

3RD
EDITION



FUEL CELL SYSTEMS EXPLAINED



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WILEY

Fuel Cell Systems Explained

Fuel Cell Systems Explained

Third Edition

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Brief Biographies



Andrew L. Dicks

Andrew L. Dicks, PhD, CChem, FRSC, was educated in England and graduated from Loughborough University before starting a career in the corporate laboratories of the UK gas industry. His first research projects focused on heterogeneous catalysts in gas-making processes, for which he was awarded a doctorate in 1981. In the mid-1980s, BG appointed Andrew to lead a research effort on fuel cells that was directed predominantly towards molten carbonate and solid oxide systems. The team pioneered the application of process modelling to fuel-cell systems, especially those that featured internal reforming. This work, which was supported by the European Commission during the 1990s, involved collaboration with leading fuel-cell developers throughout Europe and North America. In 1994, Andrew was jointly awarded the Sir Henry Jones

(London) Medal of the Institution of Gas Engineers and Managers for his studies on high-temperature systems. He also took an interest in proton-exchange membrane fuel cells and became the chair of a project at the University of Victoria, British Columbia, in which Ballard Power Systems was the industrial partner. In 2001, he was awarded a Senior Research Fellowship at the University of Queensland, Australia, that enabled further pursuit of his interest in catalysis and the application of nanomaterials in fuel-cell systems. Since moving to Australia, he has continued to promote hydrogen and fuel-cell technology, as director of the CSIRO National Hydrogen Materials Alliance and as a director of the Australian Institute of Energy. He is now consulted on energy and clean technology issues by governments and funding agencies worldwide.

**David A. J. Rand**

David A. J. Rand, AM, BA, MA, PhD, ScD, FTSE, was educated at the University of Cambridge where, after graduation, he conducted research on low-temperature fuel cells. In 1969, he joined the Australian government's CSIRO laboratories in Melbourne. After further exploration of fuel-cell mechanisms and then electrochemical studies of mineral beneficiation, he formed the CSIRO Novel Battery Technologies Group in the late 1970s and

remained its leader until 2003. He was one of the six scientists who established the US-based Advanced Lead–Acid Battery Consortium in 1992 and served as its manager in 1994. He is the co-inventor of the UltraBatteryTM, which finds service in hybrid electric vehicle and renewable energy storage applications. As a chief research scientist, he fulfilled the role of CSIRO's scientific advisor on hydrogen and renewable energy until his retirement in 2008. He remains active within the organisation as an Honorary Research Fellow and has served as the chief energy scientist of the World Solar Challenge since its inception in 1987. He was awarded the Faraday Medal by the Royal Society of Chemistry (United Kingdom) in 1991, the UNESCO Gaston Planté Medal by the Bulgarian Academy of Sciences in 1996 and the R.H. Stokes Medal by the Royal Australian Chemical Institute in 2006. He was elected a fellow of the Australian Academy of Technological Sciences and Engineering in 1998 and became a member of the Order of Australia in 2013 for service to science and technological development in the field of energy storage.

Preface

Since publication of the first edition of *Fuel Cell Systems Explained*, three compelling drivers have supported the continuing development of fuel-cell technology, namely:

- The need to maintain energy security in an energy-hungry world.
- The desire to reduce urban air pollution from vehicles.
- The mitigation of climate change by lowering anthropogenic emissions of carbon dioxide.

New materials for fuel cells, together with improvements in the performance and lifetimes of stacks, are underpinning the emergence of the first truly commercial systems in applications that range from forklift trucks to power sources for mobile phone towers. Leading vehicle manufacturers have embraced the use of electric drivetrains and now see hydrogen fuel cells complementing the new battery technologies that have also emerged over the past few years. After many decades of laboratory development, a global — but fragile — fuel-cell industry is bringing the first products to market.

To assist those who are unfamiliar with fuel-cell electrochemistry, Chapter 1 of this third edition has been expanded to include a more detailed account of the evolution of the fuel cell and its accompanying terminology. In the following chapters, extensive revision of the preceding publication has removed material that is no longer relevant to the understanding of modern fuel-cell systems and has also introduced the latest research findings and technological advances. For example, there are now sections devoted to fuel-cell characterization, new materials for low-temperature hydrogen and liquid-fuelled systems, and a review of system commercialization. Separate chapters on fuel processing and hydrogen storage have been introduced to emphasize how hydrogen may gain importance both in future transport systems and in providing the means for storing renewable energy.

The objective of each chapter is to encourage the reader to explore the subject in more depth. For this reason, references have been included as footnotes when it is necessary to substantiate or reinforce the text. To stimulate further interest, however, some recommended further reading may be given at the end of a chapter.

There are now several books and electronic resources available to engineers and scientists new to fuel-cell systems. The third edition of *Fuel Cell Systems Explained* does not intend to compete with specialist texts that can easily be accessed via the Internet. Rather, it is expected that the book will continue to provide an introduction and overview for students and teachers at universities and technical schools and act as

a primer for postgraduate researchers who have chosen to enter this field of technology. Indeed, it is hoped that *all* readers — be they practitioners, researchers and students in electrical, power, chemical and automotive engineering disciplines — will continue to benefit from this essential guide to the principles, design and implementation of fuel-cell systems.

December 2017

Andrew L. Dicks, Brisbane, Australia
David A. J. Rand, Melbourne, Australia

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As emphasized throughout this publication, the research and development of fuel cells is highly interdisciplinary in that it encompasses many aspects of science and engineering. This fact is reflected in the number and diversity of companies and organizations that have willingly provided advice and information or given permission to use their images in the third edition of *Fuel Cell Systems Explained*. Accordingly, the authors are indebted to the following contributors:

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Acronyms and Initialisms

ABPBI	phosphoric acid doped poly(2,5-benzimidazole)
AC	alternating current
ADP	adenosine 5'-triphosphate
AEM	alkaline-electrolyte membrane
AEMFC	alkaline-electrolyte membrane fuel cell
AES	air-electrode supported
AFC	alkaline fuel cell
AMFC	anion-exchange membrane fuel cell
ANL	Argonne National Laboratory
APEMFC	alkaline proton-exchange membrane fuel cell
APU	auxiliary power unit
ASR	area specific resistance
BCN	Dutch Fuel Cell Corporation
BG	British Gas
BIMEVOX	bismuth metal vanadium oxide ($\text{Bi}_4\text{V}_2\text{O}_{11}$)
BOP	balance-of-plant
BPS	Ballard Power Systems
BSF	Boudouard Safety Factor
CAN bus	Controller Area Network
CBM	coal-bed methane
CCS	carbon capture and storage
CFCL	Ceramic Fuel Cells Ltd
CGO	cerium–gadolinium oxide (same as GDC)
CHP	combined heat and power
CLC	chemical looping combustion
CNR	Consiglio Nazionale delle Ricerche (Italy)
CNT	carbon nanotube
CODH-1	carbon monoxide dehydrogenase
CPE	constant phase element
CPO	catalytic partial oxidation
CRG	catalytic rich gas
CSG	coal-seam gas
CSIRO	Commonwealth Scientific and Industrial Research Organisation

CSO	cerium-samarium oxide (same as SDC)
CSZ	calcia-stabilized zirconia
CV	cyclic voltammetry
CVD	chemical vapour deposition
DBFC	direct borohydride fuel cell
DC	direct current
DCFC	direct carbon fuel cell
DEFC	direct ethanol fuel cell
DEGFC	direct ethylene glycol fuel cell
DFAFC	direct formic acid fuel cell (also formic acid fuel cell, FAFC)
DFT	density functional theory
DG	distributed generator
DIR	direct internal reforming
DIVRR	directly irradiated, volumetric receiver–reactor
DLFC	direct liquid fuel cell
DMFC	direct methanol fuel cell
DOE	Department of Energy (United States)
DPFC	direct propanol fuel cell
DPFC(2)	direct propan-2-ol fuel cell
DSSC	dye-sensitized solar cell
EC	evaporatively cooled
ECN	Energy Research Centre of the Netherlands
EFOY	Energy for You
EIS	electrochemical impedance spectroscopy
EPFL	Swiss Federal Institute of Technology
EU	European Union
EVD	electrochemical vapour deposition
EW	membrane equivalent weight
FCE	Fuel Cell Energy Inc.
FCES	Fuel Cell Energy Solutions GmbH
FCV	fuel cell vehicle
FRA	frequency response analyser
FT	Fischer–Tropsch
GDC	gadolinium-doped ceria/gadolinia-doped ceria (same as CGO)
GDL	gas-diffusion layer
GE	General Electric
GHG	greenhouse gas
GM	General Motors
GPS	Global Positioning System
GTL	gas-to-liquid
GTO	gate turn-off (thyristor)
HAZID	hazard identification
HAZOP	hazard and operability study

