties has to be overcome for such a development, since the field ionization of nonaccommodated He atoms occurs, in this case, that is, the ionization mechanism differs from that in the FIM during the imaging. Both experimental and theoretical efforts are necessary to achieve optimal spatial localization of the field ionization event.<sup>99</sup>

The wide use of the STM and other scanning probe techniques raised the problem of the atomic scale definition of the STM tips used as probes. The advantage of an atomically well-defined tip is evident: the known atomic structure predetermines the electronic structure and thus the lateral resolution of the STM. Particularly important is the knowledge of the tip structure in the combined STM and AFM experiments.<sup>100</sup> The best way to characterize and to shape the scanning tip (including the possibility to create a one-atom tip<sup>101</sup>) is to combine the FIM and the STM in one device and to create the common protocols that could be used for comparing the results obtained in different experimental setups. The first successful steps in this direction are already done; the corresponding theory linking the atomic and the electronic structures may follow soon.

Summarizing, it can be said that the potential of the FIM and the FIM-based spectroscopies is still not yet exploited: there are still many possible applications where the FIM can be used as a complementary tool and, in even few of those, where the FIM is still the only technique of choice.

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# **High-Speed Electrochemical STM**

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# Introduction

Inspired by the pioneering work by Young et al.<sup>1</sup> on scanning probe microscopy, the scanning tunneling microscope (STM) was invented by Binnig and Rohrer in 1981.<sup>2,3</sup> Soon after the invention, this technique has been applied also to achieve atomic resolution on surfaces that are submerged in liquids.<sup>4–7</sup> Remarkably, even the first electrodeposition and stripping experiments have been performed already at this time.<sup>7</sup> Simultaneously, important steps have been set<sup>8,9</sup> that eventually led to the development of a true electrochemical STM (EC-STM), in which both the tip and the sample are fully under potentiostatic control<sup>10,11</sup>: the bipotentiostat, originally developed in 1967 to enable quantitative rotating ring–disc electrochemical conditions. It was not only possible to obtain the surface structure and its changes with atomic precision, but also the electrochemical current could be monitored simultaneously. Moreover, electrochemical reactions could be triggered and controlled via the potential of the sample (working electrode) leading to completely new insights in electrochemical surface science.

Inspired by these new possibilities, the desire quickly grew to image faster in order to capture a glance of the dynamic processes. With the aim to follow electrodeposition, etching, and related processes *in operando*, Magnussen (in the former group of Behm) pushed the borders of technology and developed a video-rate EC-STM.<sup>13,14</sup> Using this instrument, it has been demonstrated that high-speed imaging in electrochemical environment can provide valuable information about the dynamics of processes that occur at an electrode surface.<sup>14–21</sup> However, all movies in these experiments are recorded on a rather small length scale with an extremely limited roughness that spans at maximum one single atomic step. In addition, most of these publications capture the dynamics of an adsorbate layer, superstructure, or tracer molecule within such a superstructure, all of which have a unit cell that is larger than the atomic distance of the underlying crystal surface. Both the limited roughness and the larger unit cell make high-speed scanning significantly easy, as it allows to operate the microscope in the so-called constant-height mode without immediately crashing the scanning tip into the surface. The image of the surface is obtained from the variation of the tunneling current, instead of the variation of the height of the piezo element that controls the tip position.

As the local surface roughness and structure influence the local chemical potential of the surface, it is of crucial importance to follow not only the atomic details, but also the macroscopic step evolution during, e.g., deposition and etching conditions to gain a deeper and complete insight. This requires a microscope that is capable of imaging rough surfaces without losing too much of its scan speed. The first steps for further developments became feasible with the availability of fast data acquisition and processing systems, high-gain high-bandwidth current preamplifiers (preamps), and high-speed feedback (FB) electronics: video-rate STM with 80 images per second has been achieved.<sup>22</sup> Based on ongoing progress in other electronic and mechanical aspects,<sup>22–24</sup> an EC-STM has been developed that can handle significant surface roughness still at sufficiently high scan speeds and resolution.<sup>25</sup> Obviously, the imaging speed has to be reduced the larger the scan size or the surface roughness is. However, 1 image in 1.7 s is still possible even on a surface with 20 steps on a  $155 \times 200 \text{ nm}^2$  area. This enabled the *in operando* observation of the influence of additives that change the morphology and structure of steps during electrodeposition.<sup>26</sup> A selection of our STM-movies is published on the internet.<sup>27</sup>

What is the aim of this article? Despite several existing publications and reviews on STM and EC-STM,<sup>22–25,28–33</sup> some of which address also high-stability, high-speed, and video-rate scanning aspects, an overview is missing that describes the interplay and its consequences of the individual electronic (and mechanical) design aspects. These insights do not only provide the necessary back-ground for anyone, who intents building a video-rate EC-STM, but they are also helpful for improving the resolution and the

reaction time of *any* STM. Speed requires a stiff mechanical design, fast FB, and sufficiently low noise in combination with high bandwidth. A microscope that is designed like this, delivers also superior resolution when operating at low scan speeds: by decreasing the bandwidth, the gains can be increased significantly without crossing the stability border. The overview described below should, therefore, be also of interest for the design of any STM, as it addresses crucial points that allow fine-tuning and improving of the resolution.

The article is organized as follows: starting with a basic overview and understanding in the mechanical loop and its FB, the resolution performance and first concept for a stability criterion is discussed. Based on this insight, the *hybrid mode* is introduced, and its advantages are highlighted and demonstrated with an example. The next section deals with the preamp, its performance, and internal FB. A more accurate version of the stability criterion for FBs is derived including the concepts of phase and gain margins. We address the consequences of unavoidable capacitances and cables, both of which dramatically alter the preamp and, therefore, also, the microscope performance. It is crucial to consider also the noise, as it can lead to an unstable, oscillating preamp. This requires insight in the difference between an ideal and a real operational amplifier (opamp) as well as in the influence of the FB resistor and the input capacitance on the noise performance. As all potentials, and therefore also the tunneling voltage, are controlled via a bipotentiostat, the next section works out its basic function and addresses the most crucial aspects in terms of resolution and stability for the microscope. Finally, as the transfer function of the tunneling junction is part of the FB loop, the junction difference between vacuum and electrolyte is addressed. The article ends with examples that demonstrate the current research possibilities, if one aims on large-scale imaging with significant roughness.

### **Piezoelectric Scanner and its Feedback Circuit**

The movement of the STM tip is achieved via a piezoelectric scanner that can be compared to a driven oscillator. If the microscope operates in the constant-current mode, a fast FB circuit that ultimately determines the resolution of the microscope, controls the height of the tip.

Fig. 1A displays the bottom part of the microscope head with the piezoelectric tube scanner in the middle. Fig. 1B shows a schematic of this scanner including a tip, which in total can be compared to a spring with a weight at the end, as indicated in Fig. 1C. Obviously, the spring constant of the tube exceeds those of standard springs, as it is given by the Young's modulus of the ceramic material. If one wants to move the tip up and down to follow the surface corrugation, or wants to move it laterally in a raster-scan



**Fig. 1** The piezoelectric tube scanner:(A) mounted in the bottom of the microscope head, (B) drawn as a schematic, (C) shown as a corresponding spring system close to the resonance with A(out)/A(in) = 5, (D) and its corresponding transfer function, with a resonance frequency of 10 kHz and a quality factor of Q = 15.

motion to span the desired image size, one has to apply input voltages to the electrodes that are converted into real motions of the tip via the piezo element. This is comparable to the mechanical spring, where one applies a movement at one side with amplitude A(in) that leads to the reaction of the mass (comparable to the tip and its holder) on the other side with amplitude A(out). This analogy can be made in both the vertical and lateral direction, as long as one keeps in mind that these two directions do have different spring constants that lead to different responses and resonance frequencies. Typical values are 10 kHz for the first bending resonance (lateral motion) and 50 kHz for the *Z* resonance (vertical motion).<sup>24</sup>

To get an insight into FB actions, it is instructive to consider transfer functions that describe the output for a given input as a function of frequency. Fig. 1D shows the amplitude transfer function of the scanner. As is discussed below, a complete description has to consider also the phase. At frequencies well below the resonance frequency, the output amplitude simply follows the input amplitude, which is represented by the value of 1. At these frequencies, the mass–spring system is so stiff that no significant internal movement of the spring occurs. The amplitude increases the closer one gets to the resonance, and reaches its maximum at the resonance frequency with an amplitude that equals  $Q \times A(in)$ . Above the resonance frequency, the amplitude decreases and (not shown here) the phase approaches a shift of 180 degrees with respect to the excitation amplitude. Note that at these frequencies stable FB operation is completely impossible: if the tip would be too close to the surface (too large tunneling current), the FB would provide a voltage for retracting A(in) that in turn would lead to an *approaching* reaction A(out) of the tip, due to the 180 degrees phase shift.

## **Height Feedback**

Keeping the above in mind, it is insightful to consider the complete FB circuit of the microscope (Fig. 2): after converting the tunneling current into a usable voltage by means of a transimpedance amplifier (preamp), its exponential distance dependence is linearized by a logarithmic amplifier (Log). This signal is compared with the chosen tunneling-current (applied as a voltage setpoint) such that the error in current can be further treated by the FB, before amplified by high-voltage (HV) drivers and delivered to the corresponding Z electrode(s) of the scanner. As a transfer function describes the ratio of the output to the input of a system, the complete FB circuit can be described by the combination of the transfer functions of the individual elements taking into account that two elements behind each other (series connection) behave as the multiplication of their transfer functions, while two elements in parallel are described by an addition.



**Fig. 2** Feedback circuit of a scanning tunneling microscope. (A) After the amplification of the tunneling current into a usable voltage via the PreAmp, its exponential distance characteristics is linearized by a logarithmic amplifier. This output is compared with a chosen setpoint to receive an error signal that it treated further by the feedback (FB) before it is amplified by HV amplifiers and applied to the *Z* (height) electrode(s) of the piezo scanner. (B) In our case, the FB consists of three elements: an integral gain and a proportional gain in parallel followed by a special low-pass filter.

As long as one stays below the bandwidth of both the electronic components and the subcircuits, the combination of the tunneling current with its exponential distance dependence, the preamp, and the Log results in a linear transfer function of  $U_{Log}$ /*d*, in which  $U_{Log}$  is the output of the logarithmic amplifier (Log) and *d* the distance between the tip and the surface. In addition, as also the transfer functions of both the comparator (used for comparison with the tunneling current setpoint) and the HV-amplifier are linear, one only has to consider the FB action and the highly nonlinear transfer function of the piezo element. The latter was shown already in Fig. 1D. The FB consists, in our case, of three elements: an integral gain, a proportional gain, and a special low-pass filter (Fig. 2B).

If one neglects, for educational purpose, in first instance the phase of the complete loop, an FB circuit is exactly stable when the overall amplitude transfer function stays below 1 for all frequencies! This approach provides enough insight for understanding the basic principles, but it is correct only as a first-order approximation. Below, we consider also the phase and use the Nyquist stability criterion to evaluate the stability of the FB.<sup>34</sup> Anyhow, as long as one stays sufficiently low in frequency, below the resonance frequency of the scanner, the phase shift is small enough justifying the current simplification.

Based on the transfer function of the piezo element, Fig. 3A shows the overall loop, which is linearly (de)amplified to receive maximal response at low frequencies:  $A_{out}/A_{in} = 1$ . This situation is unstable, as the FB loop would overreact to all signals that occur in the vicinity of the resonance frequency, where  $A_{out}/A_{in} > 1$ . Note that this situation is unstable, even when simply *standing* (without scanning) in tunneling conditions on the surface, as the noise in the tunneling current, introduced both mechanically and electronically, still requires FB action. An additional scanning motion requires an even more drastic FB action to adjust the tip height to the height variations of the sample such that this surely would lead to a tip crashing into the surface (tip crash). To get the FB stable, one could lower the gain with a frequency-independent transfer function (a proportional gain), as shown in Fig. 3B.

Although the FB would be now stable, the risk for an undesired tip crash during scanning would be extremely high! This is due to missing gain at low frequencies, which is crucial for following the (macroscopic) surface slope: it is (almost) impossible to mount a sample surface perfectly perpendicular to the axis of the tip. Note that the missing gain equals *Q* of the resonance frequency, which is rather large, as it describes the quality factor of a solid mechanical object: the piezo tube! The solution to this dilemma is the



**Fig. 3** Tuned feedback circuit: (A) maximal response is achieved for low frequencies ( $A_{out}/A_{in}=1$ ); however, the system is unstable, as  $A_{out}/A_{in}>1$  for all frequencies in the vicinity of the resonance frequency of the scanner; (B) the system has been made stable by lowering the proportional gain; however, the risk for a tip crash during scanning is very high, due to lack of gain at low frequencies that is required to follow the macroscopic surface structure; (C) a parallel integral gain has been added that provides the reactions at low frequencies: the system is stable; (D) the typical gain characteristics of a well-tuned system.

addition of a parallel integral gain in the FB (Fig. 2B), that takes care of the low-frequency corrections, whereas the proportional gain delivers the sharpness and detailed information that naturally occur at higher frequencies. Within a certain range, it is possible to tune the balance between the integral and the proportional gain to achieve an optimized performance for imaging samples with either a large-scale roughness or obtaining atomic resolution on flat terraces. Finally, the overall performance can be fine-tuned with a special, serial low-pass filter (Fig. 2B) that keeps its low-frequency gain constant when one changes the filter's corner frequency. A proper use of this filter allows for an even higher gain within the active frequency window. Fig. 3C shows an example of a decently tuned overall FB transfer function. Below it will become clear that the system still is stable with low-frequency gains above 1, as indicated with the dotted line. Stiffer scanners with higher resonance frequencies allow for significantly more usable gain.<sup>24</sup>

Fig. 3D shows the tunable range of the proportional gain, the integral gain, and the low-pass filter (yellow) as realized in our control electronics.<sup>22,24</sup> The blue lines depict switchable decades that effectively enable the tuning of the complete blue area via precision potentiometers. The red line represents a typical FB setting, in which the integral gain crosses 0 dB at 200 Hz before an attenuated proportional gain of -10 dB takes over. To avoid high-frequency noise, the low-pass filter takes over at 100 kHz. Using a standard control electronics in an experiment, one would decrease this filter bandwidth as much as possible without losing the sharpness on the features of interest. When pushing the borders, we use this filter for shifting our hybrid mode, as discussed in the next section.

#### **Hybrid Mode**

Two general STM FB-modes are well known and applied by users: the constant-height and the constant-current mode. In constantcurrent mode, the FB is tuned such that the tip follows all height variations of the surface as accurate as possible. The complete opposite applies for the constant-height mode, in which the tip is kept at constant height during scanning and the surface contour is calculated back from the variations in the tunneling current. Without FB action, this mode is only applicable on very small length scales and flat surfaces, like on a part of one terrace. In addition, thermal drift and piezo creep should be absent making this mode fully applicable only for low-temperature microscopes. Due to significantly less high-frequency movement of the piezo (no variation in height), the constant-height mode allows, in general, fast measurements with higher scan speeds than the constant-current mode. The video-rate experiments of Magnussen<sup>14–19</sup> are all obtained in this mode.

Less known is the hybrid mode, which works at any FB setting between the constant-height and the constant-current mode. It can also been seen as an improvement to the constant-current mode, as it increases its resolution. The added value can be understood when considering the steady state response of a FB (Fig. 2A). If  $h_s$  denotes the height of the sample,  $h_t$  the height of the tip, and G the open-loop gain of the FB, one derives the following equation by realizing that the error in height,  $h_t - h_s$ , is amplified by the FB to adjust the height of the tip:

$$h_t = -\mathbf{G}(h_t - h_s) \tag{1}$$

which can be rewritten to:

$$h_t = \frac{G}{1+G} h_s \approx \left(1 - \frac{1}{G}\right) h_s \tag{2}$$

Several instructive insights can be derived from the above formula.

- The larger the value of *G* is, the better does the tip follow the surface contour.
- A tip-height error of zero implies an absolute tip height of zero.
- A FB always makes an error and can never be exact! This is independent of the value of G.

Another instructive insight can be derived by considering positive FB gain  $(-G \rightarrow |G|)$ , which occurs at large enough phase shift, e.g., at the piezo resonance:

$$h_t = \frac{1}{1 - \frac{1}{|G|}} h_s \tag{3}$$

If |G| crosses one at a particular frequency in the transfer function, the FB becomes unstable, and the tip height becomes infinitely large. Note that this is independent of the height of the surface,  $h_s$ . This situation describes the oscillation of the tip, e.g., at the piezo resonance.

Realizing that any feedback always makes an error, one can consider to measure this error such that height image can be corrected. This is exactly the concept of the hybrid mode. By measuring the so-called error signal, the hybrid mode bridges *the complete* range between constant-height and constant-current mode, as depicted in Fig. 4. Note that height information is no longer lost when changing the FB settings: with settings tuned to measure in almost ideal constant-current conditions, the error signal would approach zero. With increasing scan speed or decreasing FB gain, one would lose information in the height signal. However, this information appears in the error signal. Reaching the constant-height condition, the complete information is in the error signal. In other words, any information that is not present or lost in the height signal is transferred into the error signal. The real surface contour can always be extracted by adding these two channels. Note that the hybrid mode even improves the standard constantcurrent mode when scanning slowly, as it corrects also for the unavoidable error (Eq. 2).



**Fig. 4** Hybrid Mode: As the hybrid mode measured also the error in the height simultaneously together with the height, it bridges the complete regime between constant-height and constant-current mode. Any information that is not present or lost in one of the channels is naturally occurring in the other channel. No information is lost independently how well one tunes the FB. Moreover, as the FB naturally makes an error (Eq. 2), the hybrid mode increases also the resolution for slow, constant-height mode scanning.



**Fig. 5** Example of a Hybrid Mode Measurement: The images are recorded on a Cu(100) surface in vacuum with a line rate of 3 Hz, a sample voltage of -0.7 V, and a tunneling current of approximately 70 pA. The image sizes are  $200 \times 166$  nm<sup>2</sup>: (A) constant-height image, (B) simultaneously recorded error signal of the height, and (C) the addition of both channels, which provides the real surface contour. Note the improved resolution, which is indicated by the *circles*. While scanning, the FB gains have been adjusted to the optimum settings just below the stability criterion—see the band indicated by the *dashed lines*. The response of the FB in the form of a vibration is visible, especially in the error signal. Below the band, the gains have been decreased slightly to reach the standard stable situation.

Fig. 5 demonstrates the increase in resolution for a standard, slow-speed, constant-current mode measurement when applying additionally the hybrid mode. Fig. 5A shows the standard height image that is typically recorded by any control electronics. In addition, Fig. 5B shows the simultaneously recorded error signal of the height. The addition of both signals delivers the real surface contour: Fig. 5C. Note the improved resolution, see the circles. While scanning, the FB gains have been adjusted to the optimum settings just below the stability criterion—see the band indicated by the dashed lines. The response of the feedback in the form of a vibration is visible in this band, especially in the error signal. Below the band, the gains have been decreased slightly to reach the standard stable situation again.

The advantage of the hybrid mode exceeds the aspect of resolution. Higher scan speeds than usual become possible without losing detailed information of the surface. In addition, rougher (and misaligned) surfaces can be scanned with higher speeds, as the FB action can be decreased to just follow the macroscopic surface contour.

# Preamplifier and its Stability

The preamp is a crucial element in an STM, as it often determines, next to the mechanical loop between the tip and the sample, the resolution as well as both the noise and the bandwidth of the complete microscope. Fig. 6A shows the basic electronic scheme of a typical preamp based on the application of an inverted opamp.

It is interesting to note that this circuit works on the basis of a FB, in which the output voltage  $U_{out}$  is coupled back via the FB resistor  $R_{FB}$  to the negative input of the opamp. Due to the input resistance of the opamp (current input rejection), the (tunneling) input current  $I_{in}$  is compensated with an equal negative current from the output. Therefore, the output voltage becomes  $U_{out} = -I_{in} \times R_{FB}$ . However, the considered circuit deviates from reality, and one should take into account unavoidable, hidden capacitances (Fig. 6B).  $C_{FB}$  describes the capacitance of the FB resistor, and its value depends on both the dimensions and the type of the resistor as well as the layout of the printed circuit board. As the impedance  $Z_{C_{FB}}$  of this capacitance is equal to  $1/(i2\pi fC_{FB})$ , with f being the frequency, the output voltage decreases if  $1/Z_{C_{FB}}$  approaches  $1/R_{FB}$ . This limits the bandwidth of the preamp. Similarly, one also has an input capacitance  $C_{in}$ , which is usually dominated by the used input cable and the specific opamp. Also this capacitance limits the bandwidth of the preamp.



**Fig. 6** Transimpedance Amplifier: (A) The first order, ideal scheme of a preamp used in an STM. (B) The real scheme of the preamp includes hidden capacitances at the FB resistor ( $C_{FB}$ ) and the opamp input ( $C_{in}$ ). In addition, the tip-sample impedance is included, as it also changes the transfer function.

Fig. 7 shows the transfer function (this time both amplitude and phase) of an ideal amplifier with  $C_{FB} = C_{in} = 0$  F, in which we assume a tunneling resistance of 100M $\Omega$ . All transfer functions in this section are calculated with Multisim,<sup>35</sup> which is a professional electronic simulation package linked to a huge database. It can even calculate the real (not only ideal) behavior of electronic components.

If one would lower the DC gain below 0 dB, one might think that the preamp FB is stable, in general, as it misses a resonant system that can bring the gain above one. However, the unavoidable capacitances imply phase changes such that feed-forward (180 degrees phase shift) will occur at some frequency instead of FB. If the gain at this frequency is not suppressed enough below 1, the preamp is unstable and will oscillate. The following example delivers deeper insight into the details of stability criterions.

**Fig. 8A** shows the transfer function of a realistic preamp, in which we consider also its own input capacitance with  $C_{in} = 1$  pF. In comparison to **Fig. 7**, one notices two effects due to the input capacitance: the bandwidth is significantly decreased and a "resonance feature" is suddenly present. At this point, the input cable is still neglected, which would lead to a higher effective input capacitance. There are two margins that define the stability of a circuit: the phase and the gain margin. To determine the phase margin, one



Fig. 7 Ideal Preamp: the unavoidable, hidden capacitances are set to zero:  $C_{FB} = C_{in} = 0$  F. The amplitude is shown in *black* and the corresponding phase in *red*.



**Fig. 8** Preamp with Input Capacitance: (A) In comparison to **Fig. 7**, we consider here a realistic input capacitance of  $C_{in} = 1 \text{ pF}$ . The input capacitance leads to a significant decrease of the bandwidth as well as the appearance of a "resonance feature". (B) Logarithmic Nyquist plot allowing to visualize the stability of the transfer functions. (C) The FB gain of the *gray* (and *light red*) transfer function has been decreased from 1 G $\Omega$  to 100 M $\Omega$ . Note that this increases the bandwidth and, surprisingly, even decreases the gain margin.

searches the point of 0 dB loop-gain (black arrow). If the corresponding phase shift would be 180 degrees or more, the circuit would surely oscillate. The phase margin is defined as how far one is away from the 180-degree phase shift. Similarly, to find the gain margin, one looks for the point of 180-degree phase shift (red arrow) and determines how far the loop-gain is below 0 dB. In our case, the phase and gain margin is  $1^{0}$  and 25 dB, respectively.