HCNG	hydrogen-compressed natural gas
HDS	hydrodesulfurization
HEMFC	hydroxide-exchange polymer membrane fuel cell
HEV	hybrid electric vehicle
HHV	higher heating value
HOR	hydrogen oxidation reaction
HPE	high-pressure proton-exchange membrane electrolyser
IBFC	indirect borohydride fuel cell
ICE	internal combustion engine
ICEV	internal combustion engine vehicle
IFC	International Fuel Cells
IGBT	insulated-gate bipolar transistor
IHI	Ishikawajima-Harima Heavy Industries Co., Ltd
IHP	inner Helmholtz plane
IIR	indirect internal reforming (also known as ‘integrated reforming’)
ITM	ion transport membrane, also refers to company ITM Power
IT-SOFC	intermediate-temperature solid oxide fuel cell
IUPAC	International Union of Pure and Applied Chemistry
KEPCO	Korea Electric Power Corporation
KIST	Korea Institute of Science and Technology
LAMOX	lanthanum molybdate ($\text{La}_2\text{Mo}_2\text{O}_9$)
LCA	life-cycle assessment (also known as ‘life-cycle analysis’ and ‘cradle-to-grave analysis’)
LCOE	levelized cost of electricity
LH_2	liquid hydrogen
LHV	lower heating value
LNG	liquefied natural gas
LPG	liquefied petroleum gas
LSCF	lanthanum strontium cobaltite ferrite
LSCV	strontium-doped lanthanum vanadate
LSGM	lanthanum gallate (LaSrGaMgO_3)
LSM	strontium-doped lanthanum manganite
LT-SOFC	low-temperature solid oxide fuel cell
MCFC	molten carbonate fuel cell
MCR	microchannel reactor
MEA	membrane–electrode assembly
MEMS	microelectromechanical systems
METI	Ministry of Economy, Trade and Industry (Japan)
MFC	microbial fuel cell
MFF	mass flow factor
MHPS	Mitsubishi Hitachi Power Systems
MIEC	mixed ionic–electronic conductor (oxides)
MOF	metal–organic framework
MOSFET	metal-oxide-semiconductor field-effect transistor

MPMDMS	(3-mercaptopropyl)methyldimethoxysilane
MRFC	mixed-reactant fuel cell
MSW	municipal solid waste
MTBF	mean time between failures
MWCNT	multiwalled carbon nanotube
NADP	nicotinamide adenine dinucleotide phosphate
NASA	National Aeronautics and Space Administration
NCPO	non-catalytic partial oxidation
NEDO	New Energy Development Organization (Japan)
NOMO	Notice of Market Opportunities
NTP	normal temperature and pressure
OCV	open-circuit voltage
OEM	original equipment manufacturer
OER	oxygen evolution reaction
OHP	outer Helmholtz plane
ORR	oxygen reduction reaction
P2G	power-to-gas
P3MT	poly(3-methylthiophene)
PAFC	phosphoric acid fuel cell
PANI	polyaniline
PAR	photosynthetically active radiation
PBI	polybenzimidazole
PBSS	poly(benzylsulfonic acid)siloxane
PC	phthalocyanine
PCT	pressure composition isotherm
PEC	photoelectrochemical cell
PEMFC	proton-exchange membrane fuel cell (also called 'polymer electrolyte membrane fuel cell' and same as SPEFC and SPFC)
PET	polyethylene terephthalate
PF	power factor, also PFC power factor correction
PFD	process flow diagram
PFSA	perfluorinated sulfonic acid
plc	programmable logic controller
POX	partial oxidation
PPA	polyphosphoric acid
PPBP	poly(1,4-phenylene), poly(4 phenoxybenzoyl-1,4-phenylene)
Ppy	polypyrrole
PROX	preferential oxidation
PrOx	preferential oxidation reactor
PSA	pressure swing adsorption
PTFE	polytetrafluoroethylene
PV	photovoltaic
PWM	pulse width modulation
QA	quaternary ammonium

RDE	rotating disc electrode
RFB	redox flow battery
RH	relative humidity
RHE	reversible hydrogen electrode
RRDE	rotating ring-disc electrode
RSF	rotational speed factor
SATP	standard ambient temperature and pressure
SCG	simulated coal gas
SCT-CPO	short contact time catalytic partial oxidation
SDC	samarium-doped ceria/samaria-doped ceria (same as CSO)
SECA	Solid State Energy Conversion Alliance
SFCM	standard cubic foot per minute
SHE	standard hydrogen electrode
SI	International System of Units (French: <i>Système international d'unités</i>)
SLM	standard litre per minute
SMR	steam reforming reaction
SNG	substitute natural gas (also synthetic natural gas)
SOFC	solid oxide fuel cell
m-SPAEEEN-60	sulfonated poly(arylene ether ether nitrile)
SPEEK	sulfonated polyether ether ketone
SPEFC	solid polymer electrolyte fuel cell (same as PEMFC)
SPFC	solid polymer fuel cell (same as PEMFC)
SPOF	single point of failure
STP	standard temperature and pressure
SWPC	Siemens Westinghouse Power Corporation
TAA	tetraazaannulene
THT	tetrahydrothiophene
TMPP	tetramethoxyphenylporphyrin
TPP	tetraphenylporphyrin
TPTZ	2, 4, 6-tris(2-pyridyl)-1,3,5-triazine
TTW	tank-to-wheel
UCC	Union Carbide Corporation
UK	United Kingdom
ULP	unleaded petrol
UPS	uninterruptible power system; also uninterruptible power supply
URFC	unitized regenerative fuel cell
USA	United States of America
USB	universal serial bus
UTC	United Technologies Corporation
UV	ultraviolet
WGS	water–gas shift
WTT	well-to-tank
WTW	well-to-wheels
XPS	X-ray photoelectron spectroscopy

Symbols and Units

<i>Subunits</i>			<i>Multiple units</i>		
d	deci	10^{-1}	k	kilo	10^3
c	centi	10^{-2}	M	mega	10^6
m	milli	10^{-3}	G	giga	10^9
μ	micro	10^{-6}	T	tera	10^{12}
n	nano	10^{-9}	P	peta	10^{15}

A	ampere
A	electrode area (cm^2), also coefficient in natural logarithm form of the Tafel equation
Ah	ampere hour
<i>a</i>	chemical activity; also coefficient in base 10 logarithm form of the Tafel equation
a_x	chemical activity of species <i>x</i>
atm	atmosphere (=101.325 kPa)
<i>B</i>	exergy (J)
ΔB	change in exergy (J)
bbl	barrel of oil: 35 imperial gallons (159.113 L), or 42 US gallons (158.987 L)
bar	unit of pressure (=100 kPa)
bhp	brake horsepower (=745.7 W)
<i>C</i>	constant in various equations; also coulomb (=1A s), the unit of electric charge
$^{\circ}\text{C}$	degree Celsius
C_p	specific heat capacity at constant pressure ($\text{J kg}^{-1} \text{K}^{-1}$)
C_v	specific heat capacity at constant volume ($\text{J kg}^{-1} \text{K}^{-1}$)
$\overline{c_p}$	molar heat capacity at constant pressure ($\text{J mol}^{-1} \text{K}^{-1}$)
$\overline{c_v}$	molar heat capacity at constant volume ($\text{J mol}^{-1} \text{K}^{-1}$)
cm	centimetre
D_m	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
d	separation of charge layers in a capacitor (mm)
<i>E</i>	electrode potential (V)
E°	standard electrode potential (V)
E_r	reversible electrode potential (V)
E_r°	standard reversible electrode potential (V)

EW	(membrane) equivalent weight
e^-	electron, or the charge on one electron ($=1.602 \times 10^{-19}$ coulombs)
ΔE_{act}	activation overpotential (V)
F	farad, unit of electrical capacitance ($s^4 A^2 m^{-2} kg^{-1}$)
F	Faraday constant ($=96\,458$ coulombs mol^{-1})
ft	foot (linear measurement = 305 mm)
G	Gibbs free energy (J)
ΔG	change in Gibbs free energy (J)
ΔG°	change in standard Gibbs free energy (J)
G_f°	standard Gibbs free energy of formation (J)
ΔG_f°	change in standard Gibbs free energy of formation (J)
$\bar{g}$	molar Gibbs free energy ($J mol^{-1}$)
$\Delta \bar{g}$	change in molar Gibbs free energy ($J mol^{-1}$)
$\Delta \bar{g}^\circ$	change in standard molar Gibbs free energy ($J mol^{-1}$)
$\Delta \bar{g}_f^\circ$	change in molar Gibbs free energy of formation ($J mol^{-1}$)
$\Delta \bar{g}_f^\circ$	change in standard molar Gibbs free energy of formation ($J mol^{-1}$)
g	gram
g	acceleration due to gravity ($m s^{-2}$)
H	enthalpy (J)
ΔH	change in enthalpy (J)
ΔH°	change in standard enthalpy (J)
H_f°	standard enthalpy of formation (J)
ΔH_f°	change in standard enthalpy (heat) of formation (J)
$\bar{h}$	molar enthalpy ($J mol^{-1}$)
$\Delta \bar{h}$	change in molar enthalpy ($J mol^{-1}$)
$\Delta \bar{h}^\circ$	change in standard molar enthalpy ($J mol^{-1}$)
$\Delta \bar{h}_f^\circ$	change molar enthalpy of formation ($J mol^{-1}$)
$\Delta \bar{h}_f^\circ$	change in standard molar enthalpy of formation ($J mol^{-1}$)
h	hour
IR_e'	resistive loss in electrolyte (Ω)
IR_t'	total resistive loss in electrodes (Ω)
I	current (A)
i	current density, i.e., current per unit area (usually expressed in $mA cm^{-2}$)
i_c	crossover current (A)
i_l	limiting current density (usually expressed in $mA cm^{-2}$)
i_o	exchange-current density (usually expressed in $mA cm^{-2}$)
J	joule ($=1 W s$)
K	kelvin (used as a measure of absolute temperature)
L	litre
MFF	mass flow factor ($kg s^{-1} K^{1/2} bar^{-1}$)
m	metre
$\dot{m}$	mass flow rate, e.g., of gas ($kg s^{-1}$) or of a liquid ($ml min^{-1}$)
m_x	mass of substance x (g)
mEq	milliequivalent (weight) ($mg L^{-1}$)
mol	mole, i.e., mass of 6.022×10^{23} elementary units (atoms, molecules, etc.) of a substance
N	newton (unit of force = $1 kg m s^{-2}$)

N	rotor speed of fan (revolutions per minute)
N_A	Avogadro's number, $6.022140857 \times 10^{23}$
$N\text{-m}^3$	normal cubic metre of gas (i.e., that measured at NTP)
n	number of units (electrons, atoms, molecules) involved in a chemical or electrochemical reaction; also number of cells in fuel-cell stack
n_i	number of units or moles of species i
$\dot{n}_x$	molar flow rate of species x (mol s^{-1})
P	pressure (in Pa, or bar)
P_e	power (W), only used when context is clear that pressure is not under discussion
P°	standard pressure (=100 kPa)
P_{SAT}	saturated vapour pressure
P_x	partial pressure of species x
Pa	pascal ($1 \text{ Pa} = 1 \text{ N m}^{-2} = 9.869 \times 10^{-6} \text{ atm}$)
ppb	parts per billion
pH	numerical scale used to specify the acidity or basicity of an aqueous solution
ppm	parts per million
R	gas constant (=8.1345 $\text{J K}^{-1} \text{ mol}^{-1}$)
R'	resistance (Ω)
$R_{DS,on}$	internal resistance of a transistor
RH	relative humidity (%); also denoted by the symbol ϕ (<i>v.i.</i>)
®	registered trademark/copyright
r	area specific resistance ($\Omega \text{ cm}^2$)
S	siemens, unit of conductance (Ω^{-1})
S	entropy (J K^{-1})
ΔS	change in entropy (J K^{-1})
ΔS°	change in standard entropy (J K^{-1})
S_f°	standard entropy of formation (J K^{-1})
ΔS_f°	change in standard entropy of formation (J K^{-1})
$\bar{s}$	molar entropy ($\text{J K}^{-1} \text{ mol}^{-1}$)
$\Delta \bar{s}$	change in molar entropy ($\text{J K}^{-1} \text{ mol}^{-1}$)
$\Delta \bar{s}^\circ$	change in standard molar entropy (J mol^{-1})
$\Delta \bar{s}_f^\circ$	change in molar entropy of formation (J mol^{-1})
$\Delta \bar{s}_f^\circ$	change in standard molar entropy of formation (J mol^{-1})
s	second
SLM	standard litre per minute
T	temperature
TM	trademark
t	tonne
$t_{1/2}$	half-life
V	volt
V_c	cell voltage (V)
V_r	reversible cell voltage; also known as 'open-circuit voltage' (V)
V_r°	reversible cell voltage (V) under standard conditions of temperature (298.15 K) and pressure (101.325 kPa)
ΔV_{gain}	voltage gain (V)
ΔV_{loss}	voltage loss (V)
vol.%	volume percent

W	work done, e.g., in compressing a gas (J)
W'	isentropic work (J)
W	watt
W_{el}	watt, electrical power
W_{th}	watt, thermal power
Wh	watt-hour
wt. %	weight percent
x_i	mole fraction of species i in solution
Z	impedance (Ω)
z	number of units (electrons, atoms, molecules) involved in a chemical or electrochemical reaction
α	charge transfer coefficient
γ	ratio of the specific heats of a gas $C_p:C_v$
δ_m	thickness of proton exchange membrane (cm)
ε	electrical permittivity ($F\ m^{-1}$)
ξ	electro-osmotic coefficient
η	electrode overpotential (V); also efficiency (%) (e.g., of a fuel cell)
η_+	overpotential at a positive electrode (V)
η_-	overpotential at a negative electrode (V)
η_C	isentropic compressor efficiency (%)
η_f	fuel utilization coefficient (%), a 'figure of merit' for DMFCs
ϑ	phase angle
λ	stoichiometric ratio
μ_f	fuel utilization coefficient
μ_i	chemical potential of species i ($J\ kg^{-1}$ or $J\ mol^{-1}$)
μ	gas viscosity (centipoise, $cP = 0.001\ kg\ m^{-1}\ s^{-1}$)
ϕ	relative humidity (usually expressed as a percentage); also denoted by RH
ρ	gas density ($kg\ m^{-3}$)
ω	humidity ratio, also known as 'absolute humidity' and 'specific humidity'; symbol also used for radial frequency
Ω	ohm

1

Introducing Fuel Cells

1.1 Historical Perspective

This book is an introduction to fuel-cell systems; it aims to provide an understanding of the technology — what it is, how it works and what are its applications. Essentially, a fuel cell can be defined as a device that produces electrical power directly from a fuel via an electrochemical process. In some respects, this operation is similar to that of a conventional battery except that the reactants are stored outside the cell. Therefore, the performance of the device is limited only by the availability of the fuel and oxidant supply and not by the cell design. For this reason, fuel cells are rated by their power output (kW) rather than by their capacity (kWh).

Before addressing the technology in depth, it is necessary to understand that by virtue of being electrochemical, fuel cells have both chemical and electrical characteristics. Accordingly, their development has been inextricably linked with the development of electrochemistry as a distinct branch of physical chemistry.

At the beginning of the 19th century, it was recognized that an ‘electrochemical cell’ (nowadays, commonly called a ‘battery’) could be made by placing two dissimilar metals in an aqueous salt solution. This discovery was made by Alessandro Volta, the professor of experimental physics at Pavia University, who constructed a pile of alternating discs of copper (or silver or brass) and zinc (or tin) that were separated by pasteboard discs (or ‘any other spongy matter’) soaked in brine. When the top and bottom of the pile were connected by a wire, the assembly delivered, for the first time in history, a more or less steady flow of electricity. Volta introduced the terms ‘electric current’ and ‘electromotive force’, the latter to denote the physical phenomenon that causes the current to flow. In due course, he conveyed his findings in a letter dated 20 March 1800 to Joseph Banks, the then president of the Royal Society. Known as the ‘Volta (or Voltaic) pile’, this was the first ‘primary’ (or non-rechargeable) power source, as opposed to a ‘secondary’ (or rechargeable) power source.