Note that we refine here, in comparison to sect. "Piezoelectric Scanner and Its FB Circuit", the stability criterion! In general, FB systems can still be stable even with huge gains above 0 dB, as long as the gain is decreased clearly below 0 dB at the frequency where the phase shift is 180 degrees. The stability of a system can be more easily derived via a Nyquist plot (Fig. 8B). In the polar version of this complex plot, the gain of the transfer function becomes the amplitude, and the phase, which is the *ArcTan* of the imaginary part divided by the real part of the transfer function, becomes the angle. The two red dots are the usually considered stability points. A FB is stable, if its transfer function crosses these points at the right side (or more specifically: it should never encircle them!). The point at  $(0 \text{ dB}; -180^\circ)$  defines the real Nyquist stability criterion. However, due to often unknown tolerances of precise component values, one is forced to keep some reserve. In addition, noise and jitter is present in reality, which can make circuits unstable, even if the transfer function does not encircle the Nyquist stability point. Considering these two issues in combination with the acceptable requirement for step-responses (higher frequency signal components), one practically tries to keep a phase margin of 45 degrees with a gain of -3 dB ensuring a stable FB circuit. This point is indicated at  $(-3 \text{ dB}; -135^\circ)$ . Obviously, it is possible to push the border and approach the real stability point very closely keeping just enough distance to allow for the noise and jitter that is present in the system. On the other hand, one single external disturbance, like an electromagnetic pulse, the switching of a lamp, or the movement of an elevator, might be capable to drive such an extremely fine-tuned FB system beyond the Nyquist stability point.

An example of this is the transfer function of Fig. 8A, which does encircle the 45-degree phase margin point, but does *not* encircle the Nyquist stability point at  $(0 \text{ dB}; -180^{\circ})$ . In an ideal world, this circuit would be stable. To ensure the stability, one might think that lowering the gain from 1 G $\Omega$  to 100 M $\Omega$  would help to increase the distance to the  $(0 \text{ dB}; -180^{\circ})$  stability point. The corresponding transfer function is indicated with the lighter lines in Fig. 8C. Surprisingly, when looking back to Fig. 8B, one sees that the distance to the Nyquist stability point has even decreased instead of increased (gray line). The reason for this is that the frequency-gain product is *nearly* constant. By lowering the gain, the bandwidth also increases, which brings the "resonance" closer to the stability point. Counterintuitively, in addition, this example demonstrated that decreasing the low-frequency gain might even lead to less stability if one does not limit (or decrease) the bandwidth.

Let us now also consider the unavoidable FB capacitance that originates from the FB resistor. **Fig. 9A** shows the earlier considered transfer function of **Fig. 8A** in gray. Theoretically, it is possible to compensate the "resonance", introduced by the input capacitance, by an exactly matched FB capacitance of  $C_{FB} = 500$  aF (black line in **Fig. 9A**). Electronic engineers call this "pole compensation". This would lead to a well-behaved FB circuit with a phase margin of 15 degrees and a bandwidth of 360 kHz (**Fig. 9B**). However, tuning a capacitance as low as 500 aF is far from trivial. Tunable, commercial capacitances are available only down to the low pF regime. Moreover, the parasitic capacitance of the FB resistor is usually much larger than the 500 aF, which requires tuning with an accuracy over several decades.

Realizing the importance of the input capacitance, great care had been taken on the electrical connection between the tip and the preamp during the design of our EC-STM.<sup>25</sup> We could realize a final value of only  $C_{in} = 22$  pF. The corresponding transfer functions are displayed in Fig. 10: The dotted lines are the transfer function of Fig. 9. The lightest gray line, with "resonance", corresponds to the uncompensated circuit with  $C_{in} = 22$  pF. This transfer function can be compensated with a FB capacitance of  $C_{FB} = 2.5$  fF (darker gray line). In this configuration, it delivers a stable FB with a phase margin of 20 degrees and a reasonable bandwidth of 75 kHz. Note that this preamp is pushed in performance, as it encircles the 45-degree stability point. Without fine-tuning,  $C_{FB}$  leads to an extreme reduction of the bandwidth, e.g., to only 8 kHz for  $C_{FB} \approx 20$  fF (black line in Fig.10A). Obviously, this FB is more stable, as is does no longer encircle the 45-degree stability point (Fig. 10B).

Let us now finally turn our attention to the STM junction itself. The capacitances between various STM tips and samples have been measured on several different vacuum and ambient setups leading to the following results: typical tip-sample capacitances in vacuum are in the order of 150 fF, and the tip-sample capacitance can be calculated via a ball facing a surface, if the tipsample distance is smaller than the ball radius.<sup>36</sup> Realizing that the dielectric constants of standard electrolytes varies between 5 and 30, that the dielectric constant of water is 80, and that one usually works on very dilute electrolytes, the tip-sample capacitance  $C_{ts'}$  should be in the order of 12 pF. We determined the double-layer capacitances of our etched and coated tips to be in the order of 36 pF, which indicates that the electrolyte capacitance is indeed projected to the double-layer capacitances of the electrodes (36 pF/ 2=18 pF; simplified assumption of two serial-tip capacitances). How much of these capacitances will effectively contribute to  $C_{ts}$  is yet unclear, as it depends on the double-layer overlap of the sample and the tip during tunneling. As the overlap decreases the capacitance, and as (partial) capacitances with small distances are affected most, we expect a significant reduction. Nonetheless, the main message becomes evident, even by assuming  $C_{ts}$  to be only in the order of 1.5 pF.

Fig. 11 shows the corresponding transfer function with a huge "resonance" and phase shift. One would need to limit the bandwidth to 600 Hz in order to make it stable (dashed line). The rising flank of the "resonance" is due to the decrease of the input impedance with rising frequency. This is exactly caused by the tip-sample capacitance. The falling flank is due to the limited bandwidth of the FB, given by the input and FB capacitance. It is possible to also compensate this "resonance" (at least partially) with a proper addition and tuning of an impedance in the FB: we can usually work with a bandwidth of  $\approx$  50 kHz.

In conclusion, the transfer function in Fig. 11 shows that the tip capacitance as well as the double layers of the tip and the sample do have a significant influence on the feedback system, which finally determines also the speed and resolution of an STM. Usually, the tip-sample capacitance alters the performance negatively. However, this drawback offers also opportunities, as it might be possible to design a compensation circuit that allows for a certain variation, once all details and influences of the capacitances (double layers) are fully understood.



**Fig. 9** Preamp with Compensated Input Capacitance: theoretically, the "resonance" feature of the input capacitance can be compensated by an ideally matched FB capacitance. In practice, however, this is almost impossible (see text for more details). The bandwidth of the ideally matched circuit would be 360 kHz.

# **Preamplifier Noise**

Next to the stability issues described in the above section, the noise performance of the preamp is of crucial importance. The more noise is present, the earlier the FB circuit, which controls the height of the tip tip, becomes unstable. As a consequence, one has to lower the gains and/or decrease the bandwidth, which implies lower resolution and speed.

When considering the noise of a preamp, one has to realize that an opamp is far from ideal. Fig. 12 shows the difference between an ideal opamp and a realistic model that includes the input voltage noise ( $v_n$ ) and the input current noise ( $i_n$ ) between the terminals. These values can be found in the technical data sheets of the specific opamp in question. Also the input capacitance ( $C_{in}$ ) is of crucial importance, as it increases the FB gain for higher frequencies, thereby amplifying the input noise. Note that any cable capacitance or parallel capacitance of the current source is added to  $C_{in}$ . Another dominant noise source in an FB-coupled transimpedance amplifier is the Johnson noise of the FB resistor  $v_{R_{FB}}$ . Finally, one also has 1/f noise, which becomes significant only at low frequencies when the bandwidth of both the amplifier and the signal source extend down to DC. We neglect the latter noise term in the following and assume further that the spectral noise density is constant, which means that the power of the noise is proportional to the bandwidth. This usually is a good approximation and one finds the current-noise density and the voltage-noise density in the technical specs of the opamp in units of  $fA/\sqrt{Hz}$  and  $nV/\sqrt{Hz}$ , respectively.

As the above described noise terms are usually uncorrelated, and as random noise sources add up with the root of the sumsquares, one can eliminate the input current noise ( $i_n$ ) as well as the Johnson noise of the FB resistor ( $v_{nR_{FB}}$ ) and lump them in a final voltage noise  $\tilde{v}_n$  that replaces  $v_n$ :

$$\widetilde{v}_n = \sqrt{v_n^2 + (i_n R_{FB})^2 + v_{nR_{FB}}^2} \tag{4}$$



**Fig. 10** Preamp with Input Cable: An input cable with a capacitance of only  $C_{in}=22$  pF decreases the bandwidth from 360 kHz down to 75 kHz. The system is still stable and the "resonance" is compensated with a matched FB capacitance of  $C_{FB}=2.5$  fF. Considering a standard FB capacitance of  $C_{FB}\approx 20$  fF, the bandwidth decreases further to 8 kHz.

When using opamps with metal–oxide–semiconductor field-effect transistors (MOSFETs) or junction gate field-effect transistors (jFETs),  $i_n R_{FB}$  can usually be neglected, due to the extremely small input current noise. Evaluating the total noise and calculating it back via the FB resistor  $R_{FB}$  leads to the total current noise density:

$$\widetilde{i}_n \ge \sqrt{\left(\nu_n 2\pi f C_{in}\right)^2 + \frac{4k_B T}{R_{FB}}} \quad \left[fA/\sqrt{Hz}\right],\tag{5}$$

in which  $k_B$  is the Boltzmann constant and *T* the temperature of the FB resistor.

Fig. 13 shows the total equivalent current-noise density as a function of frequency. Note that the noise is significantly increasing when either lowering the FB gain or increasing the input capacitance! From Eq. (5) it also becomes clear that cooling of the FB resistor would lower the noise density considerably, thereby improving the signal-to-noise of the preamp.

In the above evaluation, we neglected the noise that is introduced by the tunneling voltage variation as well as the noise of the tunneling process itself. The bipotentiostat, the cabling, and the cable shielding are the reason for the first noise term, whereas the stochastics of the tunneling process is subject to actual research <a href="https://www.nature.com/articles/ncomms13009">https://www.nature.com/articles/ncomms13009</a> and probably negligible in size for the considered stability arguments. Anyhow, due to the additional noise, one has to downtune the FB such that still enough stability margin exists.

### **Bipotentiostat**

As indicated in the previous section, the tunneling-voltage noise plays an important role in the FB stability, and thereby also for the performance of the microscope. This voltage is controlled and delivered by a bipotentiostat, which unfortunately consists of several FBs.



Fig. 11 Preamp with Tip-Sample Capacitance Contribution: With a tip-sample capacitance of only 1.5 pF, the effective bandwidth drops down to 600 Hz if the circuit is not compensated.



**Fig. 12** Real versus Ideal Opamp: The performance of a real opamp can be derived by considering a noiseless, ideal opamp in combination with its input capacitance as well as input voltage noise ( $v_n$ ) and input current noise ( $i_n$ ) between the terminals.

A not yet introduced FB circuit is the so-called voltage follower (Fig. 14). By using the positive terminal of the opamp for the input voltage, the output voltage is coupled back in a FB loop to the negative input terminal. The combination of the huge gain, A, together with the FB ensures that the output voltage is (almost) the same as the input voltage. Using a voltage follower, one can minimize a possible measurement influence on a system. Due to the high input resistance, (almost) no current is dragged from the system of interest, thereby decoupling it effectively from the measurement circuit.



Fig. 13 Equivalent Current-Noise Density: The final noise is significantly increasing when either lowering the FB gain or increasing the input capacitance.



**Fig. 14** Voltage Follower: due to the FB and the high gain, A, the output voltage is almost the same as the input voltage. A voltage follower minimizes a possible measurement influence, as it effectively decouples the system via the high input resistance of its positive terminal.

Fig. 15 shows a simplified diagram of our bipotentiostat.<sup>37</sup> The positive tip and the inverted sample potential are applied to external inputs via the opamps OP1 and OP2, respectively. These are voltage followers with a low-pass-filtered FB (F in Fig. 15), to remove high-frequency noise of the DAC controller system as well as to smoothen the digital steps when performing a cyclic voltammogram. The voltage at the output of OP1 is  $+ U_t$  (indicated in blue), which is fed forward via a resistor bridge to the negative terminal of OP3. OP3 together with OP4 forms the most crucial FB circuit (indicated in red) of the bipotentiostat that is closed via the complex impedances of the electrolyte between the counter electrode ( $Z_{CE}$ ) and the reference electrode ( $Z_{RE}$ ). To cancel the input current at the negative terminal of OP3 (induced by  $+ U_t$ ), the output voltage of OP3 increases until OP4 reaches and applies  $- U_t$  via the other resistor to the same negative terminal of OP3. As OP4 is a voltage follower, point P in the electrochemical cell is exactly at  $- U_t$ . Note the following important points:

The FB is controlled on the voltage of point P such that CE can deviate from  $-U_t$ . The voltage of CE depends on the current through the cell and equals  $-U_t$  only if no electrochemical current is flowing. The higher the electrochemical current is, the more shifts the potential of the counter electrode (CE), which in the end enables the electron transfer on this half cell. Even if the complex impedances in the cell are changing, e.g., due to a change of the double layers, point P will remain on  $-U_t$  at any time. Furthermore, any current that would flow into RE, would introduce a voltage shift via  $Z_{RE}$ . This is prevented by the application of the voltage follower OP4.

Let us now consider the voltages on the tip and the sample. To get a standard tunneling preamp running stable, it is crucial to have the tip on ground (GND). This is exactly the reason for this rather unusual bipotentiostat. The electrochemical current on the sample (WE) is measured via a low-gain preamp OP6, of which the positive terminal is raised to  $-U_t + U_s$  via OP5. In this way, the potential of WE is also  $-U_t + U_s$ , which we measure, in addition, directly via the voltage follower OP7.

If one now adds  $+ U_t$  to the real electrode potentials that are applied in the cell,  $U_{RE} = -U_t U_{Tip} = GND$ , and  $U_{WE} = -U_t + U_s$ , one realizes that the desired input potentials are made available for the tip and the sample. This concept is valid, as the complete electrochemical cell is designed fully floating (except for the tip). In other words, we can shift the "GND" of the complete cell by any potential, as long as this is applied to all other electrodes. This method allows the use of high-performance current preamps that naturally have a GND at the positive input terminal.

Both the stability and the noise of the bipotentiostat depend on the input noise, the FB gains, and their corresponding bandwidths. We neglect the real noise of the system stemming from electrochemical reactions within the cell. As the inputs are filtered and decreased in bandwidth via the Fs in the scheme, their noise contribution is negligible. To further ensure a stable FB in the system, bandwidth switches (BW) are implemented that have to be properly adjusted by the user depending on the applied electrolyte, sample, potential, and tunneling current preamp. Note that the tunneling voltage is the difference between the tip and



**Fig. 15** EC-STM Bipotentiostat: two electrodes, the tip and the sample, have to be controlled in potential for STM operation. To enable the use of high-performance tunneling preamps, a floating design is necessary that allows to connect the tip directly to ground (GND). This floating design requires a stable FB system (indicated in *red*) that keeps the reference voltage at point P exactly at  $-U_t$ . The noise and stability performance depends on the gains and bandwidth. As the noise of the tunneling current depends linearly on the noise between the tip and sample potential, the characteristics of the bipotentiostat critically influence the stability and noise of the tunneling preamp. To ensure stable tunneling, bandwidth switches (BW) in the bipotentiostat are implemented that have to be properly adjusted by the user depending on the applied electrolyte, sample, potential, and tunneling current preamp.

the sample potential, both of which are controlled via the FB circuit. This naturally introduces additional noise, which can bring a barely stable tunneling preamp that is pushed to its limits, into oscillation. The lower the operator chooses the BW bandwidth, the more stable becomes the whole system enabling the use of high-speed preamps and, therefore, video-rate operation. This, on the other hand, clearly limits the electrochemical bandwidth such that cyclic voltammograms do get distorted and Faradaic reactions on the sample are kinetically limited.

### **Tunneling Current and Work Function**

As the transfer function of the tunneling current versus the tip-sample distance is part of the (height) FB loop, one should also consider its properties. The tunneling current depends on the work function  $\Phi$  as

$$I(d) \propto \exp\left(-1.025 \times \sqrt{\Phi} \times d\right) \tag{6}$$

in which *d* is the distance between the tip and sample. The work function of metals in contact with vacuum lies typically between 3 and 5.5 eV. As it still requires some energy to free an electron from an electrolyte into the vacuum, it is obvious that the work function for a metal immersed in electrolyte is significantly reduced in comparison to the vacuum work function. Although extreme values of 0.2  $eV^{38,39}$  and 3.8  $eV^{40}$  have been reported, most of the tunneling barriers have been found to lie between 1.0 and 1.5  $eV^{.41-44}$  This has significant consequences for the resolution and the gain.

Fig. 16 shows the evaluation of the tunneling current for  $\Phi = 4.5$  eV and  $\Phi = 1.5$  eV assuming a tunneling voltage of 0.1 V. It implies that the tunneling current decays with a factor of  $e^{-2.2} = 0.11$  per Å in vacuum, whereas in electrolyte the decay is only  $e^{-1.3} = 0.27$  per Å. In electrolyte, the system does have  $\approx 2.5$  times less gain, which, in the first instance, can be compensated by the FB gain settings. However, there is also a geometric resolution issue involved that cannot be compensated.

In vacuum, the typical tunneling distance at 1 nA is about 2–3 atomic spacings (or  $\approx 7.5$  Å).<sup>45–47</sup> Due to the significantly smaller work function in the electrolyte, one would have to tunnel with  $\approx 6 \,\mu$ A to operate at the same distance. This is far beyond the maximum tunneling range of 10 nA, which corresponds to the maximum power-supply voltage of 10 V, of a preamp with a gain of 10<sup>9</sup> V/A. One would have to apply a preamp with a gain of only 10<sup>6</sup> V/A to operate under these conditions. This would seriously decrease the resolution, due to the deterioration of the signal-to-noise performance (see above). Therefore, EC-STM images are often acquired with tunneling currents between a few tens to a few hundreds of nA. Even at these high tunneling currents, the tip is still further away from the surface than under the corresponding vacuum conditions. This has impact on the resolution, as the



**Fig. 16** Tunneling Current in Vacuum versus Electrolyte: the difference in the work function leads to a different gain in the FB. It also implies a significant larger distance between the tip and the sample for the same tunneling current. As a consequence, true atomic resolution on a fcc(111) terrace is more difficult to achieve in electrolyte than in vacuum.

tunneling current is the (spherical) integral around the tip apex (ideally the last atom). With a lower decrease of the tunneling current versus distance, the tunneling contribution from neighboring atoms is higher: atomic resolution is, in general, harder to achieve, the further the tip is away from the surface.

In conclusion, low tunneling currents as in vacuum are in electrochemical environments the exception rather than the rule. Although one can compensate the lower gain due to the lower work function by the FB settings, one faces a geometric resolution problem due to either the worse signal-to-noise performance of a preamp with lower gain or increased distance of the tip to the surface. Depending on the system, one needs to find the right balance. In addition, full atomic resolution on an fcc(111) surface, like shown in,<sup>28,30,48–50</sup> (and not the imaging of some adsorbates on top) is much harder to achieve in electrolyte than under vacuum conditions.

# **Examples**

So far, we were interested in the more macroscopic evolution during copper electrodeposition. Therefore, the following examples, all obtained on Cu(100) single crystals, demonstrate the capabilities of our microscope, in which we pushed the borders in terms of large image sizes together with both significant roughness and high scan speeds. At these conditions, it is impossible to scan with 25 images per second such that these examples officially do not fall under the definition of video-rate scanning.<sup>23</sup> A proper comparison and classification of high-speed imaging should account also for the tip speed and not only the frame time. In the following examples, we reach tip speeds of 102,400 nm/s. For comparison, if one assumes that the images in figure 6 of<sup>21</sup> have been recorded with  $300 \times 300$  pixels<sup>2</sup>, their tip speed was 22,500 nm/s.

Fig. 17 shows four consecutive,  $150 \times 150$  nm<sup>2</sup> large images from a movie obtained during copper electrodeposition in the presence of chloride imaged with a frame rate of 1 Hz. There are approximately 20 monolayers (steps) within the scan size. The images are differentiated from right to left for better visibility of the step edges, which gives the impression of a light that shines from the right side onto the surface. It is interesting to notice that the step growth speed varies significantly for steps at different local positions on surface. The particular geometric configuration of the surface in the close vicinity to the step must be the reason for this.

Fig. 18 shows four consecutive,  $200 \times 200 \text{ nm}^2$  large images from a movie obtained during copper electrodeposition imaged with a frame rate of 1 Hz. These are exactly the same conditions as during the experiment shown in Fig. 17, except for the fact that now also SPS is present in the electrolyte next to chloride. The growth changes significantly! The former straight steps become more rough with the formation of many kink sites.

Fig. 19 shows that it is possible to even capture the large-scale growth evolution during deposition with several tens of steps on a  $500 \times 500 \text{ nm}^2$  large area. The growth of mounds with straight steps can be followed.

# Conclusion

In this article, I addressed all critical (mostly) electronic details one should carefully pay attention to when trying to realize a videorate or high-speed EC-STM that can deal also with significant surface roughness. Several FBs are simultaneously active. As they



Fig. 17 Copper electrodeposition in the Presence of Chloride: Although we observe  $\approx$  20 monolayers (steps) on 150  $\times$  150 nm<sup>2</sup> large area, we still can image with a frame rate of 1 Hz and a tip speed of 76.8  $\mu$ m/s.



**Fig. 18** Copper electrodeposition in the Presence of Chloride and SPS: In contrast to the straight steps of **Fig. 17**, the steps do show significantly more roughness and kinks during the growth. The scan size is  $200 \times 200 \text{ nm}^2$  imaged with a frame rate of 1 Hz and a tip speed of  $102.4 \mu \text{m/s}$ .

influence each other, it is of crucial importance to find the proper balance between low noise, high resolution, large bandwidth, and fast reaction time of the microscope in combination with the desired electrochemical experiment as well as required electrochemical current resolution.

The hybrid mode enables to measure at all conditions between the *ideal* constant-height mode and the constant-current mode. It allows one to tune the height FB less critical without losing information: disappearing surface information from the height channel is projected into the error signal. In this way, the microscope can measure also on surfaces with significant roughness, while maintaining sufficient scan speed. The hybrid mode enhances even the resolution for the standard constant-height mode, as we have seen that each FB always makes an error. Each STM can profit from this enhancement.