Sir Humphry Davy, who was working at the Royal Institution in London, soon recognized that the Volta pile produces electricity via chemical reactions at the metal–solution interfaces — hydrogen is evolved on the ‘positive’ copper disc, and zinc is consumed at the ‘negative’ disc. Indeed, this recognition of the relationship between chemical and electrical effects prompted Davy to coin the word ‘electrochemical’, from which sprang the science of ‘electrochemistry’. He gave warning that Volta’s work was ‘an alarm bell to experimenters all over Europe’. His prediction was soon to be verified.

Volta had sent his letter to the Royal Society in two parts because he anticipated problems with its delivery given that correspondence from Italy had to pass through France, which was then at war with Britain. While waiting for the second part to arrive, Joseph Banks had shown the first few pages to Anthony Carlisle (a fashionable London surgeon) who, in turn, with the assistance William Nicholson (a competent amateur scientist) assembled on 30 April 1800 the first pile to be constructed in England. Almost immediately, on 2 May 1800, the two investigators found that the current from their device when passed through a dilute salt solution via two platinum wires was capable of decomposing water into its constituents — hydrogen at one wire and oxygen at the other. Details of the discovery were published in Nicholson's own journal in July of the same year. Thus, the new technique of 'molecular splitting' — to be coined 'electrolysis' by Michael Faraday much later in 1834 and derived from the Greek 'lysis' = separation — was demonstrated before Volta's own account of the pile was made public in September 1800. A schematic representation of the process is shown in Figure 1.1a.

It was left to Michael Faraday, Davy's brilliant student, to identify the mechanisms of the processes that take place within 'electrolytic' cells and to give them a quantitative basis. In addition, he was also the guiding force behind the nomenclature that is still in use today. First, Faraday with the assistance of Whitlock Nicholl (his personal physician and accomplished linguist) devised the name 'electrode' to describe a solid substance at which an electrochemical reaction occurs and 'electrolyte' to describe the chemical compound that provides an electrically conductive medium between electrodes. (Note that in the case of dissolved materials, it is fundamentally incorrect to refer to the 'electrolyte solution' as the 'electrolyte'; nevertheless, the latter terminology has become common practice.) To distinguish between the electrode by which conventional current (i.e., the reverse flow of electrons) enters an electrolytic cell and the electrode by which

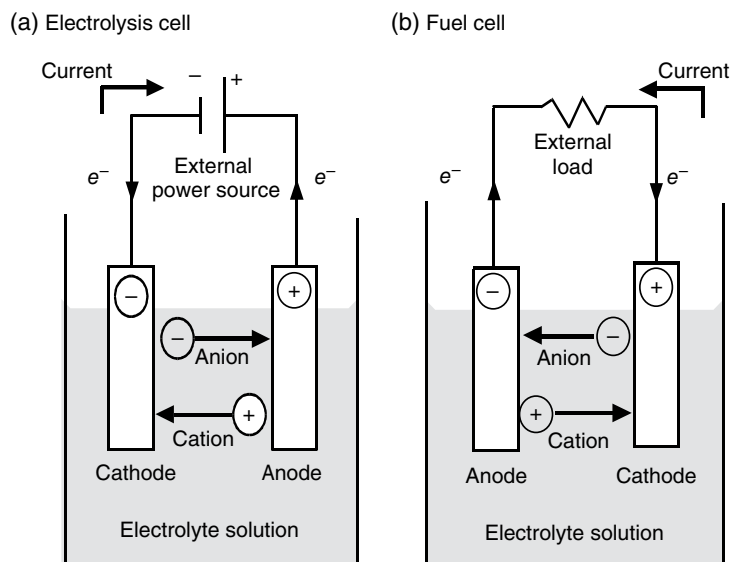


Figure 1.1 Terminology employed in operation of (a) electrolysis cells and (b) fuel cells.

it leaves, Faraday sought the assistance of the polymath William Whewell, the Master of Trinity College at the University of Cambridge. In a letter dated 24 April 1834, he asked Whewell:

‘Can you help me out to two good names not depending upon the idea of a current in one direction only or upon positive or negative?’

In other words, he wanted terms that would be unaffected by any later change in the convention adopted for the direction of current. Eventually, they settled on calling the positive electrode an ‘anode’ and the negative electrode a ‘cathode’, which were coined from Greek ‘ano-dos’ (‘upwards’–‘a way’) to represent the path of electrons from the positive electrode to the negative and ‘katho-dos’ (‘downwards’–‘a way’) to represent the counter direction. For an electrolytic cell, then, the anode is where the current enters the electrolyte and the cathode is where the current leaves the electrolyte. Thus the positive electrode sustains an oxidation (or ‘anodic’) reaction with the liberation of electrons, while a reduction (or ‘cathodic’) reaction takes place at the negative electrode with the uptake of electrons.

With use of the Greek neutral present participle ‘ion’ — ‘a moving thing’ — to describe the migrating particles in electrolysis, two further terms were obtained, namely, ‘anion’, i.e., the negatively charged species that goes to the anode against the current (or with the flow of negative charge), and ‘cation’, i.e., the positively charged species that goes to the cathode with the current (or against the flow of negative charge). The operation of an electrolysis cell is shown in Figure 1.1a. It should be noted that the anode–cathode terminology for an ‘electrolytic cell’ applies to a ‘battery under charge’ (secondary system).

A fuel cell operates in the reverse manner to an electrolysis cell, i.e., it is a ‘galvanic’ cell that spontaneously produces a voltage (similar to a ‘battery under discharge’). The anode of the electrolysis cell now becomes the cathode and the cathode becomes the anode; see Figure 1.1b. Nevertheless, the directions of the migration of anions and cations with respect to current flow are unchanged such that the positive electrode remains a positive electrode and the negative electrode remains a negative electrode. Thus, in a fuel cell, the fuel is always oxidized at the anode (positive electrode), and the oxidant is reduced at the cathode (negative electrode).

There is some debate over who discovered the principle of the fuel cell. In a letter written in December 1838 and published on page 43 of the January issue of the January–June 1839 Volume XIV of *The London and Edinburgh Philosophical Magazine and Journal of Science*, the German scientist Christian Friedrich Schönbein described his investigations on fluids that were separated from each other by a membrane and connected to a galvanometer by means of platina wires. In the 10th of 14 reported tests, one compartment contained dilute sulfuric acid that held some hydrogen, whereas the other compartment contained dilute sulfuric acid that was exposed to air. Schönbein detected a current and concluded that this was caused ‘by the combination of hydrogen with (the) oxygen (contained dissolved in water)’. This discovery was largely overlooked, however, after the publication of a letter from William Robert Grove, a Welsh lawyer and a scientist at the Royal Institution; see Figure 1.2a. The letter, which was dated 14 December 1838, appeared on page 127 of the February issue of the aforementioned Volume XIV and described his evaluation of electrode and electrolyte materials for use

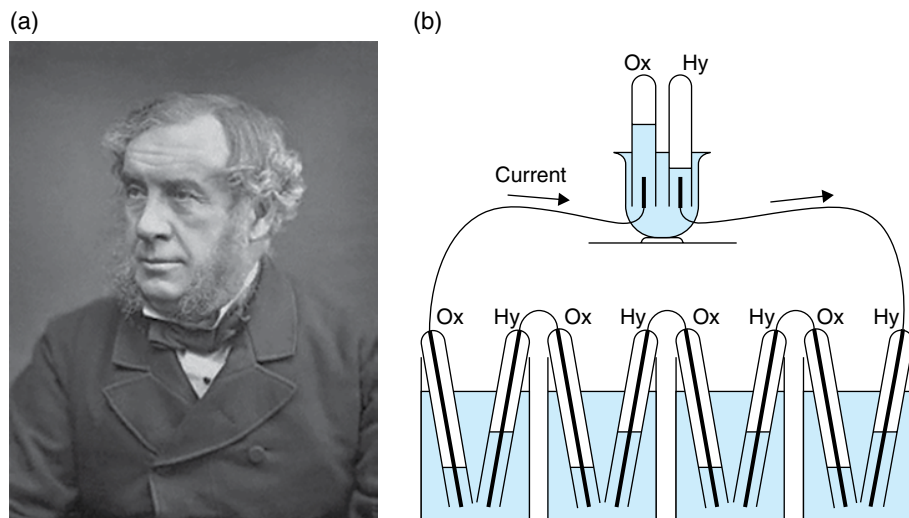


Figure 1.2 (a) William Robert Grove (1811–1896) and (b) Grove's sketch of four cells of his gaseous voltaic battery' (1842). (Source: <https://commons.wikimedia.org/w/index.php?curid=20390734>. Used under CC BY-SA 3.0; <https://creativecommons.org/licenses/by-sa/3.0/>.)

in batteries. Unfortunately, the order in which these two letters had been written is unknown as Schönbein did not date his letter in full — he gave the month, but not the day. In fact, this chronology is of little importance given the following postscript that Grove had added to his letter in January 1839:

‘I should have pursued these experiments further, and with other metals, but was led aside by some experiments with different solutions separated by a diaphragm and connected by platinum plates; in many of these I have been anticipated.’

In the same postscript, Grove went on to speculate that by connecting such cells in series sufficient voltage could be created to decompose water (by electrolysis).

Grove carried out many experiments that demonstrated the principle of the fuel cell. In 1842, he realized that the reaction at the electrodes was dependent on an area of contact between the gas reactant and a layer of liquid that was sufficiently thin to allow the gas to diffuse to the solid electrode (today, this requirement is commonly related to the formation of a ‘three-phase boundary’ or ‘triple-point junction’ where gas, electrolyte and electrocatalyst come into simultaneous contact, *v.i.*). At that time, Grove was the professor of experimental chemistry at the London Institution in Finsbury Circus, and in the same communication he reported the invention of a ‘gaseous voltaic battery’. The device employed two platinized platinum electrodes (to increase the real surface area), and a series of fifty such pairs when semi-immersed in dilute sulfuric acid solution was found ‘to whirl round’ the needle of a galvanometer, to give a painful shock to five persons joining hands, to give a brilliant spark between charcoal points, and to decompose hydrochloric acid, potassium iodide and acidulated water. An original sketch of four such cells is reproduced in Figure 1.2b. It was also found that 26 cells were the minimum number required to electrolyse water. Grove had indeed realized

the desire expressed in his 1839 postscript in that he had achieved the beautiful symmetry inherent in the ‘decomposition of water by means of its composition.’

The aforementioned apparatus became widely recognized as the first fuel cell and Grove was designated as the ‘Father of the Fuel Cell’. Historically, this title is not fully justified. More accurately, Schönbein should be credited with the discovery of the fuel-cell effect in 1838 and Grove with the invention of the first working prototype in 1842. Happily, such accreditations were of little concern to the two scientists and they became close friends. For almost 30 years, they exchanged ideas and developments via a dynamic correspondence and visited each other frequently.

It is interesting to note that many latter-day authors have attributed the introduction of the term ‘fuel cell’ to Ludwig Mond and Charles Langer in their description of a new form of gas battery in 1889. Remarkably, however, there is no mention of ‘fuel cell’ in this communication. Other claims that William W. Jacques, in reporting his experiments to produce electricity from coal, coined the name are equally ill founded. A. J. Allmand in his book *The Principles of Applied Electrochemistry*, published in 1912, appears to attribute the appellation ‘fuel cell’ to the Nobel Laureate Friedrich Wilhelm Ostwald in 1894.

Grove concluded his short paper in 1842 with the following modest entreaty:

‘Many other notions crowd upon my mind, but I have occupied sufficient space and must leave them for the present, hoping that other experimenters will think the subject worth pursuing.’

Unfortunately, however, the invention of the first internal combustion engine to become commercially successful by Jean Joseph Étienne Lenoir in 1859, coupled ironically with Faraday’s earlier discovery of electromagnetic force, diverted the course of electricity generation from electrochemical to electromagnetic methods. As a result, the fuel cell became merely an object of scientific curiosity during much of the next half-century. Meanwhile, knowledge of electrochemical conversion and storage of energy progressed largely through the development of battery technologies.

In 1894, a well-documented criticism against heat engines was expressed by Friedrich Ostwald, who drew attention to the poor efficiency and polluting problems associated with producing electrical power via the combustion of fossil fuels rather than by direct electrochemical oxidation. A fuel cell is inherently a more thermodynamically efficient device since, unlike an engine in which heat is converted to mechanical work, the cell is not subject to the rules of the Carnot cycle. By virtue of this cycle, the efficiency of a thermal engine is always lowered to a value far below 100%, as determined by the difference between the temperature at which heat is taken in by the working fluid and the temperature at which it is rejected. On this basis, Ostwald advocated that:

‘The path which will help to solve this biggest technical problem of all, this path must be found by the electrochemistry. If we have a galvanic element which directly delivers electrical power from coal and oxygen, [...] we are facing a technical revolution that must push back the one of the invention of the steam engine. Imagine how [...] the appearance of our industrial places will change! No more smoke, no more soot, no more steam engine, even no more fire, [...] since fire will now only be needed for the few processes that cannot be accomplished electrically, and those will daily diminish. [...] Until this task shall be tackled, some time will pass by.’

Regrettably, Ostwald was proven to be correct as regards his closing prediction for although attempts were made at the turn of the century to develop fuel cells that could convert coal or carbon into electricity (for instance, the work of William W. Jacques in the United States), the need for an expensive platinum catalyst and its poisoning by carbon monoxide formed during the coal gasification limited cell affordability, usefulness and lifetime. Consequently, interest in such 'direct carbon fuel cells' dwindled.

In the 1930s, Emil Bauer and H. Preis in Switzerland experimented with solid oxide fuel cells (SOFCs). Given the limitations of solid oxides at that time (i.e., poor electrical conductivity and chemical stability), G.H.J. Broers and J.A.A. Ketelaar in the late 1950s turned to the use of fused salts as electrolytes. The work gave birth to the molten carbonate fuel cell (MCFC), which eventually became one of the main types of fuel cell in commercial production.

The renaissance of the fuel-cell concept in the 20th century can be attributed largely to the work of Englishman F.T. (Tom) Bacon. He was an engineer by profession and thus appreciated the many potential advantages of the fuel cell over both the internal combustion engine and the steam turbine as a source of electrical power. His interest in fuel cells dated as far back as 1932, and he ploughed a lone furrow, with little support or backing, but showed enormous dedication to the challenge of developing practical cells. Early in his career, Bacon elected to study the alkaline-electrolyte fuel cell (AFC), which used nickel-based electrodes, in the belief that platinum-group electrocatalysts would never become commercially viable. In addition, it was known that the oxygen electrode is more readily reversible in alkaline solution than in acid. This choice of electrolyte and electrodes necessitated operating the cell at moderate temperatures (100–200°C) and high gas pressures. Bacon restricted himself to the use of pure hydrogen and oxygen as reactants. Eventually, in August 1959, he demonstrated the first workable fuel cell — a 40-cell system that could produce about 6 kW of power, which was sufficient to run a forklift truck and to operate a welding machine as well as a circular saw.

A major opportunity to apply fuel cells arose in the early 1960s with the advent of space exploration. In the United States, fuel cells were first employed to provide spacecraft power during the fifth mission of Project Gemini. Batteries had been employed for this purpose in the four earlier flights, as well as in those conducted in the preceding Project Mercury. This switch in technology was undertaken because payload mass is a critical parameter for rocket-launched satellites, and it was judged that fuel cells, complete with gas supplies, would weigh less than batteries. Moreover, the objective of Project Gemini was to evolve techniques for advanced space travel — notably, the extravehicular activity and the orbital manoeuvres (rendezvous, docking, etc.) required for the moon landing planned in the following Project Apollo. Thus, lunar flights demand a source of power of longer duration than that available from batteries.

A proton-exchange membrane fuel cell (PEMFC) system manufactured by the General Electric Company was adopted for the Gemini missions (two modules, each with a maximum power of about 1 kW), but this was replaced in Project Apollo by an AFC of circulating electrolyte design, as pioneered by Bacon and developed by the Pratt and Whitney Aircraft Company (later the United Technologies Corporation). Both

types of system were fuelled by hydrogen and oxygen from cryogenic tanks. The AFC could supply 1.5 kW of continuous power, and its in-flight performance during all 18 Apollo missions was exemplary. In the 1970s, International Fuel Cells (a division of United Technologies Corporation) produced an improved AFC for the Space Shuttle orbiter that delivered eight times more power than the Apollo version and weighed 18 kg less. The system provided all of the electricity, as well as drinking water, when the Space Shuttle was in flight.