**Fig. 19** Large-Scale Evolution in the Presence of Chloride: macroscopic surface evolution during copper electrodeposition capturing several tens of steps on a  $500 \times 500 \text{ nm}^2$  large area. Without crashing the tip, the development of several mounds with straight steps can be observed. It took 260 s to record one of the  $512 \times 512 \text{ pixel}^2$  images with a tip speed of 2.0  $\mu$ m/s (A–D). Panel (E) is a slow standard recording after the movie to inspect the larger area.

The preamp is the next crucial element of an STM. It also works with an (internal) FB. We have seen that tiny details in its design as well as internal and external, unavoidable capacitances do have a dramatic influence on its performance. Cable and tip-sample capacitances lower the bandwidth of the preamp and/or can lead to an unstable behavior due to oscillations. It is possible to compensate for these capacitances; however, it must be a perfect match not to worsen the complete characteristics. Realizing that the double layers depend on the particular electrolyte, surface, surface area, and electrode potential, one should, in principle, retune the matching, when changing one of these quantities. As this is not workable, one needs to find a suboptimal setting that fits most of the operation conditions.

Finally, there is the bipotentiostat, which again consists of various FBs. It keeps the potential of a fixed point in the electrochemical cell constant independently of any flowing current. Furthermore, it ensures the proper sample and tip potential, and enables to read out the electrochemical current without influencing the system. It is important to realize that the noise and stability of the preamp crucially depends also on the noise and stability of the bipotentiostat, as the latter regulates the tunneling voltage via the tip and sample potentials.

In general, one would like to achieve as high as possible gain for all FBs. However, due to the constant frequency-bandwidth product, this would lower the bandwidth, and thereby limit also the video-rate capabilities and reaction time of the microscope. Lower gain, on the other hand, implies also a lower signal-to-noise ratio. One carefully has to consider the desired circumstances. This allows the best tuning such that the FB and the preamp is just critical. Unfortunately, one has to consider also the electrochemical requirements. Certain reactions need certain currents such that one might need to increase the bandwidth of the bipotentiostat FB. In doing so, more noise is present in the cell and therefore also in the tunneling voltage. A critically tuned preamp and height FB might easily become unstable due to this additional noise.

Therefore, I conclude in general:

Depending on both the particular electrochemical system of interest and on the particular question regarding the surface structure—resolution or speed—it is possible to fine-tune an EC-STM to deliver the best performance for this experiment. This requires also fine-tuning of all active FBs considering their influences on each other!

# **Further Reading**

The following provides a selection of works that contain additional and further information for the interested reader divided into different topics: general electronics,  $^{51-53}$  smart control systems,  $^{54-57}$  advanced piezo control,  $^{58-60}$  scan generation,  $^{61,62}$  and the STM-"bible"  $^{63}$ .

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See also: Atomic Scale STM Imaging of Alloy Surfaces With Chemical Resolution; Electrochemical Scanning Tunneling Microscopy; Scanning Electrochemical Microscopy in the AC-Mode; STM and STS of Oxide Ultrathin Films.

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# How to Probe Structure, Kinetics, and Dynamics at Complex Interfaces In Situ and Operando by Optical Spectroscopy

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# Glossary

**Absorption spectroscopy** Investigation of wavelength (or equivalently, photon energy) dependence of absorption of light by a sample. Absorption happens typically by excitation of an electronic transition, a molecular vibration, or a lattice vibration, following certain transition rules. The absorbed fraction of light is characteristic for the amount of absorbing species present. Quantification is typically performed after combination with a reference measurement, of a "blank" state, but is straight forward. Combined with reflection techniques, "reflection absorption" spectroscopy can be used to characterize interfaces. **Electronic transition** A change in the occupation of the allowed electronic energy levels in a system.

**Emission spectroscopy** After excitation of the system in a certain form, the light emitted by a certain mechanism is spectroscopically analyzed. This group of techniques is very heterogeneous; different excitation mechanisms can be used to probe different transitions.

**Evanescent wave** A wave that exponentially decays into the rarer optical medium under conditions of total reflection. As this evanescent wave interacts with the rarer medium, species near the interface to the denser medium can be probed by this evanescent wave. This approach is used for example, in attenuated total reflection spectroscopy or surface plasmon resonance.

The characteristic decay length of evanescent waves excited in the spectral range discussed in this article is typically larger than 100 nm. In a wider context, evanescent waves are modes that are present only near an interface, that is, they are not propagating. Evanescent waves can help to enhance the interface specificity of a large variety of optical techniques. **Ex situ** The opposite of "in situ"; in ex situ analysis, a sample is typically removed from its native environment, and subjected to conditions required for a certain analysis. In other words, the sample is made suitable to work with a certain method. Ex situ analysis yields typically extremely detailed information; there are more techniques available, and data is easier to gather. However, only some features of a sample may be analyzed, and interactions with its environment are excluded.

In situ Meaning "in its (original) place; in position"<sup>1</sup>; in the context of in situ analysis refers to the analysis of a sample without removing it from its original native environment, and including the interactions with its native environment in the analysis. In an ideal experiment, it implies making the analysis method suitable to the sample and analytical problem. Typically, the information obtained from in situ analysis is less detailed, and more noisy than in ex situ analysis. There are also fewer techniques available.

Lattice vibration A vibrational mode of a crystal lattice, for example, a phonon. The equivalent of a molecular vibration in a crystal.

**Molecular vibration** A mode in which a molecule or a part of a molecule oscillates. Certain modes are characteristic for individual bonds, because only individual bonds participate, for example, C–H stretching. Other modes are delocalized over larger parts or the whole structure of a molecule with many bonds participating, and are thus characteristic for a complete molecule. There are also "collective" vibrational modes of several molecules with respect to each other, typically low in photon energy.

**Operando** Meaning "during operation." Analysis of a sample "operando" shares many features with "in situ." It may be defined as in situ analysis during a running process.

Reflectance absorbance (also known as reflection absorbance) *RA* The reflection equivalent of absorbance  $A = -\log_{10}(I_{smp}/I_0)$ , where  $I_s$  denotes the intensity of light recorded after reflection from a surface in a certain state to be probed, while  $I_0$  denotes the intensity of light reflected from a surface in a reference state. In transmission geometry, Lambert-Beer's law applies, according to which light intensity decreases exponentially with thickness *d* of an absorbing medium with absorption coefficient  $\alpha$  through which light passes, that is,  $I_s = I_0 \cdot e^{-\alpha d}$ . The same logarithmic normalization as used in transmission geometry is also useful in reflection geometry.

**Surface enhancement and tip enhancements** Local, time-averaged electric field amplitudes are high around certain structures, for example, in nanosized gaps, or around sharp tips. As all optical spectroscopic processes depend on the local field strength, the sensitivity of a spectroscopic experiment is greatly enhanced by and in the presence of structures yielding such "surface enhancement."

Nomenclature Abbreviations	
ATR	Attenuated total reflection
DBTA	2,2'-dibenzothiazole disulfide, an oxidation product of MBT
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
FIR	Far IR
IR	Infrared
IRRAS	Infrared reflection absorption spectroscopy
NIR	Near IR
MBT	2-mercaptobenzothiazole; a corrosion inhibitor used to exemplify some techniques
MIR	Mid-IR
PL	Photoluminescence
РМ	Polarization modulation
SEIRAS	Surface-enhanced IR absorptionspectroscopy
SERS	Surface-enhanced Raman spectroscopy
SFG	Sum frequency generation
SPR	Surface plasmon resonance
TERS	Tip-enhanced Raman spectroscopy
UHV	Ultra-high vacuum
UV	Ultraviolet
VIS	Visible

Symbols	
с	Velocity of light in vacuum
Ε	Photon energy, $E = hf$
E	Electric field
f	Frequency
h	Planck constant
Ι	Intensity of light ("irradiance"), $I =  \mathfrak{G} ^2$
i	Imaginary unit, $i = \sqrt{-1}$
n	Real part of the complex refractive index
k	Imaginary part of the complex refractive index
r	Amplitude reflection coefficient, $r = \mathfrak{G}_{\text{reflected}} / \mathfrak{G}_{\text{incident}}$
R	Reflectivity, $R = I_{\text{reflected}}/I_{\text{incident}}$
RA	Reflectance absorbance
Δ	Ellipsometric phase shift, $\Delta = Phase_p - Phase_s$
٤	Complex dielectric function, $\epsilon(f) = [n(f) + ik(f)]^2$ for nonmagnetic materials
λ	Wavelength of light in vacuum
$\widetilde{\nu}$	Wavenumber, $\widetilde{\nu} = 1/\lambda$
Ψ	Ellipsometric amplitude ratio, $\tan \Psi =  r_p / r_s $
W <sub>0</sub>	Index 0 denotes a reference state, for example, a clean surface without adsorbate
Wp	Index p denotes p (parallel) linear polarization
Ws	Index s denotes s (perpendicular) linear polarization
W <sub>smp</sub>	Index smp denotes a sample surface, for example, a surface with an adsorbate to be analyzed

# Why "In Situ"? Scope of This Chapter

Interfaces between a solid phase and gas, a liquid or complex fluid phase are important in nature and technology. Surfaces as interfaces between a solid phase and UHV have been used as model systems to yield extremely detailed and important insight into fundamental physical phenomena. UHV surface science usually employs methods enabling detailed experimental characterization of atomic and electronic structure, often based on spectroscopic, diffraction, or scattering techniques involving electrons.<sup>1,2,3</sup> Interactions between liquids and a solid, however, lead to qualitatively different interface structures. In addition, the same techniques that yield detailed information about the solid side of a solid/liquid interface cannot be used to obtain information about the liquid side.

While the application of UHV-based techniques after removal of a solid from solution or a specific atmosphere is an option for detailed analysis, samples are often prone to changes.<sup>4</sup> Consider a metal/solution interface. In solution, the work function of the metal is often determined by the electrode potential. The latter can be controlled, for example, by redox couples or a connection to an external electric circuit. While drying a metal surface, the electrode potential will change. It changes especially when the system undergoes intermediate states where a low liquid volume is in contact with the surface. Control of the potential under these conditions is extremely challenging. A solvent itself will have a certain dynamic structure at interfaces, which is different from the structure in the solvent bulk. "Soft" interfaces pose intrinsically special challenges, as these form often only by presence of two phases which are easily changing. Proteins as an important class of biomolecules often present at interfaces may denature. Self-assembled or self-organized structures form only in contact with a solution phase, and many of the latter will disintegrate if removed from their environment.<sup>5–9</sup>

Consequently, there is a need for experimental techniques which are suitable for nondestructive characterization of interfaces with limited accessibility. This has typically been the domain of photon-based techniques, which shall be introduced in this article. These techniques have in common that they require at least one side of the interface to be transparent to the photons in the energy range needed to probe the system. With this requirement, metal/metal interfaces are not easily studied with these techniques. Optical techniques can by and large be used in a noninvasive and nondestructive manner.

This article shall discuss spectroscopic methods, using photon energies below  $\approx$  7 eV, that is, wavelengths above  $\approx$  175 nm, and leave out diffraction and scattering methods. Data analysis for the latter is involved and gives typically information on morphological features at mesoscopic or macroscopic length scale. The wavelength range limitation also means that the X-ray range is completely left out of this article, though some conceptual similarities exist. The UV range as the highest energy range to be dealt with here is typically defined with wavelengths above 121 nm, the wavelength of characteristic fundamental transitions in the spectrum of the H-atom. However, for interface characterization, the transparency requirement makes only part of the UV range suitable.

This article shall only briefly summarize the analytical value of the corresponding bulk analytical techniques. In-depth introductions into these methods are available, covering physical basics,<sup>10</sup> as well as analytical applications.<sup>11,12</sup> A brief coverage of physical fundamentals of optical absorption and in particular its relation to interface characterization is also available from our group.<sup>13</sup> Instead of repeating these, this article focuses on specifics of interface analysis with the respective methods, and should give a brief introduction into the different methods, linking to overview sources for the respective methods, as well as pointing out some specific applications. With respect to the latter, the authors do not attempt to present an unbiased overview over the whole field. This article shall also not focus in detail on the instrumentation for the individual methods, but rather conceptually on the mechanisms and type of information available through the individual methods. It is important to know that from the method point of view, optical spectroscopy is useful for investigating a large class of substances at interfaces, including inorganic compounds, for example, oxides, small organic molecules, and macromolecules such as proteins. Likewise, the techniques can be used both at "hard" and "soft" interfaces, as long as refractive index differences exist across the interface.

In general, the techniques here can be employed for the study of structural aspects, kinetics as well as dynamics of species at interfaces. Every spectroscopic experiment probes intrinsically dynamics, as a dynamic photon–material interaction is involved. The examples will contain all three aspects. However, we will not discuss in detail advanced experiments.

#### **Overview Over In Situ and Operando Spectroscopic Techniques**

Depending on the spectral range used, different spectroscopic transitions can be excited (Table 1; Fig. 1). The type of information to be obtained is essentially the same as in the respective bulk techniques. The transitions will briefly be discussed in the respective sections.

Light is characterized by its vacuum wavelength  $\lambda_i$  its photon energy  $E_i$  its frequency  $f_i$  or its wavenumber  $\tilde{\nu}_i$ 

$$E = hf = h\frac{c}{\lambda} = hc\tilde{\nu} \tag{1}$$

In different scientific communities, different quantities are predominantly used. Therefore, several common yet different quantities will be used in different parts of this article. The use of the photon energy *E*, typically measured in eV, is common in the context of solid-state physics. Wavenumber  $\tilde{\nu}$  is frequently used in vibrational spectroscopy. Wavelength  $\lambda$  is common in general spectroscopy, especially in the visible range.

For interface characterization, at least one phase must have sufficient transparency in the spectral range to be used. For instance, using a solvent with strong absorption bands in the MIR might cause problems by blocking relevant parts of the spectrum through total absorption. On the other hand, strong absorption means also high sensitivity toward a small amount of species at an interface. In the NIR, many solvents are transparent, and consequently, sensitivity toward most species at interfaces is rather low. Techniques in which the excited mode has a significantly different energy than the detected wavelength, such as Raman spectroscopy, decouple the transparency of the environment from the probing energy, hence suffer less from a transparency problem.

Region	Wavelength range	Wavenumber range	Photon energy range	Typical type of excitation
Far-Infrared (FIR)	666.7–20 μm	15–500 cm <sup>-1</sup>	0.0019-0.062 eV	Collective modes, localized vibrational modes, or lattice vibrations involving motion of heavy atoms, rotational modes, free carrier absorption
Mid-Infrared (MIR)	20–2.5 μm	500–4000 cm <sup>-1</sup>	0.062-0.496 eV	Localized vibrational modes involving motion of light atoms, delocalized vibrational modes of for example, organic molecules (e.g., molecules consisting mainly of light atoms), free carrier absorption
Near-Infrared (NIR)	2.5–0.75 μm	4000–13,333 cm <sup>-1</sup>	0.496–1.653 eV	Harmonics (overtones) of vibrational Modes, electronic transitions of molecules with a very widely delocalized electronic system, electronic transitions of semiconductors with very low band gap, free carrier absorption
Visible (VIS)	0.75–0.4 μm	13,333–25,000 cm <sup>-1</sup>	1.653-4.000 eV	Main electronic transition of molecules with a widely delocalized electronic system or low band gap semiconductors, electronic transitions in complexes, defect level-related transitions in semiconductors or insulators, free carrier absorption
Ultraviolet (UV)	0.4–0.122 μm	25,000-81,967 cm <sup>-1</sup>	4.000-10.163 eV	Main electronic transition of all other molecules, semiconductors with sufficiently high band gap, and insulators

Table 1 Which transitions are excited in which spectral and photon energy ranges? The given spectral ranges should be treated as approximate only

The methods for in situ spectroscopy treated in this article are summarized in Table 2.



**Fig. 1** Transitions excited in different spectroscopic experiments used to probe interfaces, on the example of a molecular system, using the terminology used for describing molecular systems with singlet states  $S_0$ ,  $S_1$ , and  $S_2$ , and triplet state  $T_1$ . A similar scheme applies for the same processes in solids with a band structure; in this case,  $S_0$  would correspond to the valence band (VB), and  $S_1$  to the conduction band (CB). The different processes and techniques described in this article are labeled. Solid arrows belong to processes related to light absorption or light emission. Dashed arrows indicate processes without emission of electromagnetic radiation. Solid lines represent allowed energy states in the system. Dashed lines represent virtual states. Color coding is used to link the respective process to the description in the inset. The processes discussed in this article are labeled at the bottom.

# Absorption Spectroscopy

An important feature is the absorption of light, which can be directly measured also for interface characterization. Absorption of electromagnetic radiation can take place when the energy of the radiation matches the energy difference between two states with energies  $E_1$  and  $E_2$ . In addition, a dipole moment change must be associated with the transition (dipole transition). The two states can be two electronic states, such as those labeled S<sub>0</sub> or S<sub>1</sub> in Fig. 2. The two states may also be vibrational states, which are substates in the respective electronic states and denoted by black lines in Fig. 1. Both short<sup>13</sup> and long<sup>10</sup> introductory descriptions of the involved processes are available elsewhere.

#### UV/VIS

## **General principles**

In the UV/VIS region of the electromagnetic spectrum, predominantly electronic transitions are excited, see Fig. 1. In addition to the nonvanishing dipole moment required for a transition to be active in the UV/VIS, there are rules for the spin in the involved states. Multiplicity M = 2S + 1, with total spin quantum number *S*, may not change during an electronic transition (spin–forbidden transition). Consequently, during a transition induced by light absorption, molecules in singlet states will remain in singlet states, and those in triplet states remain in triplet states.<sup>14</sup>

In certain cases, the symmetry of the wavefunctions associated with the states involved can have a symmetry which forbids transitions between the levels (symmetry–forbidden transition). In a centrosymmetric molecule, the wavefunctions can be symmetric (s) or antisymmetric (as) with respect to the symmetry center. Transitions between orbitals of the same symmetry are not allowed. Allowed are transitions that comply with  $s \rightarrow as$  and  $as \rightarrow s$ , but transitions of the types  $\rightarrow s$  and  $as \rightarrow as$  are forbidden.

# Table 2 Overview over different in situ spectroscopic techniques discussed in this article

Technique	Short description	Surface specificity	Typical limits	Section
Absorption spectroscopy in UV/VIS	Absorption of light typically by excitation of electronic transition which change the dipole moment in molecules or solids. Yields information on the presence of certain species, quantity of species with high sensitivity, conformation, orientation, effect of solvation on electronic states.	None intrinsically; can be obtained for example, by surface enhancement, ATR, polarization modulation, ellipsometry	Absorption from dissolved species, often broad bands of only few species, low specificity	"UV/VIS" section
Absorption spectroscopy in IR	Absorption of light typically by excitation of vibrational modes with change in dipole moment, or by excitation of electronic transitions in metals. Yields information on the presence of certain species with high specificity, quantity of species, conformation, orientation, state of solvation. Most molecular systems and compound solids show absorptions.	None intrinsically; can be obtained for example, by surface enhancement, ATR, polarization modulation, ellipsometry	Absorption from dissolved species or solvents leads to decreased transparency. Low sensitivity. Complex spectra.	"IR" section
Spectroscopic ellipsometry	Quantitative absorption spectra (e.g., UV/VIS/IR) of substrates and interfacial regions are obtained via probing the change in polarization upon interaction with a sample. Yields information on thickness of interfacial region by measurements of a relative phase shift. Determination of complex refractive index possible. From this data, same information obtained as by absorption spectroscopy in respective spectral region. Information on anisotropy. Absolute method.	Specific to regions in which the refractive index of a sample changes; down to molecular level.	Simple qualitative spectrum interpretation is often not possible. Quantitative interpretation often requires involved modeling. Data from rough surfaces is hard to analyze.	"Ellipsometry" section
Polarization modulation (PM) spectroscopy	Via modulating polarization of incident light and lock-in detection, only anisotropic regions contribute to the spectrum. Yields information on the presence of ordered/anisotropic structures at interfaces. For these, same information as absorption spectroscopy in respective spectral region.	Region near an interface in which sample can discriminate polarization of light, up to quarter wavelength.	Disordered species which are present are not detected. Involved baseline shape over large spectral range, maximum signal to noise ratio in a limited spectral range.	"Polarization Modulation" section
Raman spectroscopy (RS)/Surface-enhanced RS (SERS)/Tip-enhanced RS (TERS)	Excites Raman active vibrational modes. Yields qualitative information on presence of certain structures, conformation, sometimes about defects in solids. High sensitivity, down to single molecule level. Complementary to IR absorption.	None intrinsically; limited for example, by confocal optics to $\approx 1 \ \mu$ m; Below few nm for SERS and TERS through field enhancement near sharp structures or in nano-gaps.	Strong on certain structures with ill- defined morphology, not necessarily representative for a surface. Strong on certain materials with certain excitation wavelengths. Quantification difficult.	"Raman" section
Photoluminescence (PL) spectroscopy/fluorescence spectroscopy	System is excited electronically, and emitted radiation is spectroscopically analyzed. Highly sensitive, down to single molecule level. Yields qualitative information on the presence of a certain structure, band gaps, defects and defect levels.	None intrinsically. Can be enhanced, for example, by excitation via evanescent wave, or field enhancement near sharp structures or in nano-gaps.	Limited to certain systems. Systems may undergo reactions in the excited state, which makes PL sometimes a destructive technique.	"PL" section
Sum frequency generation spectroscopy (SFG)	Nonlinear optical technique. Superimposing two strong beams of light yields the Raman spectrum of a vibrationally excited state. Requires a mode to be active in IR and Raman. Yields qualitative information on presence of structures at an interface, quantitative information about orientation to a great level of detail. Phase-sensitive SFG-direction of molecules can be determined. Selectively excludes bulk contributions for many systems.	Region with deviation from centrosymmetry; down to molecular level near interface.	Experimentally demanding. Requires transparency over large wavelength range (IR + VIS). Disordered species may be invisible at interface. Quantification of amounts difficult.	"SFG" section



Fig. 2 Example of a UV/VIS spectrum of 0.005 mM of the corrosion inhibitor MBT in 0.1 M aqueous NaOH. The spectrum is characterized by one asymmetric peak with maximum at 309 nm. The exact peak position is affected by the environment, as electronic interactions slightly shift the energy levels of the involved electronic states.

Finally, the wavefunctions of the states involved in the transition need a certain overlap for the transition dipole moment to be sufficiently high in order to allow excitation. This can be a limitation, for example, in intermolecular charge–transfer transitions in complexes which form by adsorption of a species to an interface.

Electronic excitations are marked as red arrows between the states in Fig. 1. Upon excitation from the ground state, which is frequently a singlet state in molecular systems, singlet  $S_1$  or higher singlet states  $S_n$  are reached. A return to  $S_0$  is possible via several pathways, which are labeled in Fig. 1. Some of these are also relevant for interface characterization:

- From  $S_n$  to  $S_{n-1}$  (and rarely over more than one step) via "fluorescence," emission of radiation ("PL" section),
- From  $S_n$  to  $S_{n-1}$  via radiationless deactivation, called internal conversion,
- From  $S_n$  via intersystem crossing toward a triplet state  $T_{n-1}$
- From T<sub>n+1</sub> to singlet states via intersystem crossing,
- From  $T_{n+1}$  to lower lying singlet states via "phosphorescence," emission of radiation in a spin-forbidden transition ("PL" section).

In addition, bimolecular processes are possible. More sophisticated excitation schemes are employed in Raman and SFG spectroscopy.

An example for a UV/VIS spectrum in solution is shown in Fig. 2. The spectrum is rather broad, and there is only one strong feature in the wavelength range between 250 and 800 nm. In general, bands in the spectrum, which arises from the energy difference of the energetic level, are characterized by position, intensity, shape, and fine structure. The width is affected by the number of involved vibrational or rotational levels. In addition, the solvent affects the band.<sup>14,15</sup>

#### What is special at interfaces?

The interpretation of a spectrum in reflection will have to follow similar approaches as for bulk spectra. Frequently, however, one is interested in the differences of a spectrum of an interfacial species compared to a bulk species. By and large, similar considerations apply as for IR spectroscopy. The optical peculiarities at interfaces have been discussed elsewhere.<sup>13</sup>

One important difference to bulk spectroscopy is that at interfaces, one is typically in a region with some symmetry break due to the presence of the respective other phase. Transitions may hence become active which are inactive in bulk materials.<sup>16</sup> This is illustrated in the *RA* spectrum in Fig. 3, where the maximum at  $\approx 550$  nm ( $\approx 2.2$  eV) is likely from a transition in Cu<sub>2</sub>O that is symmetry-forbidden in bulk material.

Fig. 3 also shows a minimum, which is another feature that is impossible in transmission spectra of homogeneous media. Minima and maxima are related to a large extent to the optical properties of the substrate. For instance, the spectra of self-assembled monolayers on gold also show minima, which are verified by simulation on the basis of continuum electrodynamics,<sup>17</sup> and clearly related to the interplay between reflection and absorption of light at interfaces. In UV/VIS, also negative *RA* values can be obtained on transparent substrates, as commonly observed in the IR.<sup>18</sup>



**Fig. 3** *RA* spectrum of the surface film formed on copper in phosphate-buffered saline (PBS; 140 mM Cl<sup>-</sup>, 10 mM phosphate; pH 7) at 0.1 V versus Ag/AgCl/3 M KCl. The spectrum is characterized by a minimum at  $\approx$  370 nm, a maximum at  $\approx$  480 nm ( $\approx$  2.6 eV) with a shoulder at  $\approx$  550 nm ( $\approx$  2.2 eV). The first maximum can be attributed to the formation of CuO, while the second maximum is attributed to a symmetry-forbidden transition from Cu<sub>2</sub>O, which becomes active due to the presence of point defects near the interface. The ordinate axis is labeled "PRA," because the *RA* in this spectrum was obtained from ellipsometric measurements according to a procedure described elsewhere.<sup>16</sup>

#### **Applications**

As the character of a band is dependent on the chemical structure of the measured molecule and its surrounding (solvent, complexation), UV/VIS spectroscopy can help to identify unknown molecules. If a functional group is involved in steric interaction, conjugation, or is attached to electron-releasing groups, its properties are often different from isolated functional groups. These differences can be semiquantitatively predicted for molecules.<sup>14,15,19</sup>

UV/VIS spectroscopy is essentially an old technique, and therefore has been used for in situ studies already for decades.<sup>20,21</sup> Applications of UV/VIS spectroscopy in electrochemistry have been reviewed recently.<sup>22</sup> UV/VIS has among many applications been useful in the study of redox proteins at interfaces.<sup>23</sup>

When light impinges on a glass/metal interface with an angle higher than the critical angle of total reflection, surface plasmons may be excited at the dielectric/metal interface. The corresponding technique, SPR spectroscopy, has an increased surface specificity, as it is based on evanescent waves.<sup>24</sup> SPR allows to study the growth and depleting of layers and kinetics of binding,<sup>25</sup> or the characterization of gold nanoparticles.<sup>26</sup>

# IR

#### General principles

In the IR, typically vibrational or rotational transitions are excited. Detailed descriptions of information on principles of IR spectroscopy and instrumentation of Fourier transform spectroscopy—today still the most common practical approach to spectroscopy in the IR—are available in the literature.<sup>10,27,28</sup> In the near future, the application of quantum cascade laser-based setups is likely to become more widespread.<sup>29–31</sup>

In the IR region, rotational transitions are relevant only in the gas phase. In liquids, librational modes, that is, restricted rotations, are frequently observed at low frequencies in the FIR. Lattice vibrations of solids are also probed in the IR. The energy required for vibrational transitions lies in the MIR for most organic functional groups. Molecular vibrations are subdivided into stretching and deformation modes.<sup>12,14</sup> Stretching modes are characterized by a change of bond length. For molecules with three atoms or more, symmetric and antisymmetric stretching modes are observed. Deformation modes involve a change of bond angle while the bond length stays nearly constant. Deformation modes for molecules comprise, among others, scissoring, rocking, twisting, and wagging. Some modes are delocalized over the full molecule, that is, a large part of the molecule participates. In general, molecular as well as lattice vibrations can be classified by their symmetry.<sup>12,14,32</sup> Dipole moment changes associated with a vibration are lower than those associated with an electronic transition. Therefore, absorption coefficients and hence sensitivity are lower in the IR than in the UV/VIS.

Absorption bands can also occur due to overtones or combination bands. Overtones, often observed in the NIR, are observed approximately at integer multiples of the fundamental frequency, or because of the anharmonicity of most potentials governing the vibrational modes, at slightly lower frequencies. Combination modes can be found at the sum or difference frequency of the fundamental modes involved. Both overtones and combination bands are usually considerably lower in absorbance than the fundamental. Hence, NIR is not as frequently applied for the analysis of interfacial structures, as for these, higher sensitivity is required.<sup>11,12,14</sup> Nevertheless, in situ applications for interface characterization exist of NIR, for example, in electrochemistry.<sup>33</sup>

The FIR range is used to get information regarding various vibrations in heavy atoms or molecules, crystal lattice vibrations or molecular torsional modes.<sup>34</sup> Torsional modes include both the intramolecular symmetric and asymmetric modes which arise due

to the movement of smaller organic or organometallic groups attached to a heavier group, as well as skeletal bending modes.<sup>34</sup> Information is also obtained about different lattice vibrational and phonon modes present in crystalline materials.<sup>35</sup>

#### What is special at interfaces?

IR spectroscopy is not intrinsically surface specific. Still, interfaces can be probed via reflection techniques, ATR,<sup>36–39</sup> or surface enhancement by small particles, SEIRAS,<sup>40</sup> as discussed in detail elsewhere.<sup>13,41</sup> Furthermore, the techniques can be applied combined with techniques analyzing polarization of light, such as ellipsometry ("Ellipsometry" section) or polarization modulation ("Polarization Modulation" section).

IR spectroscopy in external reflection mode can also be used as a probe for flat and smooth surfaces as a noncontact and nondestructive sampling technique. This is referred to as IRRAS, or as RAIRS (Reflection absorption IR spectroscopy), and has applications in the characterization of molecular orientation and chemical composition of thin monolayers and films down to nm thickness.<sup>42</sup> On metal surfaces, the "surface selection rule" presents an important constraint as to which modes can be detected: only modes with a transition dipole moment perpendicular to the interface can be excited because of interactions with the image dipole.<sup>13</sup>

Another reflection technique is DRIFTS which is also used for the characterization of thin films. Using DRIFTS, a rough surface, or a powder can be analyzed. DRIFT can be used to provide both chemical and structural details for different types of solid surfaces.<sup>43–45</sup>

In addition to the possibility to extract qualitative information on the presence of certain species near an interface, molecular conformation, and quantitative information on surface coverage, the single most important application in of IR absorption in interface characterization is possibly the determination of molecular orientation with respect to the interface.<sup>13</sup>

The bulk techniques of IR absorption and Raman spectroscopy ("Raman" section) are typically seen as "just" exciting vibrational modes with different symmetry. Complementarity is, however, reaching much further in the investigation of interfaces. In addition to different modes being active in the different experiments, the differences in illumination geometry make the two experiments significantly different at interfaces. Raman spectroscopy can be carried out in a confocal microscope, routinely with sub-µm lateral resolution. IR reflection studies are often done at illumination at an angle, leading in classical spectrometers to large illuminated areas. While Lamber–Beer's law permits a straightforward quantification of IR absorption, this is not directly the case in Raman spectroscopy. Likewise, the possibility to determine molecular orientation using Raman is not as general as in IR absorption. Further differences are highlighted in "Raman" section.

An example of a reflection IR spectrum of the corrosion inhibitor MBT, recorded in ATR-SEIRAS configuration, is shown in Fig. 4. The spectrum does show characteristic peaks, as would be the case in the respective bulk absorption spectrum. The spectrum is much richer in peaks than the UV/VIS spectrum of a solution (Fig. 2). Detailed analysis of the shifts of the individual peaks in IR can yield a detailed picture of environment of different groups or conformation.

#### **Applications**

In ATR geometry, solid/liquid as well as solid/solid and solid/gas interfaces are accessible. ATR-MIR has been used successfully for various in situ applications in combination with other spectroscopic and electrochemical techniques. Infrared reflection absorption



**Fig. 4** In situ ATR-SEIRA spectrum of a complex of corrosion inhibitor MBT and copper, on a rough, particulate copper surface. Spectrum was recorded in a 1 mM MBT solution in 0.1 M aqueous NaOH at a controlled electrode potential of -0.2 V versus Ag/AgCl/3 M KCl. The presence of MBT in a complex with Cu<sup>1</sup> can be deduced from the characteristic vibrational modes showing as peaks in the spectrum.

spectroscopy has been used for the study of biomolecules bound to the air/water interface.<sup>39,46,47</sup> In situ ATR-IR spectroscopy combined with electrochemical technique has been used for the study of catalytic reactions of various enzymes, for example, hydrogenase and nitrogenase,<sup>48-50</sup> the detailed investigation of interaction of various reactants and intermediate species of heterogeneous catalysts in water at electrode/water interface. $^{51-54}$  surface interactions of bacteria. $^{55}$  or the adsorption of intermediates on noble metal fuel cell electrocatalysts.<sup>56</sup> Semiconductors are well suited for model studies combining electrochemistry and ATR-IR. In situ polarized ATR-IR has thus been used to investigate in detail the electron transfer mechanism of the electrochemical oxygen reduction reaction on germanium, and germanium surface transformation from a hydroxide terminated surface to hydride terminated one.<sup>57-59</sup> The transformation of germanium surfaces to the hydrophobic H-termination leads to a weakening of the H-bond network of the interfacial water, and development of a "hydrophobic gap."<sup>60</sup> This work also represents the power of combining ATR-MIR spectroscopy with electrochemical potential jumps and an appropriate referencing scheme to enable an extraction of modes from interfacial water in front of the background of bulk water, which has previously been done using SEIRAS.<sup>61</sup> ATR-IR spectroscopy has been used recently to investigate biomolecules in subnanoliter fluidic channels on germanium surface,<sup>62</sup> pushing down the limit of the typically used sample amounts for IR analysis. ATR-IR spectroscopy is used in various studies on adsorption of ligands on nanomaterials including kinetic data.<sup>63</sup> The orientation of siloxane monolayers on silicon was found to be disordered with nearly isotropic orientation.<sup>64</sup> ATR-IR spectroscopy can only be conducted with thin metal films deposited on an IRtransparent material. The use of metal interlayers improves transparency of metals in the IR.65,66

Combining MIR spectroscopy with surface enhancements, as in SEIRAS, has been employed for the investigation of chemical structures and various reactions at solid/liquid interfaces. SEIRAS technique has become a useful tool in ATR mode for various electrochemical catalytic reactions and biomolecules at interfaces.<sup>67–71</sup> Surface enhancement can be used not only in ATR-SEIRAS configuration but also in transmission, external reflection, and diffuse reflection modes for the study of various reactions.<sup>70,72</sup> Approaches for rational analysis of surface enhancement exist.<sup>73,74</sup>

External reflection spectroscopy has been used as a probe for chemically modified surfaces.<sup>75,76</sup> IRRAS has been used for the study of biomolecules or organic films bound to the air/water interface.<sup>18,77–79</sup> DRIFTS spectroscopy has been used for the characterization of various solids without smooth interfaces, for example, asbestos in bulk building materials, crystallinity change of hydroxyapatite in bone tissues and teeth.<sup>45,80,81</sup> It has been also used for the in situ characterization of different heterogeneous catalysts in the presence of reactive gases.<sup>44</sup>

FIR, also referred to as "Terahertz" spectroscopy, has applications for detection of the phonon interface modes in semiconducting materials, for example, GaN epilayers on GaAs or GaP substrates.<sup>82</sup> Raman spectroscopy ("Raman" section) has been widely used to give information regarding intermolecular water interactions,<sup>83,84</sup> though FIR can also be used to extract information between water molecules on a molecular scale. This has been used heavily in bulk water in recent years,<sup>85,86</sup> but is still less commonly used for interfaces.

FIR has been used for the study of intermolecular interactions due to the presence of librational modes  $>300 \text{ cm}^{-1}$ ,<sup>87</sup> for example, in water/ionic liquid mixtures,<sup>88</sup> for the investigation of intermolecular hydrogen bonding in water or in different organic molecules,<sup>89</sup> to observe isolated water molecules by diluting water in different hydrophobic solvents,<sup>90</sup> and for the in situ spectroe-lectrochemical studies of electrode/solution interfaces.<sup>91,92</sup> Interpretation of the observed modes is, however, always involved in the FIR so that one must be careful with following interpretation on a purely empirical basis. Protein modes can also be studied by FIR.<sup>93</sup>

The use of synchrotron IR radiation with brightness of 1000 times higher compared to the conventional sources in FIR enables the study of various adsorbed species/substrate interaction and frustrated IR modes of adsorbed species.<sup>94</sup> This technique has been used for the in situ spectroscopy, imaging, or pump probe type of experiments at different electrode surfaces and interfaces. It has been used for the investigation of catalysis, corrosion inhibition and determining the structure at the electrode/solution interface; all of these show low energy modes characteristic for substrate–adsorbate interaction.<sup>95</sup> High brightness allows in situ experiments in solution. Synchrotron-based FIR has been also used for microscopy studies,<sup>96</sup> and to identify very weak modes from isotopic shifts,<sup>97</sup> due to its good signal to noise ratio.

## **Techniques Exploiting Polarization of Light**

#### Ellipsometry

## **General principles**

Ellipsometry is an optical technique which measures the relative change in polarization of light upon reflection, transmission, or scattering. Here, we are dealing with reflection at the ambient/sample interface. Texts introducing ellipsometry are available as extensive and thorough textbooks, <sup>98-100</sup> as well as reduced introductions.<sup>101,102</sup>

Before interaction with the sample, the state of polarization of the light is set to a certain state, and after interaction with the sample, the state of polarization is analyzed. In the simplest setup, a linear polarizer is placed before the sample, and an analyzer after the sample. More sophisticated experiments are enabled by inserting compensators between sample and linear analyzers. Rotating elements may be replaced by photoelastic modulators.<sup>99,102</sup> With these geometries, arbitrarily elliptically polarized light can be analyzed. Ellipsometry is most sensitive to interfacial structure if the difference in reflectivity between the two linear polarizations is large. In a typical external reflection geometry, this happens at the Brewster angle, where reflected and refracted light beams include an angle of 90 degrees.

When considering a planar interface, it is most useful to decompose any arbitrarily polarized beam of light into two linearly polarized components with polarization perpendicular to each other. The linear polarizations are "eigenpolarizations" of a flat interface, that is, incoming linearly polarized light will be reflected as linearly polarized light. (Incoming light with polarizations other than linear will undergo a change in polarization.) When considering reflection from an interface, parallel (p) and perpendicular (s) polarizations of light provide the most useful frame of reference. The amplitudes of reflected and incident light are related to each other by the complex amplitude reflection coefficients  $r_p$  and  $r_s$ , respectively, for the two linear polarizations. A simple and common form of ellipsometry measures the ratio of these two as<sup>98,99</sup>

$$\rho = \frac{r_{\rm p}}{r_{\rm s}} = \frac{|r_{\rm p}|}{|r_{\rm s}|} \cdot e^{i({\rm Phase_{\rm p}-Phase_{\rm s}})} = \tan(\Psi) \cdot e^{i\Delta}$$
(2)

Modern forms of ellipsometry, such as full Mueller matrix ellipsometry, provide a more detailed characterization of the interaction of polarized light with a sample.<sup>103,104</sup> In situ applications are so far often limited to simpler ellipsometric detection schemes, often analyzing the parameters  $\Psi$  and  $\Delta$ .

Ellipsometric spectroscopy is a highly quantitative and absolute technique of getting detailed data on the optical properties, in form of the complex refractive index or dielectric function of a sample. Such data includes the absorption spectrum, but is more comprehensive than this. The state of polarization of reflected light is strongly influenced by the state of the interface. Therefore, ellipsometry provides a good way to extract structural features from interfacial films, down to submonolayer coverage. The most common application is probably the determination of film thicknesses. The ellipsometric parameter  $\Delta$  (Eq. 2) represents the phase shift between fields with s and *p*-polarization of reflected light.  $\Delta$  changes with thickness of a thin layer, and this change is rather sensitive. In the simplest form, the shift in  $\Delta$  can be calibrated to a thickness.<sup>105</sup> The ability to measure a phase shift via  $\Delta$  makes ellipsometry a unique measurement technique. But also the absorption spectrum of thin layers can be extracted. Parameter  $\Psi$  represents the amplitude ratio of the two linear polarizations upon reflection, and is affected by absorption of light by interfacial films.<sup>98,99</sup> Due to the surface selection rule, extraction of a spectrum becomes particularly easy on metal surface.<sup>16</sup> The UV/VIS spectrum of copper oxide shown in Fig. 3 has been extracted from an ellipsometric measurement by using

$$PRA = -\log_{10}\left(\frac{\tan^2\Psi_{\rm smp}}{\tan^2\Psi_0}\right) \tag{3}$$

as "pseudo reflectance absorbance," in analogy to RA.<sup>16</sup>

The term "pseudo-dielectric function" is frequently used to denote spectra obtained from analyzing ellipsometric data, to distinguish them from the true complex dielectric function,  $\varepsilon(f)$ . In the ellipsometric analysis, often idealizations are made, for example, concerning homogeneity or isotropy of samples. While ideally the pseudo-dielectric function equals the dielectric function, this is in reality often not the case, justifying the usage of a dedicated term.

Ellipsometry is an absolute method, due to the intrinsic referencing by calculating the ratio between the two different linear polarizations. Nevertheless, in actual applications, especially in situ measurements, the measurement of a sample with a known reference state can be beneficial. In order to obtain quantitative data, often a modeling of the obtained spectra is needed, which can be rather demanding. Simplified analysis versions exist to extract information for very thin layer by a perturbation treatment.<sup>106</sup> However, it is often difficult to interpret spectra qualitatively without quantitative analysis, as opposed to the situation in many other techniques discussed here, where qualitative information is easily obtained, but quantitative information is hard to extract. The simple calculation of *PRA* as in Eq. (3) helps to make data easier accessible, especially in complex measurement situations. Application of ellipsometry is quite wide because it can measure from a single atomic layer up to µm range. The most remarkable features of ellipsometry are the high precision of the measurements and high thickness sensitivity. In this context, the surface roughness is often a restriction in the data analysis. This is likely to be an active area of research in the coming years. Special analysis schemes can be used to limit the effect of distributions of polarization states, for example, from roughness, on the results.<sup>107,108</sup>

#### Applications

In situ spectroscopic ellipsometry can be performed, amongst others, to investigate the modification of interfaces during layer growth, etching, cleaning, electrochemical processes or biomolecular modifications.<sup>99</sup> In biomedical research, in situ ellipsometry can be used to study the adsorption of proteins at solid/liquid interfaces.<sup>99,109</sup> Ellipsometry is also commonly applied to study film growth during physical and chemical vapor deposition to optimize the process.<sup>110</sup> One can control the film thickness during the synthesis and also initial nucleation behavior and film growth rate can be investigated. Specifically, during atomic layer deposition (ALD), spectroscopic ellipsometry can be performed to control the growth of ultrathin films with submonolayer resolution. Overall, two different approaches are applied to process SE data obtained during growth of the ALD films, which can be used as examples for general data analysis strategies. In the first approach, a certain relationship between the optical constants and the model parameters is postulated. This "dispersion relation" is then used to determine the film thickness and to optimize the model parameters in an iterative process. Most commonly, the Cauchy relationship or a Tauc Lorentz oscillator model is used in the literature. Examples of such analysis for example, for Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, Er<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> can be found in the literature. <sup>110</sup> Conductive phases can be parametrized by a Drude–Lorentz model.<sup>110</sup> In the second approach, the thickness and dielectric function of a sample are obtained directly from the pseudo-dielectric function. A combination of both approaches can be applied where appropriate.

Coupling spectroscopic ellipsometry and electrochemistry provides significant insight on the understanding of solid/liquid interfaces, for example, the formation of oxides.<sup>111,112</sup> This technique was applied, for example, for Zn and Cu, to investigate the interfacial reactions and oxide growth during electrochemistry.<sup>16,113–115</sup> To analyze the in situ SE data recorded during electrochemical oxidation of Zn, a model-free analysis scheme on the basis of Lekner's perturbation parameter was applied.<sup>106</sup> The only assumption in this method is that the thin oxide film is nonlight-absorbing.<sup>114</sup> Results from this approach may, however, also be used as first approximation in case of absorbing films. The approach was later extended to also yield absorption spectra of thin layers.<sup>16</sup> Data can also be obtained under conditions of chemical reactions, such as the oxygen evolution.<sup>113</sup> Adsorption of biomolecules to interfaces can be quantified by ellipsometry.<sup>116</sup> The desorption and readsorption of self-assembled monolayers to gold show a nontrivial chain-length dependence, and desorbed structures help to stabilize gas near the interface.<sup>117</sup> Ellipsometry is also useful for the investigation of the properties of polymer thin films.<sup>101,118,119</sup> A classical application is the characterization of the interface between Si and an oxide layer on top.<sup>120</sup>

A technique closely related to ellipsometry is reflection anisotropy spectroscopy, which is used specifically to probe surface and interface anisotropy both in situ and ex situ.<sup>121</sup>

#### **Polarization Modulation**

#### **General principles**

External reflection spectroscopy ("Absorption spectroscopy" section) by itself is not surface specific. Species interacting with the beam propagating to an interface contribute to the spectrum. Combining PM with for example, IRRAS makes the reflection spectroscopy a surface-specific technique, if all other materials that the light passes are isotropic. In PM spectroscopy, isotropic contributions are averaged out in the spectrum, suppressing bulk absorptions. At an interface, differences exist in the reflection of the two polarizations of light. PM spectroscopy is most frequently performed in the IR, but this is by no means a limitation. It can be seen as a special form of ellipsometry ("Ellipsometry" section). As the reflectivity from a surface changes strongly with the angle of incidence, PM spectroscopy is strongly dependent on the incidence angle as well.<sup>122,123</sup>

A PM experiment combines a spectrometer with a fast modulation of the incident light's polarization. In the IR, a photoelastic modulator generates alternating linear states of polarization. Signal processing enables the extraction of two signals,  $(I_p - I_s)$  and  $(I_p + I_s)$ , where *I* stands for intensity and s and p denote the polarization. Especially on metals, spectrum analysis is simplified by the surface selection rule,<sup>13</sup> which enables a simple calculation of a differential reflectance spectrum,  $\frac{\Delta R}{R}$ ,<sup>122-124</sup>

$$\frac{\Delta R}{R} = \begin{pmatrix} I_{\rm p} - I_{\rm s} \\ I_{\rm p} + I_{\rm s} \end{pmatrix} \tag{4}$$

By modulating the polarization, no additional background measurement is in principle required, as for absorption spectroscopy ("Absorption spectroscopy" section). Measurement of absorption spectra of both polarizations occurs virtually simultaneously. Nevertheless, due to the intrinsic way of working of the photoelastic modulators, modulation is ideal only in a limited spectral range, which results in complicated, Bessel-function like baselines. These need to be calculated or calibrated before or after the actual experiment in order to use data over an extended spectral range. PM spectroscopy enables the detection of anisotropic structures near an interface, and a quantification of the optical anisotropy, for example, in the form of molecular tilt angles. As such, the method is sensitive also to unwanted anisotropy in the optical path. Quantitative results on interfacial molecular orientation can only be obtained if anisotropy at an interface between two isotropic media is investigated.