The successful exploitation of fuel cells in the space programme drove research activity worldwide during the 1970s to develop systems that would generate power with high efficiency and low emissions for terrestrial applications. Research was stimulated further by the hiatus in the global oil supply in 1974. What followed was the emergence of various national initiatives on fuel-cell development. In the United States, demonstrations of phosphoric acid fuel cell (PAFC) technology by the American Gas Association led to a Notice of Market Opportunities (NOMO) initiative. This activity, in turn, renewed interest in the MCFC by US researchers, and in the mid-1980s, national research and development programmes were established in Japan and Europe. Renewed interest in the PEMFC was championed in the late 1980s by Geoffrey Ballard, a Canadian pioneer, who saw the potential for the technology to replace internal combustion engines. Since then, this system has been the subject of much advancement for a variety of applications, so much so that it merits two chapters in this book.

1.2 Fuel-Cell Basics

To understand how the reaction between hydrogen and oxygen produces an electric current, and where the electrons are released, it is necessary to consider the reaction that takes place at each electrode. The reactions vary for different types of fuel cell, but it is convenient to start with a cell based around an acid electrolyte, not only because this system was used by Grove but also because it is the simplest and still the most chosen for commercial applications.

At the anode of an acid fuel cell, hydrogen is oxidized and thereby releases electrons and creates H^+ ions, as expressed by:



This reaction also releases energy in the form of heat.

At the cathode, oxygen reacts with electrons taken from the electrode, and H^+ ions from the electrolyte, to form water, i.e.,



Thus the overall cell reaction is:



Clearly, for both the electrode reactions to proceed continuously, electrons produced at the negative electrode must pass through an electrical circuit to the positive. Also, H^+ ions must pass through the electrolyte solution — an acid is a fluid with free H^+ ions and so serves this purpose very well. Certain polymers and ceramic materials can also be made to contain mobile H^+ ions. These materials are commonly called ‘proton-exchange membranes,’ as an H^+ ion is also known as a proton. The PEMFC is examined in detail in Chapter 4.

The cell reaction (1.3) shows that two hydrogen molecules will be needed for each oxygen molecule if the system is to be kept in balance. The operating principle is illustrated in Figure 1.3.

In a fuel cell with an alkaline electrolyte (AFC), the overall reaction of hydrogen oxidation is the same, but the reactions at each electrode are different. In an alkaline solution, hydroxyl (OH^-) ions are available and mobile. At the anode, these ions react with hydrogen to release electrons and energy (heat) together with the production of water:



At the cathode, oxygen reacts with electrons taken from the electrode, and water in the electrolyte and thereby forms new OH^- ions:



Comparing equations (1.4) and (1.5) shows that, as with an acid electrolyte, twice as much hydrogen is required compared with oxygen. The operating principle of the AFC is presented in Figure 1.4.

There are many other types of fuel cell, each distinguished by its electrolyte and the reactions that take place on the electrodes. The different systems are described in detail in the following chapters.

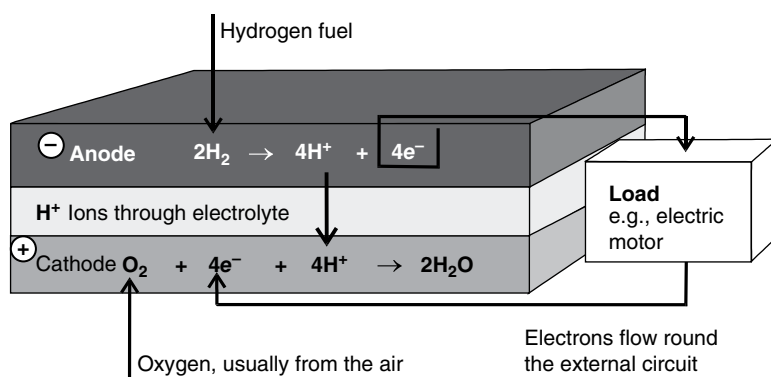


Figure 1.3 Electrode reactions and charge flow for fuel cell with an acid electrolyte. Note that although the negative electrons flow from the anode to cathode, the ‘conventional positive current’ flows from cathode to anode.

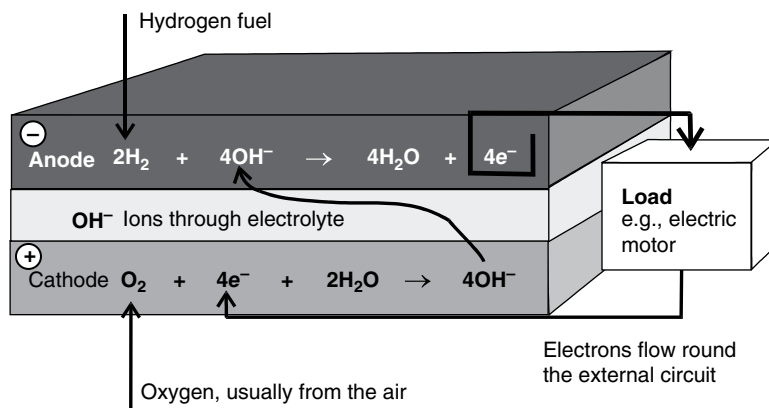


Figure 1.4 Electrode reactions and charge flow for a fuel cell with an alkaline electrolyte. Electrons flow from negative anode to positive cathode, but 'conventional positive current' flows from cathode to anode.

1.3 Electrode Reaction Rates

The oxidation of hydrogen at the negative electrode liberates chemical energy. It does not follow, however, that the reaction proceeds at an unlimited rate; rather, it has the 'classical' energy form of most chemical reactions, as shown in Figure 1.5. The schematic represents the fact that some energy must be used to excite the atoms or molecules sufficiently to start the chemical reaction — the so-called 'activation energy'. This energy can be in the form of heat, electromagnetic radiation or electrical energy. In visual terms, the activation energy helps the reactant to overcome an 'energy hill'.

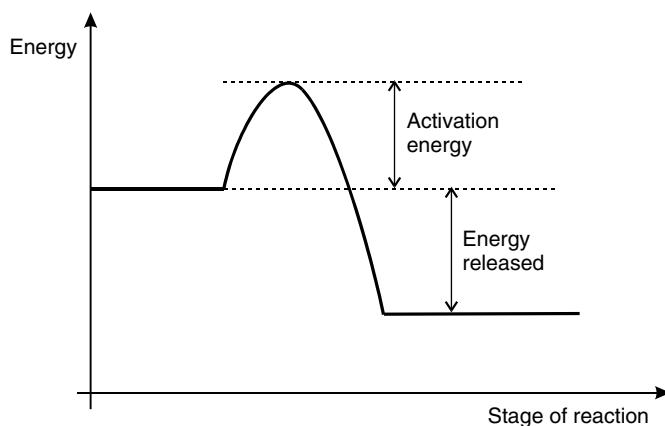


Figure 1.5 Classical energy diagram for a simple exothermic chemical reaction.

and once the reaction starts, everything rolls downhill. Thus, if the probability of an atom or molecule having sufficient energy is low, then the reaction will only proceed slowly. This is indeed the case for fuel-cell reactions, unless very high temperatures are employed.

The three main ways of dealing with the slow reaction rates are to (i) use catalysts, (ii) raise the temperature and (iii) increase the electrode area. Whereas the first two options can be applied to any chemical reaction, the electrode area has a special significance for electrochemical cells. The electrochemical reactions take place at the location where the gas molecules (hydrogen or oxygen) meet the solid electrode and the electrolyte (whether solid or liquid). The point at which this occurs is often referred to as the 'three-phase boundary/junction' or the 'triple-phase boundary/junction' (*v.s.*).

Clearly, the rate at which either electrode reaction proceeds will be proportional to the area of the respective electrode. Indeed, electrode area is such an important issue that the performance of fuel cells is usually quoted in terms of the current per cm^2 . Nevertheless, the geometric area (length $\times$ width) is not the only issue. The electrode is made highly porous so as to provide a great increase in the 'effective' surface area for the electrochemical reactions. The surface area of electrodes in modern fuel cells, such as that shown in Figure 1.6, can be two to three orders of magnitude greater than the geometric area. The electrodes may also have to incorporate a catalyst and endure high temperatures in a corrosive environment; catalysts are discussed in Chapter 3.