#### **Applications**

PM-IRRAS is a powerful technique used for the molecular orientation and conformation analysis of thin films such as ultrathin polymer films, liquid crystals, surfactants, and monolayers from peptides and proteins, phospholipids, and model Langmuir films on reflective surfaces.<sup>18,123–125</sup> It has been used for example, for the orientation analysis of self-assembled monolayers (SAMs) formed from alkanethiols mostly on Au substrates.<sup>126</sup> This technique is also used for the characterization of the SAMs in the finger-print IR region by eliminating the absorption from water vapor.<sup>126</sup> PM-IRRAS has also been used for studies of the air/water interface.<sup>127</sup> It has various in situ applications. It has been used for the in situ investigation of various SAMs on metal surfaces in liquid electrolytes, such as D<sub>2</sub>O and CD<sub>3</sub>CN.<sup>128</sup> It has also been used for the in situ electrochemical study of surface chemical reactions occurring on SAMs on an Au substrate,<sup>129</sup> and for the study of the Stark effect on CO during adsorption at fuel cell Pt/Nafion interfaces.<sup>130</sup> PM-IRRAS has also been used for in situ corrosion studies of metals, for example, Cu, exposed to corrosive environments such as reactive gases (SO<sub>2</sub>,NO<sub>2</sub>, HCl) and high humidity.<sup>131</sup> The combination with SFG ("SFG" section) has been used to study the effect of organic inhibitors on the protection efficiency against atmospheric corrosion.<sup>132,133</sup>

#### **Techniques Based on Excitation and Emission**

Detecting emitted light has the big advantage that sensitivity is only limited by the efficiency of the collecting optics and the detector. As only few photons are sufficient to give a signal, methods such as Raman and PL spectroscopy can be employed with single

molecule sensitivity. This sensitivity does, however, come at a price. Quantification of the intensities is typically challenging, and requires a detailed knowledge of the collection efficiency of photons, and the detector response.

# Raman

#### **General principles**

Raman spectroscopy is a technique complementing infrared absorption ("IR" section) to study vibrational and rotational modes of a system.<sup>12,27,134,135</sup> The excitation scheme is shown in Fig. 1. In an inelastic scattering process, the system is excited into a virtual state and re-emits photons into a vibrational state higher (Stokes) or lower (anti-Stokes) than the original state. Raman emission occurs with a low quantum yield, typically on the order of  $10^{-6}$ . Instead of a virtual state, the system may be excited into an excited state, for example, the  $S_1$  state in Fig. 1. This case is called resonance Raman spectroscopy. As the initial excitation occurs to a permitted state in resonance Raman, that is, a state with a longer lifetime, resonance Raman peaks are significantly more intense. On the other hand, the system may show more of the photophysical processes sketched in Fig. 1, as for example, fluorescence or phosphorescence.<sup>27,134,135</sup>

Stokes Raman scattering occurs at lower photon energies, that is, higher wavelengths, than the initial excitation. The excitation photon energy is always much higher than the energy of the transition to be excited. Consequently, fluorescence, for example, in the form of defect-induced photoluminescence of solids, is problematic. Broad intensive fluorescence peaks can easily completely cover the Raman spectrum. Anti-Stokes Raman spectroscopy detects the emitted photons on the higher photon energy, that is, lower wavelength side of the excitation. Hence, fluorescence can easily be excluded by filters, as it occurs only on the low photon energy side of the excitation. On the downside, anti-Stokes Raman is less intense than Stokes Raman scattering, due to the different occupations of the involved levels.

The transition rules for a Raman process are distinctly different from those in absorption. In absorption spectroscopy in general,<sup>3</sup> dipole transitions are dominating the spectrum. On the other hand, the Raman process requires a change in polarizability during the transition. In simple molecules, a transition is therefore either Raman- or IR-active. In complex molecules, many modes can be excited in both experiments. At interfaces, the symmetry break also often makes modes active in both experiments, a phenomenon that shall be very useful in sum frequency generation spectroscopy ("SFG" section).<sup>27,134,136</sup> As for IR absorption ("IR" section), vibrational modes are specific to composition, structure, and conformation.<sup>27,135</sup>

# What is special at interfaces?

Raman spectroscopy is not intrinsically surface specific. Without any enhancement, it can therefore be challenging to probe interfaces. This drawback can be overcome by using SERS or TERS.<sup>41,134,137–139</sup> In SERS, rough metal island surfaces are used, where gaps or sharp structures produce large local electric fields  $\mathfrak{E}$ . As the Raman intensity is proportional to  $|\mathfrak{E}|^4$ , field enhancement leads to quite large enhancement in Raman signals from interfaces. The information from these spectra becomes quite surface specific also, with the drawback that the technique typically analyzes very ill-defined surfaces. (In absorption, such as SEIRAS, absorbance increases only with  $|\mathfrak{E}|^2$ , making the effects of surface enhancement much stronger in Raman.) Field enhancement is particularly strong at certain metals with certain dielectric functions at the excitation wavelength. Ag is a popular choice in the visible. SERS therefore works easily only on special morphologies and special materials. (Field enhancement is in general present, however, also in nanogaps or other metal structures.<sup>140</sup>) Resulting enhancement is highly local, and it remains doubtful whether results are representative for a surface. For TERS, nanostructures are specially manufactured and placed near an interface to be studied. TERS can be performed in scanning probe microscopy type of experiments, or in fabricated structures.<sup>140–144</sup>

A new variant to overcome the problems of SERS and TERS is shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS).<sup>134,139,145</sup> In this variant, nanoparticles are prepared from a material yielding large field enhancement, and are insulated by shells, for example, SiO<sub>2</sub>, against the environment.<sup>145</sup> Such particles can subsequently be placed at an arbitrary surface, and the surface becomes accessible to Raman experiments. Still, the results may be nonrepresentative of the surface, as enhancement is highly local. Absolute quantification is also challenging. Mass transport to the interface is locally affected by the particles, which make them highly suitable for in situ studies, with limits for operando experiments.

#### Applications

In biological systems, Raman is widely used to study hard/soft tissue interfaces.<sup>146</sup> Raman was used to probe collagen damage within tissue. The state of the extracellular matrix can also be analyzed in situ.<sup>147</sup> Changes of biomechanical properties of bone due to chemical perturbation have been investigated.<sup>148</sup> When coupling with electrochemical experiments, Raman spectroscopy can help to understand reactions at the electrode/electrolyte interface.<sup>134</sup> For example, Raman is used to study lithium–ion battery materials, which can give insight into the mechanism in batteries.<sup>149</sup> Besides, it can be utilized to study corrosion processes which occur at solid/liquid interfaces.<sup>150</sup> Raman was used to monitor oxide formation on copper as a function of electrode potential, which showed different vibrational modes, hence different structures, in situ and ex situ.<sup>16</sup> Different types of copper oxide can be easily distinguished by their vibrational spectra,<sup>151</sup> which is true for many other compound phases as well. Strongly light-absorbing surface species may transform under illumination,<sup>152–154</sup> and keeping them wet by a solvent may circumvent transformations.<sup>155</sup> Applied between a metallic zinc surface and a delaminating coating, pH oscillations were detected by in situ Raman spectroscopy.<sup>156</sup> During observation of the growth of ZnO, the presence of defects changes the local symmetry and hence the activity of the otherwise inactive LO phonon so that Raman can be used as a sensitive probe of defects in ZnO.<sup>157–159</sup>



**Fig. 5** In situ Raman spectrum, recorded at a controlled electrode potential of 0.4 V w.r.t. Ag/AgCl/3 M KCl, of corrosion inhibitor MBT, adsorbed from 1 mM MBT solution in 0.1 M NaOH, to a surface of copper. The peaks labeled with \* originate from DBTA, an oxidation product of MBT. The spectrum shows a number of peaks corresponding to vibrational modes of the Cu-MBT complex, and DBTA molecules. The presence of the oxidation product shows that MBT oxidizes partly under the conditions of the experiment. The presence of copper oxides can in principle also be detected if peaks at the characteristic frequencies for copper oxide were observed. The broad peak around 1640 cm<sup>-1</sup> originates from the deformation mode of water. Detailed analysis of the water spectrum can hence also yield insight into the state of solvation of the interface.

The interaction between corrosion inhibitors and metals was also studied by Raman.<sup>160</sup> SERS was used to investigate the interfacial reaction of the corrosion inhibitor MBT, with copper, silver, and gold.<sup>161</sup> As the electrode potential increased, the structure of the complex formed on the interface changed, leading to shifts of Raman peaks. An example of an in situ Raman spectrum of MBT on Cu is shown in Fig. 5.

## PL

#### **General principles**

PL spectroscopy uses fluorescence and phosphorescence. The excitation scheme is shown in Fig. 1.<sup>162,163</sup> PL is widely used in biochemistry and molecular biology to characterize complex molecules, their environment, or their location.<sup>164–167</sup> PL is equally used to characterize the optoelectronic properties of semiconductors.<sup>162,168</sup> The photon energy of the emitted photon is a direct measure of the energy difference between the involved orbitals or bands. In this way, the direct band gap of semiconductors can be determined, or the HOMO–LUMO gap in molecules.<sup>162,163,168</sup> In semiconductors, it is also common that point defects yield states in the band gap so that PL is observed at photon energies below the band gap. This PL is characteristic of different defects.<sup>168</sup>

PL is not observed for metals, as these have a continuum of electronic states around the Fermi level, and no radiative transitions are possible between states above and below the Fermi level. Instead, the system will relax via the path shown on the left of Fig. 1. This relaxation leads to heating of the sample.

#### What is special at interfaces?

PL is not intrinsically specific to interfaces. It is possible to combine it for example, with excitation via an evanescent wave or a surface plasmon, which helps to suppress bulk contributions. On the other hand, the continuum of states around the band gap in metals makes it possible that molecular or semiconductor states near a metal interface couple with those of the metal, which suppresses luminescence. Interfaces can also be labeled by for example, fluorescent species.

### **Applications**

PL has also been used in in situ experiments to characterize interfaces. PL spectroscopy has, for example, been applied to understand the surface processes in the field of semiconductor photocatalysis. The technique provides important information on the optical and photochemical properties of semiconductors, electronic structure of the materials, and also point defects in the interfacial region.<sup>169–173</sup> It is widely employed in environmental photocatalysis since a relationship was observed between PL and photocatalytic activity toward certain processes.<sup>173</sup> It is also a powerful method to investigate the quantum confinement effects in nanocrystals.<sup>172</sup> PL spectroscopy can be performed in situ and operando during electrochemical reactions, which could provide significant insight on the defect formation during surface oxidation and in oxide films when electrochemically treated.<sup>16,113,156,174</sup> The

electronic structure of classical semiconductors such as silicon can be studied in contact with liquids by PL.<sup>175,176</sup> In general, PL is useful for the characterization of semiconductors in contact with solution.<sup>177</sup> Fluorescence imaging of molecules near surfaces is applied more widely these days than detailed analysis of spectra.<sup>178,179</sup> Electrochemical in situ use of PL has been described comprehensively recently.<sup>180</sup> An interesting possibility arises for the in situ characterization of particle interfaces, if PL is coupled to whispering gallery modes in the particle, probing the surrounding via an evanescent wave.<sup>181,182</sup>

## SFG

## **General principles**

SFG as a nonlinear optical technique is a powerful tool to observe surface and interface phenomena, for example, in physical chemistry and biochemistry. Recent introductory and overview texts are available, relating to more in-depth treatments.<sup>41,183,184</sup> Experimentally, two input laser beams of frequency  $f_1$  and  $f_2$  are superimposed at a sample surface to generate an output beam which has a sum frequency of the two sources,  $f_3 = f_1 + f_2$ , to be detected by an appropriate detector. The excitation scheme is shown schematically in Fig. 1, and the experimental geometry in Fig. 6. Second harmonic generation (SHG), a technique which might have deserved its own subsection in this article, can be considered as a special case of SFG in which  $f_1 = f_2$ . Consequently, in SHG, the output beam has a doubled frequency compared to the input beam. Only pulsed lasers can generate the high electric fields needed for SFG or SHG to be observed, as these are phenomena with only low efficiency. Nonlinear optical effects were firstly reported in the study of bulk media,<sup>185,186</sup> and were later applied to probe surfaces.<sup>187,188</sup>

In practice, the most commonly applied combination is IR/VIS-SFG. A tunable IR laser excites the system from the vibrational ground state to a vibrationally excited state (Fig. 1). This excitation corresponds to the same excitation probed by IR absorption spectroscopy ("IR" section). The vibrationally excited state is then excited to a virtual state by a fixed wavelength visible laser, corresponding to the same process as exploited in Raman spectroscopy ("Raman" section). If the tunable IR laser is tuned to a frequency where a transition is permitted, intensity will be observed at  $f_1 + f_2$ . If not, only the background will be detected. As SFG combines a typical dipole excitation with a Raman process, SFG transitions must be active in both the IR and the Raman spectrum.

SFG is a typical second-order nonlinear optical process. As such, contributions to the spectrum from regions which are centrosymmetric (including isotropic media) will not be visible. Consequently, if the only break from inversion symmetry occurs at the interface, SFG can be interface specific down to molecular dimensions.<sup>41,183</sup> It is, however, also possible that quadrupolar terms dominate the surface SHG/SFG signal because of the field variation across the surface region.<sup>189–194</sup> The resulting spectrum detected in reflection geometry, as typically performed for interface characterization, represents no bulk multipolar contributions, while detectable bulk multipolar contributions can then be found in the transmission geometry. A main challenge is then to quantitatively measure the bulk quadrupole, or distinguish the signal of the surface dipole contributions from the bulk, either by computation or by experiment.<sup>189,195</sup> Care is therefore still required when the SFG spectrum is directly interpreted as interface-related, but other contributions are possible.

The line shapes of SFG spectra can be analyzed quantitatively, and thorough descriptions of the procedure are available in the literature.<sup>183,196</sup> It must be noted that the shapes in the spectra, that is, in plots of intensity versus wavenumber, are not only affected by the emitted SFG intensities but also by the reflectivities of the respective interfaces. Therefore, for a quantitative analysis of actual vibrational spectra, the reflectivities need to be considered as well.<sup>183</sup> This thorough analysis was not common practice in many early works employing SFG.

With proper choice of incident and detected polarization combinations, it is possible to selectively excite components in certain orientations. SFG is therefore a well-suited technique to investigate details of the orientation of species at interfaces, including details of the orientation distribution.<sup>184</sup> The angle of incidence can also be varied, and offers an additional method to probe details of interfacial structure.



Fig. 6 Schematic beam geometry in an SFG experiment, superimposing in space and time an IR laser and a VIS laser.

### **Applications**

With its interface specificity, SFG has been widely applied in interface science, both ex situ and in situ. Method development in SFG, for example, for phase-sensitive detection schemes,<sup>197</sup> in these days is also largely driven by applications in interface science. Characterization of the interface of water has been one very important field of application of SFG, with SFG leading to insight on the molecular level.<sup>198,199</sup> Likewise, proteins or other biological molecules at interfaces have been studied in detail,<sup>200</sup> as well as processes relevant in environmental chemistry.<sup>201</sup> Buried interfaces have been investigated between polymers and other substances.<sup>199,202</sup> SFG has been an important method to learn more about the structure of ionic liquids at interfaces to solids.<sup>203</sup> SFG has also been applied to study fundamental aspects of corrosion processes.<sup>204,205</sup> In combination with in situ ellipsometry, interfacial process during electrochemical hydrogen evolution under a self-assembled monolayer has been studied by SFG.<sup>206</sup> As SFG is a nonlinear optical process originating from the coupling of two high frequency fields, coupling to a static field may affect the signals obtained in SFG.<sup>207</sup>

#### Summary

A toolbox with several optical techniques exists, which can be used to study interfaces in situ and operando. All the techniques treated in this chapter can be applied in UHV, as well as in volatile liquids and gas atmospheres. Experiments under different conditions (in situ vs. ex situ) can therefore even provide a direct comparison of how a system transforms when removed from its surrounding. Current developments in the availability of IR lasers will likely lead to a wider application of these also in the study of interfaces. For virtually all methods introduced here, time resolution is constantly increasing. Therefore, optical in situ and operando spectroscopy will likely increase its potential in the years to come.

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# **Imaging Chemical Reactions One Molecule at a Time**

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# Nomenclature

General Apprev	lations
DOb	Deuterated bridging hydroxyl-deuterium bonded on top of Ob
DOt	Deuterated terminal hydroxyl-OD on top of Ti <sub>5c</sub>
H2TBPP	Meso-tetrakis(3,5-di-tertiarybutylphenyl)-porphyrin
HOb	Bridging hydroxyl—hydrogen bonded on top of Ob
HOt	Terminal hydroxyl—OH on top of Ti <sub>5c</sub>
I <sub>HT</sub>	High-temperature intermediate
It	Tunneling current
ML	Monolayer
Oa	Oxygen adatom—O bonded on top of Ti <sub>5c</sub>
Ob	Bridging oxygen
Ob(CH2)nOTi	Dioxy species bound on Ob and Ti5c sites
O <sub>b</sub> (CH <sub>2</sub> ) <sub>n</sub> OH	Hydroalkoxy species bound on Ob site
PS-b-PMMA	Poly(styrene-block-methyl methacrylate)
ROb	Bridging alkoxy—alkyl group bonded on Ob
ROH	Alcohol
Ti <sub>5c</sub>	5-Fold coordinated surface titanium cation
Ti <sub>6c</sub>	6-Fold coordinated surface titanium cation

vdW	Van der Waals
V <sub>G</sub>	Gap voltage, tunneling bias
Vo	Bridging oxygen vacancy
Abbreviations	
AES	Auger electron spectroscopy
AFM	Atomic force microscopy
AIMD	Ab initio molecular dynamics
DFT	Density functional theory
DOS	Density of states
IETS	Inelastic electron tunneling spectroscopy
IR	Infrared
IRRAS	Infrared reflection absorption spectroscopy
MD	Molecular dynamics
SPM	Scanning probe microscopy
STM	Scanning tunneling microscopy
STS	Scanning tunneling spectroscopy
TERS	Tip-enhanced Raman spectroscopy
TPD	Temperature programed desorption
UHV	Ultra-high vacuum
UPS	Ultraviolet photoemission spectroscopy
XPS	X-ray photoelectron spectroscopy

# Introduction

The invention of scanning tunneling microscopy  $(STM)^1$  changed our atomistic understanding of surface processes in a revolutionary way and allowed for unprecedented progress in many areas of science. Seeing structural motifs in real space allowed us to determine the configuration of atoms on complex surfaces and identify and quantify various structural defects such as dislocations, steps, missing or added atoms, and impurities. Now famous, the first STM image of Si(111) surface (Fig. 1A) from 1983 resolved its complex (7 × 7) reconstruction<sup>2</sup> and earned Rohrer and Binnig Nobel Prize in Physics in 1986. Currently, many flavors of scanning probe methods exist and employ a variety of tip–surface interactions to generate space-resolved maps of surface properties that include conductivity, electrostatic and van der Waals interactions, magnetization, spin, hydrophilicity, work function, and others.<sup>3</sup> However, the scanning probe methods are nowadays not only employed as imaging techniques. They can provide information about the local electronic and vibrational structure of the imaged features, the tip functionalization with molecules is used to enhance resolution and to obtain specific information about physical and chemical properties at the atomic scale, and the tip manipulation can be employed to assemble nanostructures with atomic precision and to induce local reactions. The list of processes that can be followed with modern scanning probes is practically endless.



**Fig. 1** A timeline illustrating the progression of imaging from clean surfaces to adsorbates and reactions. (A) One of the first STM images illustrates  $7 \times 7$  reconstruction of Si(111) (Reproduced with permission from Binnig, G.; Rohrer, H.; Gerber, C.; Weibel, E.  $7 \times 7$  Reconstruction on Si(111) Resolved in Real Space. *Phys. Rev. Lett.* **1983**, *50*, 120–123). (B) An example of early study of molecularly adsorbed CO island on Pt(111) (Reproduced with permission from Stroscio, J. A.; Eigler, D. M., Atomic and Molecular Manipulation with the Scanning Tunneling Microscope. *Science* **1991**, *254*, 1319–1326). (C) One of the earliest studies where STM was used to study chemical reactions on metal oxide surfaces. Here TiO<sub>2</sub>(110) (used as a primary model system throughout this review) was exposed to formic acid and the formate intermediates and their diffusion was imaged. Adapted with permission from Onishi, H.; Iwasawa, Y. STM Imaging of Formate Intermediates Adsorbed on a TiO<sub>2</sub>(110) surface. *Chem. Phys. Lett.* **1994**, *226*, 111–114.

In this review, we focus on demonstrating the utility of the scanning probe methods in one specific area, imaging of the chemical reactions. While the surface reactions are critical in many different areas such as materials science, geoscience, electrochemistry, corrosion, precipitation and dissolution, tribology, and others, heterogeneous catalysis represents a prime example where understanding the role catalysts' make-up and structure play in determining the rates and selectivity of the product formation is essential. The speedy progress from the imaging of bare surfaces to adsorbates and reactions is illustrated in Fig. 1 (Refs. 2,4,5).

We first illustrate the utility of different imaging schemes and highlight their strengths and weaknesses (Section "Basics of Scanning Probe Techniques"). Subsequently, we select a number of examples to illustrate different surface processes including adsorption, dissociation, diffusion and rotation of adsorbed molecules, formation of reaction intermediates, and conclude this section (Section "Imaging Elemental Steps in Surface Reactions") with complex reactions. In these examples, we mainly focus on the STM, which is most extensively employed as a method of choice. To limit the complexity of the article we have selected only a few systems for the discussion. In particular, elemental steps in the reactions of water, alcohols, and diols on TiO<sub>2</sub>(110) surface are utilized to illustrate the power of imaging techniques in our understanding of surface chemistry. In the last part (Section "Future Directions and Challenges"), we provide a brief outlook on both current and future challenges in this exciting area of research.

# **Basics of Scanning Probe Techniques**

Shortly after the introduction of STM,<sup>6</sup> many variations quickly followed.<sup>3,7</sup> The techniques are now commonly referred to as scanning probe microscopies (SPM), as they all rely on the probe scanning in the proximity of the surface. The key difference among various SPM methods is the type of probe-sample interaction (signal) being measured. We have selected two most popular methods used in the imaging of surface reactions: STM and atomic force microscopy (AFM) and briefly introduce both below (Fig. 2). For further details, the reader is referred to numerous books and review articles in the literature.<sup>3,7</sup>

#### Scanning Tunneling Microscopy

Scanning tunneling microscopy, the original SPM technique, relies on probing the local electronic density of states at the surface. The image contrast is based on electron tunneling through a controllable gap,<sup>1</sup> with a bias voltage,  $V_{G}$ , applied between the sample and the sharp metallic tip (usually made from tungsten). This technique utilizes a decay of the tip and sample wavefunctions into the vacuum and their overlap within very short distances (~1 nm). The range of states below (filled) and above (empty) the Fermi level is sampled by setting a negative or positive sample bias, respectively. Tunneling current,  $I_{t}$ , depends exponentially on the distance between the sample and the tip, z, and the measured tunneling current is used as a reference signal for the *z*-feedback loop. While the STM is the most commonly used SPM technique, its applications are limited to samples with sufficient surface electrical conductivity, leaving a broad class of insulating materials inaccessible.

Traditionally, STM is used in the topographic mode, where the tip is scanning in the *xy* plane while keeping the tunneling current constant and recording the *z* position. In the second imaging mode, a constant height mode, the feedback loop is disabled, and scanning is performed at a constant height *z*. The recorded variation in the tunneling current then reflects the atomic structure of the surface.

The great advantage of STM for the reactivity studies is that it can operate in a broad range of temperatures (mK to 1000 K) and pressures. The high-pressure/high-temperature STM instruments are typically contained within a high-pressure cell to limit the exposure of the whole UHV system to the reactants and have been termed reactorSTM.<sup>8,9</sup>

#### Atomic Force Microscopy

The development of the AFM extended the SPM capability to nonconductive samples.<sup>10,11</sup> The imaging mechanism is based on the measurement of attractive/repulsive forces (van der Waals, electrostatic, etc.) between the tip and the sample. The tip is mounted on

#### Scanning Tunneling Microscopy Atomic Probe Microscopy



Fig. 2 Schematic view of two SPM techniques (STM and AFM) most commonly employed in the studies of adsorbates on surfaces.

a cantilever that works as a spring and allows to be used as a force detector. The cantilever is rigid along the *x*- and *y*-axis while being relatively soft along the *z*-axis.

AFM can be used in a number of modes, but for imaging of adsorbates, a noncontact mode is the most appropriate. In this dynamic mode the cantilever vibrates with a frequency modulation of the force sensor that is similar to the timekeeping element in modern watches. Such quartz tuning fork (qPlus) sensors provide an excellent frequency stability over time and temperature variations with little energy consumption.

AFM is inherently more complex than STM, and it took almost 10 years since its invention before the atomic resolution on reactive surfaces was achieved.<sup>10</sup> Even now AFM is rarely used to study chemical reactions. In contrast with STM, in AFM, the force between the sample and the tip has both short- and long-range components. This force is not monotonic, being attractive for large tip-sample distances, and repulsive for short tip-sample distances, making an establishment of a stable *z*-feedback loop more complex. In addition, since the sum of the overall tip to sample forces is measured, the source of atomic resolution is often hard to identify. In recent years, chemically functionalized tips operated at cryogenic temperatures became popular in many groups. A CO molecule is typically used to image adsorbates with submolecular resolution. This high resolution is attributed to Pauli repulsion between the CO molecule and the probed molecule on the surface (see Section "Adsorbate Structure Imaging with Functionalized Scanning Probes").<sup>12</sup>

## Benefits and Drawbacks of Single Molecule Imaging by STM

Since the STM is by far the most commonly used SPM technique and its examples are used extensively throughout this review, we briefly summarize its strengths and weaknesses as compared to ensemble average techniques that are typically employed in the reactivity studies.

One of the key advantages of STM is its ability to follow extremely low adsorbate coverages. The detection limit is simply defined by the largest area one is willing to analyze, but typically coverages below 0.001 monolayer (ML) can be easily studied (1 ML is typically defined as a density of surface atoms and is generally on the order of  $10^{15}$  atoms/cm<sup>2</sup>). In contrast, ensemble average techniques, such as X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRRAS), and temperature programmed desorption (TPD), provide at best the detection limit of ~0.01 ML.

Another key strength of STM is the ability to directly identify the preferential adsorption sites. For example, one can easily follow the adsorbate coverages on terrace sites, steps, and point defects. In an example that is used extensively here, rutile  $TiO_2(110)$  surface (schematically shown in Fig. 3A), the adsorption and reactions on five-fold coordinated surface titanium sites ( $Ti_{5c}$ 's), and missing surface oxygen sites (bridging oxygen vacancies,  $V_O$ 's) are often compared and contrasted.<sup>13–15</sup> Temperature-dependent measurements can yield further details about the delivery of the adsorbates to specific active sites and their conversion to other surface intermediates.

While the advantages of the imaging of single molecules on surfaces are indisputable, numerous challenges are present in such experiments. First of all, the studies of adsorbates are generally limited to well-ordered single crystalline surfaces. The complexities of ill-defined substrates such as polycrystalline surfaces and supported nanoclusters quickly impede any possibility of successful interpretation of the data when adsorbates are used. Nanoparticles on its own are very difficult to image at atomic resolution, and only a very few successful examples were reported to date.

Second, STM lacks the chemical sensitivity. For example, on our prototypical  $TiO_2(110)$  surface, the imaging contrast is reversed from the actual surface topography (see Fig. 3) due to electronic effects and the low-lying  $Ti_{5c}$  atoms are imaged bright while the



**Fig. 3** (A) Structural model of TiO<sub>2</sub>(110) surface. (B) Empty-state STM image ( $V_G = +1$  V,  $I_t = 0.1$  nA) depicting the same area, illustrating reversed imaging contrast (The low-lying Ti<sub>5c</sub> ions appear high and the geometrically protruding O<sub>b</sub> ions appear low) dominated by electronic effects. Reproduced with permission from Dohnálek, Z.; Lyubinetsky, I.; Rousseau, R. Thermally-Driven Processes on Rutile TiO<sub>2</sub>(110)–(1 × 1): A Direct View at the Atomic Scale. *Prog. Surf. Sci.* **2010**, *85*, 161–205.

ridge O<sub>b</sub> atoms are imaged dark. Similarly, the missing oxygen atoms (V<sub>O</sub> defects) are imaged bright. Analogous issues persist for adsorbates, and in the Section "Molecular Adsorption" we focus on different approaches that can be employed in determining their chemical identity.

When STM is used to image the chemical reactions, one of the limiting factors is the slow scanning speed (typically 1 image per minute). The acquisition speed ultimately determines the rate of changes one can follow. As such the ability to adjust the temper-ature of the sample to limit the rate of diffusion or reaction becomes critical.

While we have highlighted the ability of STM to follow extremely low coverages, imaging higher coverages becomes increasingly difficult, especially when the molecules do not form ordered structures or the structures are highly fluctuational.

#### **Delivery of Reactants**

Reagent delivery while avoiding contamination represents one of the critical elements in the studies of adsorbates. Often, other molecules that are present in the chamber background such as  $H_2O$ , CO, and  $H_2$  can adsorb and interfere with the experiment. Similarly, care has to be taken to assess possible presence of contaminants in the reagents. Due to the lack of chemical sensitivity of STM, this becomes critical as the identification of the surface species is not straightforward. In many instances, this resulted in serious erroneous assignments and confusion in the literature.

There are three basic adsorbate delivery methods that are currently being used (Fig. 4). The easiest but also highly questionable method involves simple backfilling of the vacuum chamber with the molecules of interest. This approach inevitably results in complications as the whole system is being exposed, and molecules can displace other molecules from the chamber walls or even react forming other products. Additionally, when a low-temperature STM is used, a large buildup of molecular layers on the cooled components can occur.

Only slightly more complicated method involves the use of tube dosers.<sup>16</sup> This method lowers the gas load of the system dramatically and delivers the flux of molecules locally on the sample. Components needed include a tube with desired diameter mounted on a retractable stage and a pinhole gasket ( $\sim 3 \mu m$ ) or a leak valve to control the flux. Many groups attach such dosers directly to the chamber with STM, allowing to image the same area of the sample before and after dosing. During the dose, the STM tip needs to be often retracted several micrometers to avoid tip shadowing of the imaged area. Probing the same area on the sample before and after dosing molecules is experimentally challenging as finding the same nanoscale area can be difficult due to thermal drift. During dosing, the molecules can also adsorb on the apex of the STM tip, making the tunneling conditions unstable.

The most sophisticated method employs molecular beams.<sup>17</sup> This allows for ultimate control over the dosed area. Additionally, the translational energy of the molecules can be varied by seeding the molecule of interest in light gasses (i.e., helium or hydrogen) and by heating the orifice that the molecules are emanating from. Such molecular beam sources are complex and consist of several differential pumping stages connected via beam-defining apertures. The purpose of the pumping stages is to eliminate the nondirectional component in the beam. Due to the complexity of such sources, only a limited number of reports exist in the literature.<sup>18</sup>

## **Imaging Elemental Steps in Surface Reactions**

Every encounter, reactive or unreactive, of a molecule with a solid surface can be dissected into a sequence of elementary steps that can include adsorption, dissociation, diffusion and rotation, the formation of reaction intermediates, and desorption. Many of such steps can be imaged with a single molecule resolution as a function of time and temperature yielding a wealth of information about the kinetics and dynamics of such processes. Ultimately, when corroborated by theoretical calculations, these measurements can yield unprecedented level of understanding of reaction mechanisms.



Fig. 4 Three basic adsorbate delivery methods for dosing molecules under UHV conditions.

#### **Molecular Adsorption**

The initial encounter of a molecule with the surface leads to energy transfer, and if sufficient, the molecule thermalizes and adsorbs. For unreactive events, the molecule remains adsorbed on the surface if the substrate temperature is insufficient to provide the energy required for the desorption. Since the energy barriers for the molecules to diffuse on the surface are generally lower than the desorption energies, the adsorbed molecules explore the surface potential energy landscape. The molecules probe various adsorption sites (terrace sites, step sites, point defects), ultimately populating the ones with the highest binding energies. They can also lower their adsorption energy by arranging in preferred configurations relative to other molecules on the surface, e.g., by forming two-dimensional clusters.

One of the key strengths of STM over ensemble-average techniques such as XPS, TPD of IRRAS is its ability not only to follow the coverage, but also the arrangement, exact adsorption sites at the atomic level, and mutual interactions between adsorbed molecules. A prototypical example is shown for nonreacting CO molecules adsorbed on Pt(111) substrate, which adsorb as isolated molecules at low coverages, form islands of mutually interacting CO molecules at intermediate coverages, and ultimately yield ordered high-coverage structures.<sup>19</sup> All these structures can be easily imaged and unambiguously identified with STM, as shown in Fig. 5.

#### Reactive Systems—Understanding What You See

For the reactive events, additional processes can lead to dissociation, new surface intermediates, reactions with other adsorbed species, and ultimately to the formation of products. One of many possible sequences of such steps is illustrated in Fig. 6 for the reaction of a simple alcohol molecule (ethanol) on rutile  $TiO_2(110)$ ,<sup>14</sup> the surface already introduced in Fig. 3. The structure of the catalyst can be altered by interactions with adsorbates as well. In this section, we present simple examples that illustrate studies of such elemental steps, highlight the quantitative information one can extract from a careful analysis, and point out the difficulties and possible pitfalls.

The first step in understanding the reaction mechanisms is a proper identification of adsorbed species. Even something as simple as a water molecule on  $TiO_2(110)$  will appear differently depending on the substrate temperature, water coverage, and the site the



**Fig. 5** CO ordering on Pt(111) as a function of increasing coverage: From isolated molecules to high-coverage superstructures. Adapted with permission from Yang, H. J.; Minato, T.; Kawai, M.; Kim, Y. STM Investigation of CO Ordering on Pt(111): From an Isolated Molecule to High-Coverage Superstructures. *J. Phys. Chem. C* **2013**, *117*, 16429–16437.



Fig. 6 Schematic representation of elemental steps in alcohol dehydration reaction on TiO<sub>2</sub>(110) surface.



**Fig. 7** Adsorption of water on  $TiO_2$  (110) at 80 K yields water monomers and dimers on  $Ti_{5c}$  rows,  $HO_b-HO_t$  pairs on neighboring  $O_b$  and  $Ti_{5c}$  sites, and  $HO_b-HO_b$  pairs on  $O_b$  rows. Adapted with permission from Wang, Z.-T.; Wang, Y.-G.; Mu, R.; Yoon, Y.; Dahal, A.; Schenter, G. K.; Glezakou, V.-A.; Rousseau, R.; Lyubinetsky, I.; Dohnálek, Z. Probing Equilibrium of Molecular and Deprotonated Water on  $TiO_2(110)$ . *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 1801–1805.

molecule occupies. This is illustrated in an image presented in Fig. 7. Four types of features can be seen: molecularly bound water monomers, water dimers on bright  $Ti_{5c}$  rows, and two different pairs of hydroxyl species,  $HO_b-HO_b$  and  $HO_t-HO_b$ . The  $HO_b-HO_b$  pair is a result of water dissociation on the  $V_O$  site:

$$H_2O + V_O + O_b \rightarrow 2HO_b \tag{1}$$

and the HO<sub>t</sub>-HO<sub>b</sub> pair is formed by dissociation of Ti<sub>5c</sub>-bound water monomer:

$$H_2O + O_b \rightarrow HO_t + HO_b \tag{2}$$

Why do the species shown in Fig. 7 coexist on the surface? The expectation is that the most stable configuration would dominate as indicated earlier. The key is that this experiment has been performed at 80 K, well below the onset of diffusion ( $\sim$  170 K), and hence all the species are formed by a direct adsorption on the specific site. The image, therefore, illustrates a nonequilibrated scenario with kinetically frozen intermediate states.

How does one go about determining the chemical identity of the observed species? The helpful starting point is understanding as much as possible about the chemistry using the ensemble averaged techniques. For example, TPD can provide information about at what temperature the reactants and products desorb, and IRRAS and XPS can provide chemical fingerprints of certain surface intermediates. While not necessary, such information can help to avoid mistakes in the subsequent STM assignments. Below we illustrate the procedures one can apply in pursuing the assignment of the surface species with STM.



**Fig. 8** STM images (*top panels*) and corresponding ball models (*bottom panels*) of  $H_2O$  adsorption, dissociation to bridging hydroxyls (Reaction 1), and hydroxyl hydrogen diffusion on TiO<sub>2</sub>(110). Light blue ball: O<sub>b</sub>, red ball: Ti atom. Reproduced with permission from Dohnálek, Z.; Lyubinetsky, I.; Rousseau, R., Thermally-driven processes on rutile TiO<sub>2</sub>(110)-(1 × 1): A direct View at the Atomic Scale. *Prog. Surf. Sci.* **2010**, *85*, 161–205.

## Same area imaging

Comparing the same area before and after adsorption is critical as the initial image provides the map of initial surface sites including defects, steps, and molecules already adsorbed on the surface. Fig. 8 illustrates this approach in imaging H<sub>2</sub>O dissociation on  $V_O$  sites on TiO<sub>2</sub>(110).<sup>20</sup> The identification of the initial  $V_O$  concentration and their positions are the key (Fig. 8, left). After H<sub>2</sub>O adsorption, the same area image shows one bright species centered on the original  $V_O$  (Fig. 8, middle) and one on neighboring O<sub>b</sub> site. The observation of two features and their relative positions with respect to the original  $V_O$  is a key piece of evidence leading to the conclusion that water dissociated in the  $V_O$  (see the reaction scheme above) and formed a pair of bridging hydroxyl species (HO<sub>b</sub>). Further time-dependent evolution of the area illustrates the diffusion of one of the HO<sub>b</sub>'s (Fig. 8, right) confirming the assignment. Line profiles along the low-index crystallographic directions over the observed features facilitate the analysis further. While this process seems simple, it is not often adopted as imaging the same area during the adsorption is difficult.

#### Bias- and tunneling current-dependent imaging

Another key approach utilizes the bias and tunneling current dependence to identify/distinguish the surface species. For example, the HO<sub>b</sub> appearance on TiO<sub>2</sub>(110) can change dramatically relative to the underlying lattice and V<sub>O</sub> defects.<sup>21</sup> As shown in Fig. 9, for one particular bias, a simple variation of the tunneling current can make them stand out very clearly (Fig. 9A), make them appear practically identical with V<sub>O</sub>'s (Fig. 9C), or make them invisible (Fig. 9D). When the initial surface becomes completely hydroxylated prior to the initial imaging one could easily arrive to the conclusion that the surface is clean and contains only V<sub>O</sub>'s.

## Scanning tunneling spectroscopy<sup>22</sup>

In addition to the imaging, scanning tunneling spectroscopy (STS) provides site-resolved information about the available empty and filled density of states (DOS) as a function of energy. The STS spectra are obtained by placing the STM tip above a particular site on the sample. With the height of the tip fixed, the electron tunneling current is measured as a function of electron energy by varying the voltage between the tip and the sample. STS obtained at different sites allows for the correlation of the DOS with specific atomic sites or adsorbed species. While the measurements are relatively simple, a stable and well-defined metallic tip apex is







**Fig. 10** STS *IV* (*inset*) and *dl/dV* spectra of the site-dependent occupied DOS in the vicinity of a  $V_0$  site on TiO<sub>2</sub>(110) surface measured at 78 K. Spectra are acquired (A) at the center of a lobe in the occupied STM image between the second and third Ti<sub>5c</sub> sites away from the  $V_0$ , (B) at a Ti<sub>6c</sub> site, and (C) at the  $V_0$  site. Measurements demonstrate that the charge state at -0.8 eV is located on the Ti<sub>5c</sub> sites that are between one and four sites away from the  $V_0$ . Reproduced from Minato, T.; Sainoo, Y.; Kim, Y.; Kato, H. S.; Aika, K.; Kawai, M.; Zhao, J.; Petek, H.; Huang, T.; He, W.; Wang, B.; Wang, Z.; Zhao, Y.; Yang, J. L.; Hou, J. G. The Electronic Structure of Oxygen Atom Vacancy and Hydroxyl Impurity Defects on Titanium Dioxide (110) Surface. *J. Chem. Phys.* **2009**, *130*, 124502 with the permission of AIP Publishing.

a prerequisite for reliable STS measurements. Such conditions are generally hard to achieve on complex materials such as oxides, in particular, if the tip is held at room temperature.

Fig. 10 shows a nice set of the STS spectra for the  $TiO_2(110)$  prototype (see Fig. 3) that were used to identify the spatial distribution of the excess charge created by  $V_O$  defects.<sup>23</sup> The spectra taken at the  $V_O$  and nearby  $Ti_{5c}$  sites show that the excess electron density spreads from the  $V_O$  onto the neighboring  $Ti_{5c}$  sites retaining very negligible density on the proximate  $Ti_{6c}$  ions. STS confirms the presence of occupied  $Ti^{3+}$  defect states as observed in ultraviolet photoemission spectroscopy (UPS).

#### Tip-induced manipulation

Ultimately, harsh imaging conditions (high bias and/or current) can be used to alter the adsorbed species.<sup>24</sup> When done in a controlled way, such tip-induced manipulations can serve as a diagnostic method to distinguish or identify certain types of species. For example, the tip-induced removal of the HO<sub>b</sub> hydrogen, illustrated in Fig. 11, settled the long dispute in the identification of HO<sub>b</sub>'s and V<sub>O</sub>'s.<sup>25</sup> A word of caution: while the tip-induced processes can be used as a diagnostic or even to induce surface reactions and changes in the adsorbate conformation, they can also result in unintended consequences. For example, for sensitive adsorbates,



**Fig. 11** Controlled desorption of individual H atoms from HO<sub>b</sub> pair (labeled as  $OH_{br}$  in the figure) on TiO<sub>2</sub>(110). Reproduced with permission from Acharya, D. P.; Ciobanu, C. V.; Camillone, N.; Sutter, P. Mechanism of Electron-Induced Hydrogen Desorption from Hydroxylated Rutile TiO<sub>2</sub> (110). *J. Phys. Chem. C* **2010**, *114*, 21510–21515.

such as  $O_2$  on TiO<sub>2</sub>(110), the dissociation can occur efficiently even under the mildest imaging conditions and lead to erroneous conclusion about the dissociation of  $O_2$  at low temperatures (< 150 K).<sup>26</sup> Interpreting the STM images while taking into account the results of prior ensemble averaged studies cannot be stressed enough.

# Simulation of STM images

To further understand the adsorption configuration of the surface species, theoretical calculations of the optimized geometry, electronic structure, and the charge density distribution are often carried out. The results of such calculations can be utilized to simulate the STM images<sup>27</sup> that can be compared with the experimentally measured images.

For example, for  $H_2O$  adsorbed on anatase TiO<sub>2</sub>(101), the arch-like features are observed (Fig. 12A).<sup>28</sup> It is not clear from the STM image whether these features are isolated water molecules, water clusters, or dissociated water. Density functional theory (DFT) simulations yielded the adsorption structure (Fig. 12B), charge distribution of water monomer (Fig. 12C), and the STM images (Fig. 12D). The agreement between the simulations and the experimental images strongly supports the fact that water is bound molecularly on this particular surface.

#### Inelastic electron tunneling spectroscopy

One of the advanced approaches to chemical fingerprinting of the adsorbed species involves inelastic electron tunneling spectroscopy (IETS). In the experiment, the tunneling current,  $I_{t}$ , is measured as a function of voltage,  $V_{G}$ , across the junction. Small, sharp steps in the conductance, dI/dV, can be observed when the energy of the tunneling electrons reaches the energy of a vibrational mode for molecules in the junction and the  $d^2I/dV^2$  spectra are normally plotted to clearly see the changes in the conductance. This increase is the result of electrons losing their energies to the vibrational mode, giving rise to an inelastic tunneling channel, which is forbidden when tunneling electrons have energies below the quantized vibrational energy. The IETS measurements are experimentally involved, require extremely high signal-to-noise ratio, and have to be carried out at liquid He temperatures.