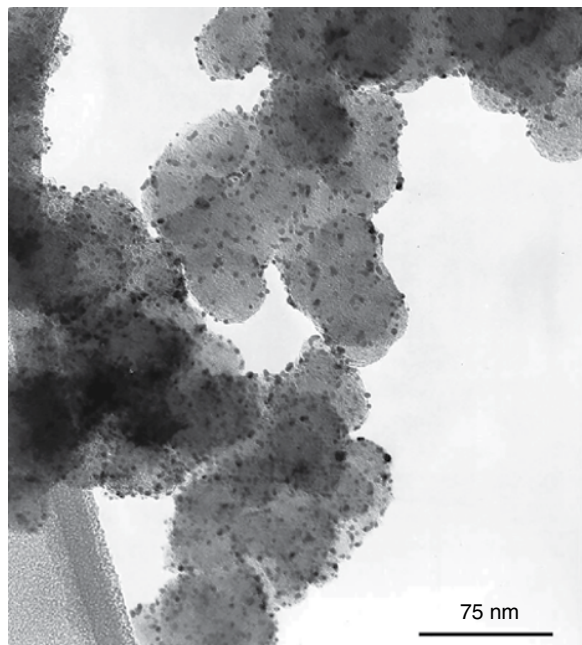


Figure 1.6 Transmission electron microscope image of a fuel-cell catalyst. The black spots are the catalyst particles that are finely divided over a carbon support. The structure clearly has a large surface area. (Source: Courtesy of Johnson Matthey Plc.)

1.4 Stack Design

Because a fuel cell functions at a low voltage (i.e., well below 1 V), it is customary to build up the voltage to the desired level by electrically connecting cells in series to form a 'stack'. There are a number of different designs of fuel cell, but in each case the unit cell has certain components in common. These are as follows:

- An electrolyte medium that conducts ions. This may be a porous solid that contains a liquid electrolyte (acid, alkali or fused salt) or a thin solid membrane that may be a polymer or a ceramic. The membrane must be an electronic insulator as well as a good ionic conductor and must be stable under both strong oxidizing and strong reducing conditions.
- A negative fuel electrode (anode) that incorporates an electrocatalyst, which is dispersed on an electronically conducting material. The electrode is fabricated so that the electrocatalyst, the electrolyte and the fuel come into simultaneous contact at a three-phase boundary (*v.s.*).
- A positive electrode (cathode), also with a triple-point electrocatalyst, at which the incoming oxygen (either alone or in air) is reduced by uptake of electrons from the external circuit.
- A means of electrically connecting individual cells together. The design of inter-connector depends on the geometry adopted for the cells.
- Seals that keep the gases apart and also prevent cell-to-cell seepage of liquid electrolyte, which otherwise would give rise to partial short-circuits.

A stack also has current-collectors that are located at the two ends of the stack and are connected by end-plate assemblies.

Historically, the flat plate is by far the preferred geometry for fuel cells, and one way of assembling such cells in series is to connect the edge of each negative electrode to the positive of the next cell through the string, as illustrated in Figure 1.7. (For simplicity, the diagram ignores the difficulty of supplying gas to the electrodes.) The problem with this method, however, is that the electrons have to flow across the face of the electrode to the current collection point at the edge. The electrodes might be quite good conductors, but if each cell is only operating at about 0.7 V, even a small voltage drop can be significant. Consequently, this type of stack design is not used unless the current flows are very low, the electrodes are particularly good conductors and/or the dimensions of the stack are small.

A much better method of cell interconnection for planar fuel cells is to use a 'bipolar plate'. This is an electrically conducting plate that contacts the surfaces of the positive electrode of one cell and the negative electrode of the next cell (hence the term 'bipolar'). At the same time, the bipolar plate serves as a means of feeding oxygen to the negative anode and fuel gas to the positive cathode of the adjacent cells. This is achieved by having channels machined or moulded on either side of the plate along which the gases can flow and the products, i.e., pure water in the case of hydrogen fuel, can exit. Various designs of channel geometry have been proposed to maximize the access of gases and the removal of water, e.g., pin-type, series-parallel, serpentine, integrated and interdigitated flow-fields. The different types are described in later chapters when considering the stacking arrangement of each type of fuel cell. The arrangement of the

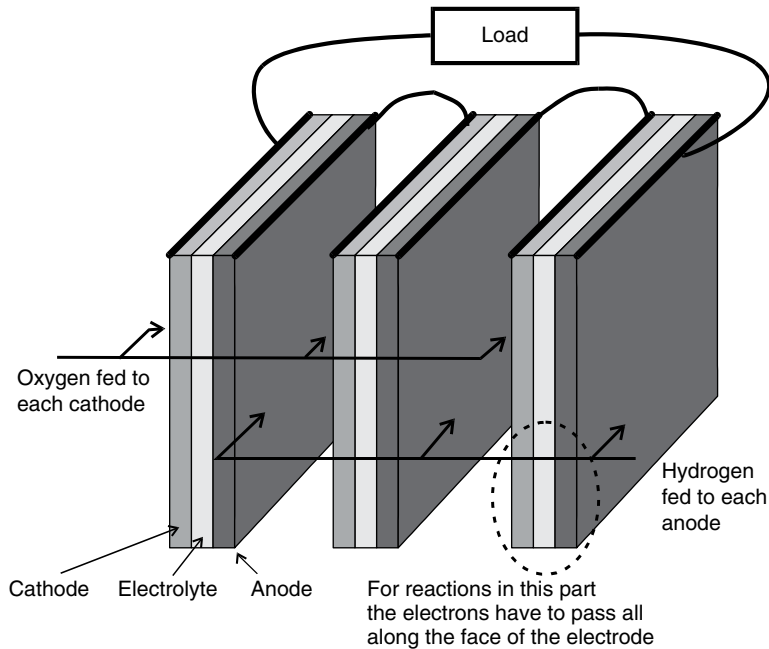


Figure 1.7 Simple edge connection of three-planar fuel cells in series. When the electrolyte is a membrane, the cathode–electrolyte–anode unit is generally known as a membrane–electrode assembly (MEA).

channels (also known as the ‘flow-field’) leads the bipolar plate to be also known as the flow-field plate. Bipolar plates must also be relatively impermeable to gases, sufficiently strong to withstand stack assembly and easily mass produced. They are made of a good electronic conductor such as graphite or stainless steel. For transport applications, low weight and low volume are essential. The method of connecting two plates to a single cell is illustrated in Figure 1.8; the respective gases are supplied orthogonally.

To connect several cells in series, anode–electrolyte–cathode assemblies have to be prepared. These are then ‘stacked’ together with bipolar plates placed between each pair of cells. In the particular arrangement shown in Figure 1.9, the stack has vertical channels for feeding hydrogen over the anodes and horizontal channels for feeding oxygen (or air) over the cathodes. The result is a solid block, in which the electric current passes efficiently more or less straight through the cells, rather than over the surface of each electrode one after the other.

The electrodes and electrolytes are also well supported, and the whole structure is clamped together to give a strong and robust device. Although simple in principle, the design of the bipolar plate has a significant effect on fuel-cell performance. If the electrical connection between cells is to be optimized, then the area of contact points should be as large as possible, but this would mitigate good gas flow over the electrodes. If the contact points have to be small, at least they should be frequent. This may render the plate more complex, difficult and expensive to manufacture, as well as fragile. Ideally, bipolar plates should be as thin as possible so as to minimize both the electrical resistance between individual cells and the stack size. On the other hand, such an

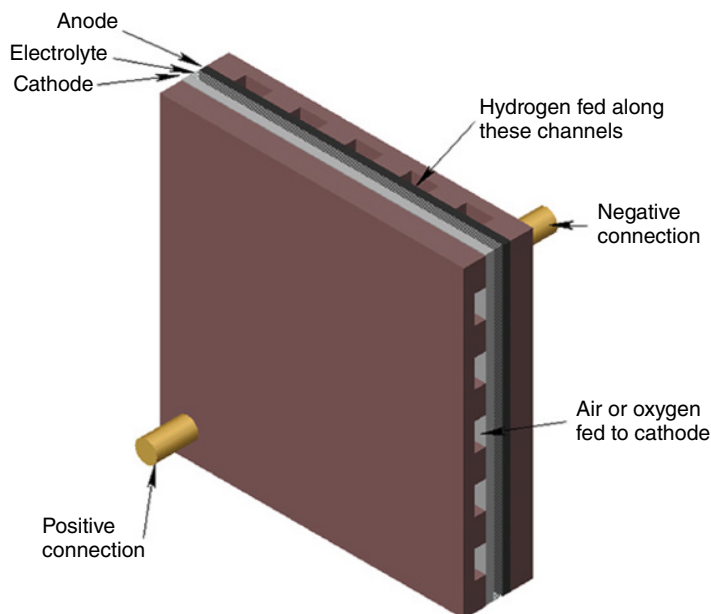


Figure 1.8 Single cell with end-plates for collecting current from the whole face of the adjacent electrode and applying gases to each electrode.