An example from the pioneering work of Ho's group is shown in Fig. 13.<sup>29</sup> Here, the inelastic electron tunneling spectra for an isolated acetylene ( $C_2H_2$ ) molecule on Cu(100) showed an increase in the tunneling conductance at a vibrational voltage of 358 mV, resulting from excitation of the C–H stretch mode. An isotopic shift to 266 mV was observed for deuterated acetylene ( $C_2D_2$ ). While a  $C_2H_2$  and a  $C_2D_2$  appear the same in the regular STM image (Fig. 13B), only one molecule ( $C_2H_2$  or  $C_2D_2$ ) was revealed in the vibrational imaging conducted at the correlated vibrational voltage (358 and 266 mV in Fig. 13A spectrum 1 and 2, respectively). For semiconductor surfaces, recording the IETS spectra is challenging due to the absence of states around the Fermi level. Recently, Kern's group demonstrates IETS on a highly *n*-doped anatase TiO<sub>2</sub>(101) surface to chemically identify single water molecules and hydroxyl species.<sup>30</sup>

Ho's group further pushed the spatial resolution of the STM to molecular structure and chemical bonding by employing IETS with functionalized STM tips.<sup>31</sup> They used CO-terminated tip to probe the local potential energy landscape of an adsorbed molecule. As the CO-terminated tip is scanned over the molecule during imaging, changes in the energy and intensity of the hindered translational vibration of CO on the tip are measured by IETS, revealing the skeletal structure and bonding of the molecule as shown in Fig. 14. An application of the inelastic tunneling to probe cobalt phthalocyanine in Fig. 14 reveals the sharing of hydrogen atoms among multiple centers in intramolecular and extramolecular hydrogen bonds.



**Fig. 12** a) STM images of isolated water molecules on anatase  $TiO_2(101)$  taken at a sample temperature of 190 K (+3.5 V, 0.45 nA). (B–D) Theoretical results for an adsorbed water monomer on anatase  $TiO_2(101)$ . (B) Optimized geometry (*top view*) (C) isosurface of the charge density difference resulting from the adsorption of a water molecule. Positive (electron excess) and negative (electron deficit) lobes are shown in blue and yellow, respectively. (D) Simulated constant density image, determined from the integrated local density of states in an energy window of 2.75 eV from the conduction band minimum. Adapted with permission from He, Y.; Tilocca, A.; Dulub, O.; Selloni, A.; Diebold, U. Local Ordering and Electronic Signatures of Submonolayer Water on Anatase  $TiO_2(101)$ . *Nat Mater* **2009**, *8*, 585–589.



**Fig. 13** (A) IETS  $d^2/dV^2$  spectra for  $C_2H_2$  (1) and  $C_2D_2$  (2) on Cu(100) show C–H (1) and C–D (2) vibrational peaks at 358 mV and 266 mV, respectively. (1–2) shows the difference spectrum. (B) Regular (constant current) STM image (4.8 × 4.8 nm<sup>2</sup>) of a  $C_2H_2$  (*left*) and a  $C_2D_2$  molecule (*right*). Spectroscopic  $d^2I/dV^2$  spatial imaging of the inelastic channels for (C)  $C_2H_2$  and (D)  $C_2D_2$  recorded at 358 and 266 mV, respectively. Adapted with permission from Stipe, B. C.; Rezaei, M. A.; Ho, W., Single-Molecule Vibrational Spectroscopy and Microscopy. *Science* **1998**, *280*, 1732–1735.



**Fig. 14** Skeletal images of cobalt phthalocyanine (CoPc) with two different configurations, labeled  $CoPc(\times)$  and CoPc(+), obtained by inelastic tunneling probe (itProbe). Constant-height images over (A) CoPc(+) and (B)  $CoPc(\times)$  on Ag(110). (C) Schematic diagram showing the skeletal structure of CoPc(+) and the intramolecular hydrogen bonds (*dashed lines*). Adapted with permission from Chiang, C.-I.; Xu, C.; Han, Z.; Ho, W. Real-Space Imaging of Molecular Structure and Chemical Bonding by Single-Molecule Inelastic Tunneling Probe. *Science* **2014**, *344*, 885–888.

## **Adsorbate Motion**

The delivery of reactants and intermediates to the reaction sites is often mediated by their diffusion on the catalyst surface from their adsorption or generation site. As such, this step represents an important part of many reaction mechanisms. Below we will illustrate two basic types of motion, rotational diffusion, which can lead to the proper alignment of the adsorbed species with the active site to facilitate the reaction, and translational diffusion, which facilitates delivery to the active site.

### **Rotational dynamics**

The STM images of adsorbed species are hardly ever a static representation of their structure. Depending on the temperature, the molecules can access a range of rotational and vibrational configurations which can significantly affect their appearance during long STM imaging timescales. As a result, the image often represents a time average of probability-weighted configurations accessed by the adsorbate during the image acquisition. For example, the images of acetylene shown in Fig. 13B–D appear circular despite the elliptical profile of the molecule. As suggested by the authors,<sup>29</sup> the appearance is likely a result of the fast rotational motion between two equivalent configurations on the surface. At the experimental temperature of 8 K, this represents a rotational barrier that has to be very small (< 2 kJ/mol).



**Fig. 15** The STM images of  $TiO_2(110)$  after adsorption of (A),(E) 1-, (B),(F) 2-, (C), (G) 3-, and (D),(H) 4-octanol at 300 K. Imaging was conducted at 300 K (A)–(D) and 150 K (F)–(H). The insets show magnified areas with the octoxy species overlaid by  $TiO_2(110)$  ball models ( $O_b$ : blue,  $Ti_{5c}$ : magenta). The yellow zigzag lines illustrate the octyl chains; red dots mark the anchoring position on the  $O_b$  row. Green lobes forming an "X" shape for 1-, 2-, and 3-octoxy and "I" shape for 4-octoxy indicate how fast rotation of the octoxy species lead to the formation of such features in the STM images. Adapted with permission from Zhang, Z.; Rousseau, R.; Gong, J.; Kay, B. D.; Dohnálek, Z. Imaging Hindered Rotations of Alkoxy Species on  $TiO_2(110)$ . *J. Am. Chem. Soc.* **2009**, *131*, 17926–17932.

The rotational dynamics has been clearly visualized for 1-, 2-, 3-, and 4-octoxy species anchored on the  $O_b$  rows of rutile TiO<sub>2</sub>(110) as shown in Fig. 15.<sup>32</sup> The octoxy species have been prepared by dissociating the octanol molecules (ROH) via O–H bond cleavage on the V<sub>O</sub> sites (see Fig. 6); the step analogous with the dissociation of water discussed earlier (Reaction 1 and Fig. 8):

$$R - OH + V_O + O_b \rightarrow RO_b + HO_b$$
(3)

Instead of a single bright elongated lobe as expected for the alkyl chain of a static 1-, 2-, and 3-octoxy species, bright "X"-shaped features centered above the original position of the  $V_O$  with four lobes stretching onto the neighboring  $Ti_{5c}$  rows are observed for 1-, 2-, and 3-octoxy species. These "X"-shaped features are a consequence of the alkyl chain rotation between four equivalent local energy minima around the anchoring C–O<sub>b</sub> bond with a rate that is fast compared to the slow STM acquisition rate. The acquired images, therefore, represent a time average of the alkoxy species in these four positions as schematically illustrated in the ball model insets. This trend is completed for 4-octanol, Fig. 15D, where instead of an "X"- and "I"-shaped feature perpendicular to the O<sub>b</sub> row is observed. In all cases, the alkyl chains are located on  $Ti_{5c}$  rows and minimize their overlap with the O<sub>b</sub> rows. This is simply due to increased van der Waals interaction of the hydrocarbon chains with Ti<sup>4+</sup> cations over O<sup>2-</sup> anions.

Direct evidence for the rotation of the octoxy species was further obtained by imaging the octoxy species at 150 K as shown in Fig. 15E–H. While the appearance of 1-octoxy species (Fig. 15E) remains "X" shaped, 2- and 3-octoxy (Fig. 15F and G) became "V" shaped due to frozen cross-O<sub>b</sub> row rotational motion.

A more complex example demonstrating a combination of rotational motion with a reversible reaction is shown in Fig. 16.<sup>33</sup> Here a hydroxyethoxy species,  $O_b$ -(CH<sub>2</sub>)<sub>2</sub>-OH, is formed by 1,2-ethanediol (ethylene glycol) dissociation on the V<sub>O</sub> sites of TiO<sub>2</sub>(110):

$$HO - (CH_2)_2 - OH + V_O + O_b \rightarrow O_b - (CH_2)_2 - OH + HO_b$$
(4)

This species is anchored by one oxygen on the  $O_b$  row, while its second hydroxyl oxygen is bound to the neighboring  $Ti_{5c}$  site. The species rotates slowly at 300 K between the two equivalent  $Ti_{5c}$  rows that are neighboring the anchoring  $O_b$  site. At the same time, a reversible reaction leads to deprotonation of the  $Ti_{5c}$  bound hydroxyl:

$$O_{b} - (CH_{2})_{2} - OH + O_{b} \rightleftharpoons O_{b} - (CH_{2})_{2} - O_{Ti} + HO_{b}$$
 (5)

Following the deprotonation, a stronger bond between the dioxo  $O_{Ti}$  oxygen and the  $Ti_{5c}$  site prevents further rotation until the hydroxyethoxy species is reformed.


**Fig. 16** Time-lapse sequence of STM images of the same area on  $TiO_2(110)$  obtained after the exposure to ethane-1,2-diol at 295 K. The schematics below the images indicate the observed processes. (A)  $\rightarrow$  (B) Formation of the hydroxyethoxy species,  $O_b-(CH_2)_2-OH$ , from the bridging hydroxyl, HO<sub>b</sub>, and the diethoxy,  $O_b-(CH_2)_2-O_{Ti}$ , species (not observed directly). Following its formation, the  $O_b-(CH_2)_2-OH$  rotates around its anchoring  $O_b$  site. (B)  $\rightarrow$  (C) Deprotonation of the  $O_b-(CH_2)_2-OH$  to  $O_b-(CH_2)_2-O_{Ti}$  and HO<sub>b</sub>. The energy barriers for the  $O_b-(CH_2)_2-OH$  dissociation ( $\Delta E_{rot}$ ) were determined via DFT. Reproduced with permission from Acharya, D. P.; Yoon, Y.; Li, Z.; Zhang, Z.; Lin, X.; Mu, R.; Chen, L.; Kay, B. D.; Rousseau, R.; Dohnálek, Z. Site-Specific Imaging of Elemental Steps in Dehydration of Diols on TiO<sub>2</sub>(110). *ACS Nano* **2013**, *7*, 10414–10423.

#### Surface diffusion

Surface diffusion represents a critical step in most catalytic reactions. Under reaction conditions, it efficiently supplies reagents to active sites and mediates steps that involve more than one surface species. The mobility of one species can also mediate mobility of other species. We provide several examples that illustrate such processes and quantitative information that can be obtained from imaging.

We start with a simple example of HO<sub>b</sub> hydrogen diffusion on O<sub>b</sub> rows of TiO<sub>2</sub>(110) that was illustrated in Fig. 8.<sup>20</sup> While the images provide a clear indication of the along-the-row directionality of the motion and the onset temperature of ~300 K, more detailed temperature-dependent studies coupled with theoretical simulations provide information about the mechanism and kinetic parameters.<sup>34</sup> The temperature-dependent hydrogen and deuterium isotope experiments further yield the diffusion activation energies of 0.74 eV and 0.85 eV and prefactors of  $10^{7.3}$  and  $10^{8.6}$  s<sup>-1</sup>, respectively. The differences in the parameters are a consequence of the differences in hydrogen and deuterium zero-point energy. The DFT calculations further reveal that there are two competitive pathways, one involves direct H hopping between the O<sub>b</sub> sites, and the other, two-step mechanism, involves a hop from the O<sub>b</sub> to in-plane oxygen followed by a hop from the in-plane O to the next O<sub>b</sub> (Fig. 17).



**Fig. 17** Intrinsic HO<sub>b</sub> hydrogen diffusion along the O<sub>b</sub> rows on TiO<sub>2</sub>(110) as illustrated in Fig. **8**. (A) Arrhenius plot of the HO<sub>b</sub> hydrogen and DO<sub>b</sub> deuterium hopping rates, *h*. (B) Two competitive pathways determined from DFT calculations: Path 1 involves a direct hydrogen hopping between the O<sub>b</sub> sites. Path 2 involves two steps, hop from O<sub>b</sub> to in-plane 0 atom and hop from in plane 0 to next O<sub>b</sub>. Adapted with permission from Li, S.-C.; Zhang, Z.; Sheppard, D.; Kay, B. D.; White, J. M.; Du, Y.; Lyubinetsky, I.; Henkelman, G.; Dohnálek, Z. Intrinsic Diffusion of Hydrogen on Rutile TiO<sub>2</sub>(110). *J. Am. Chem. Soc.* **2008**, *130*, 9080–9088.



Fig. 18 Schematic view of the cross-row transport of bridging hydroxyl hydrogen mediated by diffusing  $Ti_{5c}$ -bound water molecule on  $TiO_2(110)$  surface. Green ball: water oxygen, gray ball: deuterium, white ball: hydrogen.

The situation changes completely in the presence of water adsorbed on the  $Ti_{5c}$  rows, which represents a more complex diffusion process: molecule-mediated diffusion. Here, the HO<sub>b</sub> hydrogen moves from one O<sub>b</sub> row to another. The mechanistic understanding reveals that the HO<sub>b</sub> hydrogen is not simply moved from one row to another, but is incorporated into water molecule, while a different hydrogen is left behind as illustrated in Fig. 18.<sup>35</sup> This scenario is only observed when the coverage is increased to the point where all V<sub>O</sub>'s are reacted away and converted to hydroxyls (Reaction 1). Under such conditions, hydrogen starts diffusing primarily along the cross-row direction. To illustrate the mechanism, let us start with a pair of HO<sub>b</sub>'s (formed via water dissociation on a V<sub>O</sub> site, see Fig. 8) and water bound on the  $Ti_{5c}$  (we select D<sub>2</sub>O for clarity). The first step involves diffusion of D<sub>2</sub>O along the  $Ti_{5c}$  row (Fig. 18A  $\rightarrow$  B); the second step is the D<sub>2</sub>O dissociation to a pair of hydroxyls (Fig. 18B  $\rightarrow$  C) according to the equation:

$$D_2O + O_b \rightarrow DO_b + DO_t \tag{6}$$

Here, the DO<sub>t</sub> signifies terminal hydroxyl bound on the  $Ti_{5c}$  row and DO<sub>b</sub> located on the O<sub>b</sub> row neighboring the one with the HO<sub>b</sub> pair; the third step is the hydroxyl recombination leading back to water (Fig. 18C  $\rightarrow$  D). This step can involve the original DO<sub>t</sub> and DO<sub>b</sub> (reverse **Reaction 6**) or DO<sub>t</sub> and one of the HO<sub>b</sub>'s:

$$DO_t + HO_b \rightarrow HDO + O_b$$
 (7)

In the latter scenario shown in Fig. 18D, HDO is formed and a new DO<sub>b</sub> hydroxyl ends up across the row from the original HO<sub>b</sub>.

Similarly, water also mediates the transport of oxygen adatoms,  $O_a$ 's, on the  $Ti_{5c}$  rows of  $TiO_2(110)$ .<sup>36</sup> Here the reaction of water with the  $O_a$  yields two terminal hydroxyls:

$$H_2O + O_a \rightarrow 2HO_t$$
 (8)

Upon recombination of the two HO<sub>t</sub>'s to water, one of the two oxygen atoms can be utilized. When the original  $O_a$  is incorporated, the oxygen atom from the molecule is left behind on the surface, displaced by one site along the  $Ti_{5c}$  row.

Since surface reactions are an integral part of the water-mediated diffusion examples shown above, these processes also represent simple examples of surface reactions. Further examples are presented in the subsequent sections that deal with the formation of new surface intermediates and more complex reaction schemes.

#### Formation of Surface Intermediates

In this section, we provide two examples that illustrate the formation of new surface intermediates. In the first example, we demonstrate how surface defects can participate in such a process, and in the second example, we show the reaction of two adsorbed surface species.

Fig. 19 shows an example of the conversion of an  $O_b$  and Ti-bound dioxo species,  $O_b-(CH_2)_3-O_{Ti}$ , to a new dioxo intermediate,  $O_b-(CH_2)_3-O_b$ , that is bound to two neighboring  $O_b$  sites on rutile TiO<sub>2</sub>(110).<sup>33</sup> The  $O_b-(CH_2)_3-O_{Ti}$  species is formed as a result of the dissociation of 1,3-propanediol on the  $V_O$  defect site and deprotonation of the second, Ti-bound, hydroxyl group:

$$HO - (CH_2)_3 - OH + V_O + O_b \rightarrow O_b - (CH_2)_3 - OH + HO_b$$

$$\tag{9}$$

$$O_b - (CH_2)_3 - OH + O_b \rightleftharpoons O_b - (CH_2)_3 - O_{Ti} + HO_b$$

$$\tag{10}$$

These reactions parallel those for 1,2-ethanediol (Reactions 4 and 5) illustrated above.

The HO<sub>b</sub> species formed in this sequence are mobile at the imaging temperature of 460 K and diffuse away from the vicinity of the  $O_b-(CH_2)_3-O_{Ti}$  species. In addition, prior studies have shown that the  $V_O$  defects are mobile at 460 K, which is critical for the  $O_b-(CH_2)_3-O_{Ti}$  changes observed from Fig. 19A to B leading to the  $I_{HT}$  intermediate. The mechanism that was put forward is shown in the schematics in Fig. 19C–E. In the first step,  $V_O$  diffuses toward the  $O_b-(CH_2)_3-O_{Ti}$  species (Fig. 19C). In the second step, the  $O_b-(CH_2)_3-O_{Ti}$  rotates about the  $O_b$  anchor into the empty  $O_b$  site created by the diffusing  $V_O$  (Fig. 19D). This results in the formation of a new dioxo intermediate that is bound to two neighboring  $O_b$  sites (Fig. 19D). This process can be summarized by the following reaction:

$$O_b - (CH_2)_3 - O_{Ti} + V_O \rightarrow O_b - (CH_2)_3 - O_b$$
 (11)

Similar V<sub>O</sub>-assisted mechanism was also concluded for the diffusion of O<sub>b</sub>-bound alkoxy species along the O<sub>b</sub> rows.<sup>37</sup>



**Fig. 19** Time-lapse sequence of STM images of the same area on  $TiO_2(110)$  obtained at 460 K: (A) surface after 1,3-propanediol adsorption, dissociation in  $V_0$ , and deprotonation (Reactions 9 and 10). (B) same area after an additional 6 min of imaging leading to the formation of high-temperature intermediate,  $I_{HT}$ . The large  $TiO_x$  cluster labeled with  $\times$  was used to track the same area at high temperatures. (C–E) Proposed identity and mechanism of the formation for the  $I_{HT}$  intermediate. Adapted with permission from Acharya, D. P.; Yoon, Y.; Li, Z.; Zhang, Z.; Lin, X.; Mu, R.; Chen, L.; Kay, B. D.; Rousseau, R.; Dohnálek, Z. Site-Specific Imaging of Elemental Steps in Dehydration of Diols on  $TiO_2(110)$ . *ACS Nano* **2013**, *7*, 10414–10423.

Interestingly, the same  $O_b-(CH_2)_3-O_{Ti}$  intermediate formed by the Reaction 9 can also be created by the coupling reaction of two adsorbed formaldehyde, HCHO, molecules.<sup>38</sup> In the experiment shown in Fig. 20, the same area was followed, as a function of increasing temperature. This experimentally extremely challenging method enables imaging of the processes that happened at different temperatures. Here several formaldehyde molecules are imaged from their initial adsorption, to the onset of diffusion, to the formation of new intermediates, and ultimately to the C–C coupling reaction. Starting with the image of the clean TiO<sub>2</sub>(110) at 75 K (Fig. 20A), a HCHO dose leads to three formaldehyde molecules adsorbed on the Ti<sub>5c</sub> rows (Fig. 20B). Subsequently, the diffusion of two formaldehyde molecules at 145 K leads to their adsorption on the preferred V<sub>O</sub> sites (Fig. 20C). Ultimately, further diffusion of Ti<sub>5c</sub>-bound HCHO leads to an encounter with the V<sub>O</sub>-bound formaldehyde and coupling reaction that yields the diolate,  $O_b-(CH_2)_2-O_{Ti}$ , intermediate as shown in Fig. 20D.

#### Imaging Complex Reactions

Armed with the detailed understanding of elemental reaction steps for each adsorbate and arsenal of approaches to characterize each species (see Section "Molecular Adsorption"), STM can be utilized to follow complex reactions between different molecules. Often, many reaction steps occur concurrently making it difficult to follow what is happening with each of the individual species.

Such a complex reaction mechanism is illustrated for the reaction of molecular oxygen with water on  $TiO_2(110)$ .<sup>39</sup> Here water fulfills multiple roles: it serves as a reactant, product, and as a catalyst facilitating the diffusion of other species. As shown in separate experiments, water and oxygen can dissociate on  $TiO_2(110)$  via different dissociation pathways<sup>13,14,40</sup>:

$$H_2O + V_O + O_b \rightarrow 2OH_b \tag{1}$$

$$O_2 + V_O \rightarrow O_b + O_a \tag{12}$$

$$O_2 \rightarrow 2O_a$$
 (13)

The oxygen adatom,  $O_a$ , and bridging hydroxyl,  $OH_b$ , intermediates can be identified using their adsorption sites, symmetry and brightness as indicated in Fig. 21A and B. The reaction between  $OH_b$  and  $O_2$  further leads to hydroperoxo,  $HO_2$ , intermediate (Fig. 21B) that was also identified in separate studies<sup>41</sup>:

$$OH_b + O_2 \rightarrow O_b + HO_2 \tag{14}$$



**Fig. 20** STM images obtained from the same area of reduced  $TiO_2(110)$  at different temperatures, revealing the formation of dioxo  $O_b-(CH_2)_2-O_{Ti}$  species via a coupling reaction of the Ti-bound formaldehyde and the  $V_0$ -bound formaldehyde. (A) Clean surface imaged at 75 K, (B) surface imaged at 75 K after dosing 0.02 ML of formaldehyde at 75 K, (C) surface imaged at 145 K, and (D) surface imaged at 170 K. Dotted lines mark the position of Ti<sub>5c</sub> rows (*orange*) and  $O_b$  row (*blue*). Reproduced with permission from Zhu, K.; Xia, Y.; Tang, M.; Wang, Z.-T.; Jan, B.; Lyubinetsky, I.; Ge, Q.; Dohnálek, Z.; Park, K. T.; Zhang, Z. Tracking Site-Specific C–C Coupling of Formaldehyde Molecules on Rutile TiO<sub>2</sub>(110). *J. Phys. Chem. C* 2015, *119*, 14267–14272.



**Fig. 21** STM images of the same area  $(10 \times 10 \text{ nm}^2)$  on a partially hydroxylated TiO<sub>2</sub>(110) surface with 0.061 ML of V<sub>0</sub>'s and 0.043 ML of HO<sub>b</sub>'s. (A) Before and (B) after O<sub>2</sub> exposures of 5.6 × 10<sup>15</sup> O<sub>2</sub>/cm<sup>2</sup>. (C) Same area after an additional dose of 2.4 × 10<sup>15</sup> O<sub>2</sub>/cm<sup>2</sup> (cumulative dose of 8.0 × 10<sup>15</sup> O<sub>2</sub>/cm<sup>2</sup>). Reproduced with permission from Zhang, Z.; Du, Y.; Petrik, N. G.; Kimmel, G. A.; Lyubinetsky, I.; Dohnálek, Z. Water as a - Catalyst: Imaging Reactions of O<sub>2</sub> with Partially and Fully Hydroxylated TiO<sub>2</sub>(110) Surfaces. *J. Phys. Chem. C* 2009, *113*, 1908–1916.

Further, terminal hydroxyl intermediates (Fig. 21B) were shown to form via reaction of oxygen adatoms near the bridging hydroxyls:

$$OH_b + O_a \rightarrow OH_t + O_b \tag{15}$$

In the absence of  $Ti_{5c}$ -bound water, all the above-mentioned intermediates are immobile, and the surface remains static. A small additional dose of  $O_2$  should lead to the formation of additional intermediates. Contrary to this expectation, it leads to complete

disappearance of  $V_0$ ,  $O_a$ ,  $HO_t$ , and  $HO_2$  species as shown in Fig. 21C. This abrupt change is a result of water formation via reactions between the neighboring intermediates:

$$OH_b + HO_2 \rightarrow O_b + O_a + H_2O \tag{16}$$

$$OH_b + OH_t \rightarrow O_b + H_2O \tag{17}$$

$$2OH_t \rightarrow O_a + H_2O \tag{18}$$

As demonstrated earlier (Section "Adsorbate Motion"), water facilitates diffusion of HO<sub>b</sub> and O<sub>a</sub> species. This in turns brings the species together, and the reactions above accelerate. Ultimately, the amount of initial  $V_O$ ,  $O_2$ , and  $H_2O$  reagents determines the endpoint of the reaction. Here (Fig. 21C), besides desorbing  $H_2O$ , it is HO<sub>b</sub> that remains on the surface.

# **Future Directions and Challenges**

We would like to conclude this tutorial with few examples that hint us about the future of single molecule reaction imaging. This is an exciting area with bright future that provides a wealth of information that cannot be obtained otherwise. The majority of examples given in the previous sections involved STM imaging under clean UHV conditions. Hence, taking advantage of other imaging techniques such as AFM, combining STM with other spectroscopy methods to enhance its capabilities, and carrying out studies at high pressures and in condensed phase are clear frontier areas to be explored. The sections below provide few examples that illustrate progress in these areas.

## **High Pressure and Condensed Phase Studies**

The development and utility of the reactorSTM for high-pressure studies has already been briefly mentioned (Section "Scanning Tunneling Microscopy"). While adsorbate-induced changes in the catalyst structure can be followed relatively easily, studies of adsorbates, isolated molecules in particular, become very difficult, even more so in the liquid phase. Additionally, small amounts of strongly bound contaminants/adsorbates from the environment can alter the surface structure, and their effect has to be considered under realistic reaction conditions.

An example highlighting such effects is illustrated for rutile  $TiO_2(110)$  when exposed to air and liquid water. Here, the small amount of  $CO_2$  (binds weakly on  $TiO_2(110)^{42}$ ) from the atmosphere or liquid water leads to the formation of strongly bound bicarbonate (HCO<sub>3</sub>) species.<sup>43</sup> This reaction is promoted by both the strong bidentate bonding of HCO<sub>3</sub> and the nanoscale H<sub>2</sub>O film that spontaneously forms on TiO<sub>2</sub> under ambient conditions. The formation of such ordered monolayer of HCO<sub>3</sub> and H is shown in Fig. 22. The layer is stable in vacuum up to 450 K. These results demonstrate the need for studies on well-controlled catalyst surfaces in ambient and solution environments, where competition for reactive sites plays an important role.



#### Sputtered + Water Immersion

**Fig. 22** STM images of (A) a sputtered and annealed rutile  $TiO_2(110)$  sample that was then (B) immersed in  $H_2O$  for 3 min. The bicarbonate monolayer in (B) leads to periodic protrusions with a characteristic 0.60 nm spacing. Reprinted with permission from Song, A.; Skibinski, E. S.; DeBenedetti, W. J. I.; Ortoll-Bloch, A. G.; Hines, M. A. Nanoscale Solvation Leads to Spontaneous Formation of a Bicarbonate Monolayer on Rutile (110) under Ambient Conditions: Implications for CO<sub>2</sub> Photoreduction. *J. Phys. Chem. C* **2016**, *120*, 9326–9333.



**Fig. 23** (A) Relative stability and interconversion barriers for molecularly and dissociatively bound water on TiO<sub>2</sub>(110) determined from the combined molecular beam scattering and STM imaging experiments. (B) The dissociation probability of H<sub>2</sub>O molecules impinging on the TiO<sub>2</sub>(110) with different incident energies. Adapted with permission from Wang, Z.-T.; Wang, Y.-G.; Mu, R.; Yoon, Y.; Dahal, A.; Schenter, G. K.; Glezakou, V.-A.; Rousseau, R.; Lyubinetsky, I.; Dohnálek, Z. Probing Equilibrium of Molecular and Deprotonated Water on TiO<sub>2</sub>(110). *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 1801–1805.

## **Combined Molecular Beam Scattering and Scanning Tunneling Microscopy**

The power of molecular beam technology is its ability to tune the translational energy of the molecules or even prepare molecules in specific rotationally and vibrationally excited state.<sup>44,45</sup> This allows to overcome the energy barriers for low-probability processes and, in principle, bridge the pressure gap. By following the energy-dependent dissociation probabilities, one can probe energetics of specific reaction steps and quantify their barriers. Despite the maturity of molecular beam technology, its combination with STM proved challenging and successful executions are rather limited.<sup>17,46</sup> Recently, the relative stability of molecular water relative to hydroxyls on  $Ti_{5c}$  rows of  $TiO_2(110)$  (**Reaction 2**) as well as their interconversion barriers have been successfully measured (Fig. 23A)<sup>17</sup> resolving the long-standing controversy in the literature.<sup>14</sup>

The dissociation probabilities, determined by counting the molecularly and dissociatively bound water molecules in the STM images obtained at 80 K, are shown as a function of  $H_2O$  incident energy in Fig. 23B (*blue squares*). The experimental data are complemented by the results of the AIMD simulations (*red squares*) that reveal how the electrostatic field emanating from the oxide surface leads to steering and reorientation of the molecules, activation of the O–H bonds, and deprotonation. A classical MD model, constructed based on the AIMD results, allows for precise determination of the dissociation barrier of 0.36 eV.

#### Adsorbate Structure Imaging with Functionalized Scanning Probes

While atomic resolution on surfaces can nowadays be obtained routinely, the atomic resolution within the adsorbed species has been achieved only recently.<sup>12,47</sup> The key to this advancement has been the tip functionalization. Typically, this is achieved by picking up a single CO molecule with the tip. This has been first accomplished with CO-functionalized AFM tips that can produce high-resolution images that closely resemble the structure of the adsorbed molecule.<sup>47</sup> We have already discussed the IETS imaging with CO functionalized STM tips (see Section "Molecular Adsorption") that was developed later.<sup>31</sup> For the CO-functionalized AFM tips, the atomic features only become visible when working at small tip-sample distances in the regime of Pauli repulsion between the CO molecule at the tip and the imaged molecule on the surface. While first demonstrated for pentacene molecules,<sup>47</sup> the most striking example of a direct identification of the structure of more than one hundred asphaltene molecules in the mixture is illustrated in Fig. 24 (Ref. 48). The asphaltenes are the solid components of crude oil and pose an exceptional challenge for structure analysis. This study demonstrated that many different molecules can be screened by high-resolution scanning probe microscopy in a single preparation without going through a lengthy chemical synthesis, purification, and characterization for each one of them beforehand.

## **Combining Scanning Probe Techniques with Vibrational Spectroscopies**

Following surface reactions with both topographic and chemical information at the molecular level represents an ultimate challenge for imaging techniques. While IETS (see Section "Molecular Adsorption") provides some vibrational information, it does not reveal the unique vibrational fingerprint of the molecule and the experiments require liquid helium temperatures. Raman spectroscopy and IR spectroscopy can yield a complete vibrational signature of the molecules. However, their spatial resolution is limited by the diffraction limit (hundreds of nanometers). In recent developments, Raman and IR are being combined with SPM to obtain best of both worlds, vibrational spectra of molecules with a typical spatial resolution comparable to the radius of the tip  $(\sim 10 \text{ nm}).^{49-53}$ 

Tip-enhanced Raman spectroscopy (TERS) utilizes the localized surface plasmons of the noble metal tip to focus the light at its apex, which enhances the weak scattered Raman signal (Fig. 25A). The advantage of TERS is that it can operate both in ultrahigh



**Fig. 24** Laplace-filtered AFM images of selected coal-derived asphaltenes with their derived structure. Adapted with permission from Schuler, B.; Meyer, G.; Peña, D.; Mullins, O. C.; Gross, L., Unraveling the Molecular Structures of Asphaltenes by Atomic Force Microscopy. *J. Am. Chem. Soc.* **2015**, *137*, 9870–9876.



**Fig. 25** (A) Schematic tunneling-controlled TERS in a confocal-type side-illumination configuration. (B) STM image (1.5 V, 30 pA, 35 nm  $\times$  27 nm) of isolated *meso*-tetrakis(3,5-di-tertiarybutylphenyl)-porphyrin (H<sub>2</sub>TBPP) molecules on Ag(111). The inset shows the chemical structure of H<sub>2</sub>TBPP. (C) Representative single molecule TERS spectra on the lobe (*red*) and center (*blue*) of a flat-lying H<sub>2</sub>TBPP molecule on Ag(111). The TERS spectrum on the bare Ag about 1 nm away from the molecule is also shown, in black (120 mV, 1 nA, 3 s). (D) The top panels show experimental TERS mapping of a single molecule for different Raman peaks (23  $\times$  23,  $\sim$ 0.16 nm per pixel), processed from all individual TERS spectra acquired at each pixel (120 mV, 1 nA, 0.3 s; image size: 3.6  $\times$  3.6 nm<sup>2</sup>). The bottom panels show the theoretical simulation of the TERS mapping. Reproduced with permission from Zhang, R.; Zhang, Y.; Dong, Z. C.; Jiang, S.; Zhang, C.; Chen, L. G.; Zhang, L.; Liao, Y.; Aizpurua, J.; Luo, Y.; Yang, J. L.; Hou, J. G. Chemical Mapping of a Single Molecule by Plasmon-Enhanced Raman scattering. *Nature* **2013**, *498*, 82–86.

vacuum and under high pressures. Using ultrahigh-vacuum TERS, Zhang et al. conducted the chemical imaging of single H<sub>2</sub>TBPP molecule on Ag(111).<sup>54</sup> The characteristic four-lobed pattern of an H<sub>2</sub>TBPP molecule is discernible in the TERS mapping (Fig. 25D). This is because the TERS peak intensities (Fig. 25C) acquired on the molecular lobe are stronger than those in the center. Their work pushed the spatial resolution of TERS to 1 nm, which is an order of magnitude smaller than the radius of the tip.

The success of the TERS shows the great potential of imaging catalytic reactions at the molecular scale. Both experimental development and theoretical understanding of TERS experienced a rapid growth in last several years. Currently, most of the TERS studies have been done using gap mode, utilizing plasmonic metal tip and plasmonic metal substrates, to maximize the enhancement of Raman signal. The studies on nonmetal substrates are still very limited.<sup>55</sup>

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# Impedance Spectroscopy Applied to the Study of Electrocatalytic Processes

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## Introduction

Electrocatalytic reactions are the inner sphere electrochemical reactions involving interactions of reactants with the electrode surface.<sup>1</sup> Electrocatalysts can lower the activation energy but cannot affect the reaction thermodynamics. Typically the electrodes used are metallic (pure metals, alloys, monocrystals, small particles) or oxides although other surfaces were also studied (e.g., heteropolyacids, carbides, phosphides, sulfides, phosphides, borides, silicides, carbon).<sup>2</sup> The majority of the reactions of practical importance are electrocatalytic: hydrogen adsorption, oxidation or evolution, oxygen reduction or evolution, chlorine evolution,  $CO_2$  and CO oxidation or reduction, direct alcohol and other small molecules oxidation (ammonia, hydrazine, formic acid, formaldehyde) in polymer membrane fuel cells, hydrocarbons in solid oxide fuel cells, etc.

The main purpose of electrocatalysis in industrial practice is to find the best electrocatalysts and conditions to carry out the desired reactions with the highest efficiency, that is, at the smallest overpotential. Important fundamental aspect of electrocatalysis is the determination of the mechanism, kinetics, and thermodynamic parameters of reactions. Various classical electrochemical methods: cyclic voltammetry, steady-state polarizations, chronoamperometry, chronopotentiometry, and open circuit potential decay in stationary and hydrodynamic (rotating disk or rotating ring disk electrodes) conditions are initially used. They are followed with various spectroscopic techniques (infrared,<sup>3</sup> electron spectroscopy, in situ X-ray synchrotron spectroscopy: XSANES, EXAFS<sup>4</sup>), differential electrochemical mass spectrometry, DEMS,<sup>3,5</sup> electrochemical quartz crystal microbalance, EQCM,<sup>3</sup> and radiochemical methods to determine the nature and quantity of surface species. These measurements lead to a hypothesis about the mechanism of such reactions. However, testing of the mechanism and determination of the reaction parameters are the most challenging part of the research. Very often, the reaction mechanism proposed involves several reactions and adsorbed species but only some of them are rate limiting and other might be fast. The classical electrochemical methods might not always be sufficient in determination of the detailed mechanism.

Electrochemical impedance spectroscopy (EIS) is the versatile method which allows to study the details of the complex reaction mechanisms.<sup>6-8</sup> It is a mature method<sup>9</sup> which allows for fine tuning and distinction between possible electrode mechanisms. Although it is widely used in electrochemical studies, its possibilities were not yet fully exploited.

Here, some fundamental notions of the EIS will be presented followed by its applications in simple and more complicated electrocatalytic reactions.

# **Introduction to EIS**

EIS differs from the other electrochemical techniques. In typical electrochemical methods the electrical signal: current or potential is measured as a function of time (or electrical parameters proportional to time) after application of a perturbation (potential or current step, potential sweep). However, in EIS a small sinusoidal perturbation of the potential or current is applied and the sinusoidal perturbation of the same frequency of the current or potential is measured. Such a measurement is repeated for a wide series of different frequencies in the steady-state conditions. The applied signal has its amplitude and the phase (usually assumed as zero) and the measured signal has also its amplitude, but it is shifted in phase with respect to the perturbation.



**Fig. 1** Time dependence of the potential and current signals of the amplitude E=0.01 V and i=0.002 A, current precedes potential by 60 degrees (*left*), and the polar representation of the potential and current vectors (*right*).

An example of the applied sinusoidal voltage of the amplitude 0.01 V with initial phase zero and the measured current of the amplitude 0.002 A and shifted in phase by 60 degrees is shown in Eq. (1) and, in time and polar representations, in Fig. 1. Both signals have the same frequency of 3.125 Hz.

These signals, in the time domain, are:

$$E = |E|\cos(\omega t + \varphi_{\rm E}) = 0.01\cos(\omega t)$$
  

$$i = |i|\cos(\omega t + \varphi_{\rm i}) = 0.002\cos(\omega t + 60^{\circ})$$
  

$$\omega = 2\pi f; \quad f = 3.125 \text{ s}^{-1}$$
(1)

and in the polar notation:

$$E = |E| \angle 0^{\circ}; \quad i = |i| \angle 60^{\circ} \tag{2}$$

The modulus of the impedance is simply the ratio of the amplitudes of the potential and current  $|Z| = 0.01 \text{ V}/0.002 \text{ A} = 5 \Omega$  and the phase angle is of course -60 degrees (see Fig. 2). Using simple trigonometry the  $\gamma$  component is  $5 \times \sin(-60^\circ) = -4.33 \Omega$  and the x component is  $5 \times \cos(-60^\circ) = 2.5 \Omega$  (see Fig. 2). Instead of using trigonometry we can simplify the calculations by calling  $\gamma$  axis imaginary and x axis real and using complex calculus in the computations:

$$\widehat{Z} = \frac{|E|\cos(\varphi_{\rm E}) + j|E|\sin(\varphi_{\rm E})}{|i|\cos(\varphi_{\rm E}) + j|i|\sin(\varphi_{\rm E})} = \frac{0.01}{0.002\cos(60^\circ) + j0.002\sin(60^\circ)}$$

$$= \frac{0.01}{0.001 + j0.001732} = 2.5 - j4.33$$
(3)



Fig. 2 Polar representation of the impedance; it is simply the ratio of vectors E and i from Fig. 1 (right).



Fig. 3 Electrical equivalent circuit for the faradaic reaction at the electrode surface.

 Table 1
 Impedances of the electrical elements

Electrical element	R	С	L
Impedance	R	1/ <i>j</i> ωC	jωL

The impedance vector in Fig. 2 is simply the ratio of vectors E and i from Fig. 1 (right), Eq. (3). Of course more precise mathematically the impedance is the ratio of the Fourier transforms (operator F) of E and i:

$$\widehat{Z} = \frac{F(E)}{F(i)} = \frac{0.005}{0.0005 + j0.000866} = 2.5 - j4.33$$
(4)

and all the calculations are carried out using complex notation.<sup>8</sup>

In determination of the impedances of the electrochemical systems, the ideally polarizable electrode may be represented as the connection of the solution resistance,  $R_{sr}$  and double layer capacitance,  $C_{dl}$ , in series. In the presence of the faradaic reaction, the faradaic impedance,  $\hat{Z}_{fr}$  is in parallel with the double layer capacitance. The electrical equivalent model of the electrode in the presence of red-ox reaction at the surface is displayed in Fig. 3.

For each reaction mechanism one can write the corresponding impedance by linearization of the current, the equation(s) describing surface coverage by adsorbed species, and the mass transport to and from the electrode.<sup>8</sup> The obtained faradaic impedance might often be rearranged and expressed in the form of the electrical components of resistance, R, capacitance, C, and inductance, L. The impedances of these elements are displayed in **Table 1**. The use of the equivalent circuits is not obligatory when the equation describing  $\hat{Z}_f$  is known but its use helps to understand the electrochemical processes and allows for use of the popular fitting programs. It should be added that mass transfer, surface porosity, or geometry might lead to equations which cannot be represented by simple electrical elements but they are often included in the popular software as equations.

In the next chapters impedance of various electrocatalytic processes will be presented.

## Simple Electrosorption Reaction

The simplest electrocatalytic reaction is an electrosorption, and the examples are hydrogen<sup>10</sup> or metal (on other metal)<sup>11</sup> underpotential deposition (UPD). Let us consider electrosorption of species A from solution to  $B_{ads}$  adsorbed at the electrode surface M:

$$A + M + e^{-\frac{\overrightarrow{k}_{1}}{\overleftarrow{k}_{2}}} MB_{ads}$$
(5)

For example, for the hydrogen UPD:  $A = H^+$  and  $MB_{ads} = MH_{ads}$ . The rate of this reaction,  $v_1$ , neglecting the diffusion of A in solution (i.e., assuming that the surface and bulk concentrations are the same) and assuming Langmuir adsorption isotherm for  $MB_{ads}$  might be described by the equation<sup>8</sup>:

$$v_1 = k_0 e^{-\beta f (E - E_p)} (1 - \theta_B) - k_0 e^{(1 - \beta) f (E - E_p)} \theta_B = \vec{k}_1 (1 - \theta_B) - \vec{k}_1 \theta_B$$
(6)

where the rate constant  $k_0$  contains also concentration of A in solution,<sup>8</sup> f = F/RT,  $\beta$  is the transfer coefficient,  $\theta_B$  is the surface coverage by adsorbed species B,  $E_p$  is the potential corresponding to  $\theta_B = 0.5$ , and  $\vec{k}_1$  and  $\vec{k}_1$  are the potential dependent rate constants. In the further equations, the potential difference will be written as  $\eta = E - E_p$ . The equations describing current and  $d\theta_B/dt$  are:

$$i = -Fv_1 = -F\left[\overrightarrow{k}_1(1-\theta_B) - \overleftarrow{k}_1\theta_B\right]$$

$$\sigma_B \frac{d\theta_B}{dt} = -F\left[\overrightarrow{k}_1(1-\theta_B) - \overleftarrow{k}_1\theta_B\right]$$
(7)

where  $\sigma_B$  is the charge necessary for the full surface coverage by adsorbed B. The stationary current is always zero and the surface coverage by adsorbed hydrogen is changing between 0 at positive potentials to 1 at negative potentials, according to the Langmuir isotherm (see Fig. 4):

$$\theta_{\rm B} = \frac{1}{1 + \exp(f\eta)} \tag{8}$$

Linearization of Eq. (7), that is, keeping only the linear terms in Maclauren series<sup>8</sup> leads to:

$$\Delta i = -F\Delta v_1 = -F\left[\left(\frac{\partial v_1}{\partial \eta}\right)\Delta \eta + \left(\frac{\partial v_1}{\partial \theta_B}\right)\Delta \theta_B\right]$$
  
$$\sigma_1 \frac{\partial \Delta \theta_B}{\partial t} = F\left[\left(\frac{\partial v_1}{\partial \eta}\right)\Delta \eta + \left(\frac{\partial v_1}{\partial \theta_B}\right)\Delta \theta_B\right]$$
(9)

where  $\Delta p = p_0 \exp\left[j\left(\omega t + \phi_p\right)\right] = p_0 e^{j\phi_p} e^{j\omega t} = \tilde{p}e^{j\omega t}$  and parameters *p* are *i*,  $v_1$ ,  $\eta$ , and  $\theta_B$ . Vectors  $\tilde{p}$  are called phasors. Using phasors one can rewrite Eq. (9) as<sup>8</sup>:

$$\widetilde{i} = -F\left[\left(\frac{\partial v_1}{\partial \eta}\right)\widetilde{\eta} + \left(\frac{\partial v_1}{\partial \theta_B}\right)\widetilde{\theta}_B\right]$$

$$j\omega\sigma_B\widetilde{\theta}_B = F\left[\left(\frac{\partial v_1}{\partial \eta}\right)\widetilde{\eta} + \left(\frac{\partial v_1}{\partial \theta_B}\right)\widetilde{\theta}_B\right]$$
(10)





**Fig. 4** Plots of the surface coverage,  $\theta_B$ , charge transfer resistance,  $R_{ct}$ , and pseudocapacitance,  $C_p$ , on overpotential for one adsorbed species, reaction (5), assuming Frumkin adsorption isotherm,  $k_0 = 10^{-7}$  mol cm<sup>-2</sup> s<sup>-1</sup>,  $\sigma_B = 210 \mu$ F cm<sup>-2</sup>, and  $\beta = 0.5$ . Values of the interaction factor, g, are indicated in graphs; for g=0 Langmuir isotherm is obtained.