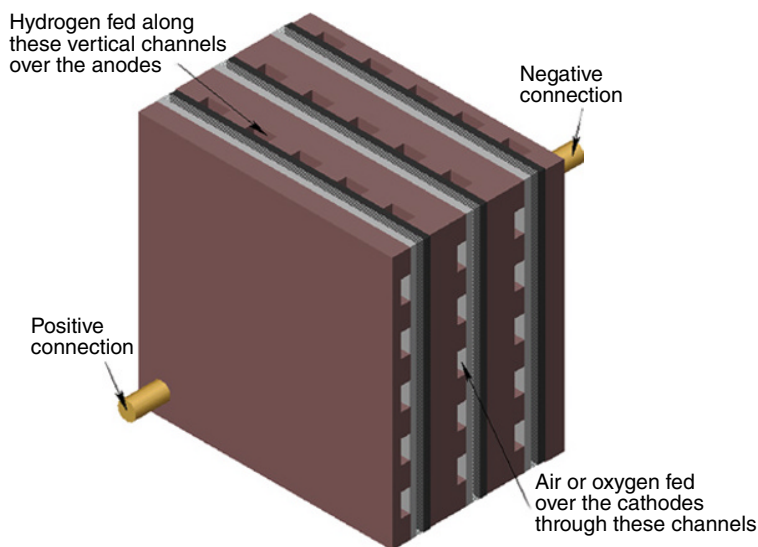


Figure 1.9 A three-cell stack showing how bipolar plates connect the anode of one cell to the cathode of its neighbour.

approach would narrow the gas channels and thereby place greater demands on the pumps for supplying gases. High rates of flow are sometimes required, especially when using air instead of pure oxygen at the positive electrode. For low-temperature fuel cells, the circulating air has to evaporate and carry away the product water. Moreover, in many

cases, additional channels have to pass through the bipolar plate to carry a cooling fluid. Some further challenges for the bipolar plate are considered in the next section.

1.5 Gas Supply and Cooling

The arrangement given in Figure 1.9 has been simplified to show the basic principle of the bipolar plate. In practice, however, the twin problems of gas supply and preventing leaks mean that the design is somewhat more complex.

Because the electrodes must be porous (to permit the access of gas), they allow leakage of the gas through their edges. Consequently, the edges must be sealed. Sometimes this is done by making the electrolyte compartment slightly larger than one, or both, of the electrodes and fitting a gasket around each electrode, as presented in Figure 1.10. Such assemblies can then be made into a stack in which the fuel and oxygen can then be supplied to the electrodes using the external manifolds as shown disassembled in Figure 1.11. With this arrangement, the hydrogen should only come into contact with the anodes as it is fed vertically through the fuel-cell stack. Similarly, the oxygen (or air) fed horizontally through the stack should only contact the cathodes and certainly not the edges of the anodes. Such would not be the case for the basic design illustrated in Figure 1.9.

The externally manifolded design suffers from two major disadvantages. The first is that it is difficult to cool the stack. Fuel cells are far from 100% efficiency, and considerable quantities of heat are generated, as well as electrical power. In practice, the cells in this type of stack have to be cooled by the reactant air passing over the positive electrodes. This means that air has to be supplied at a higher rate than that demanded by the cell chemistry — sometimes the flow is sufficient to cool the cell, but it is wasteful of energy. The second disadvantage of external manifolding is that there is uneven pressure over the gasket round the edge of the electrodes, i.e., at the points where there

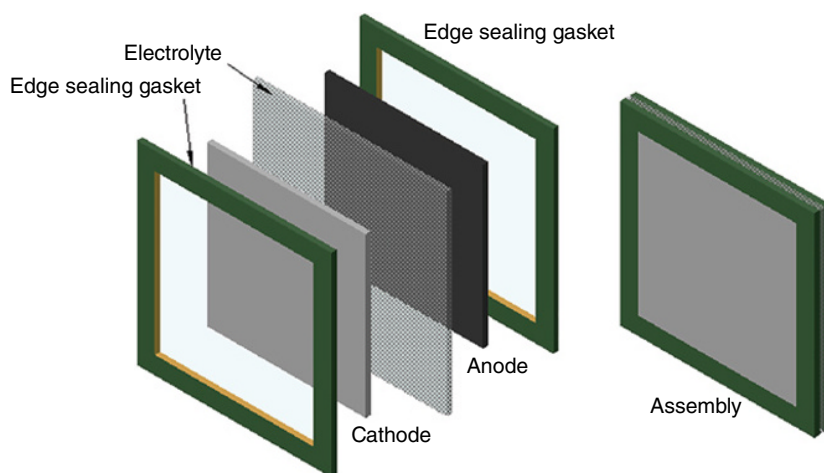


Figure 1.10 The construction of cathode–electrolyte–anode units with edge seals that prevent the gases leaking in or out through the edges of the porous electrodes.

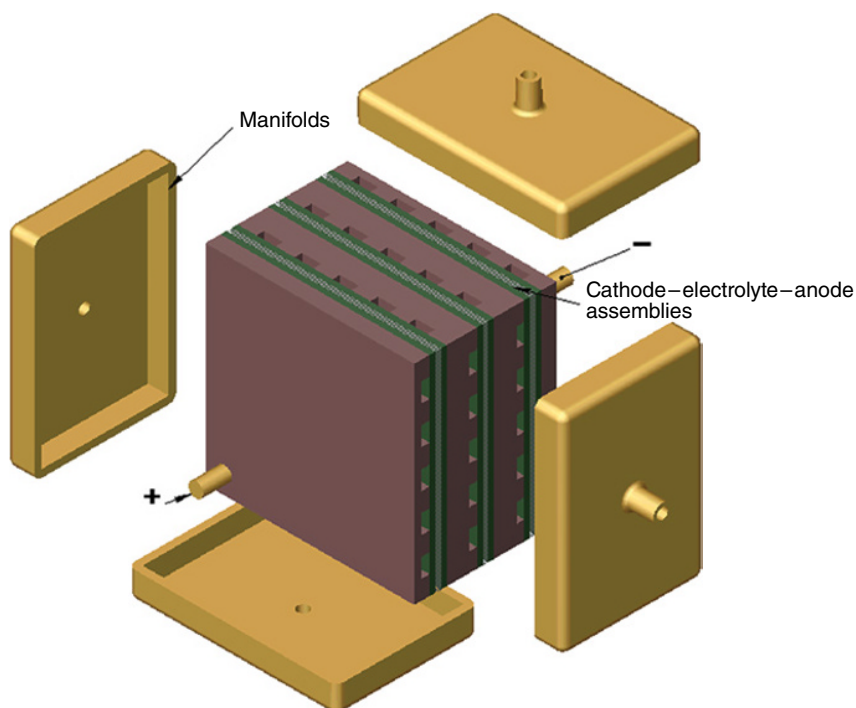


Figure 1.11 Three-cell stack, with external manifolds. Unlike the stack shown Figure 1.9, the electrodes now have edge seals.

is a channel and the gasket is not pressed firmly onto the electrode. This increases the probability of leakage of the reactant gases.

‘Internal manifolding’ is a more common stack arrangement and requires a more complex design of bipolar plate, such as that displayed schematically in Figure 1.12. In this arrangement, the plates are made larger relative to the electrodes and have extra channels running through the stack for the delivery of fuel and oxygen to the electrodes. Holes are carefully positioned to feed the reactants into the channels that run over the surface of the electrodes. Reactant gases are fed in at the ends of the stack where the respective positive and negative electrical connections are also made. An example of a commercial fuel-cell stack is shown in Figure 1.13.

A stack with internal manifolding can be cooled in various ways. The most practical method is to circulate a liquid coolant through electrically conductive metal plates that are inserted between groups of cells. In this passive approach, the heat within the plane of the plate must be conducted out to one or more of the edges of the plate for transfer to a heat-exchanger external to the fuel-cell stack. Alternatively the bipolar plates themselves can be made thicker and machined to incorporate extra channels that allow passage of cooling air or water. The preferred cooling method varies greatly with the type of fuel cell and is addressed in later chapters.

From the foregoing discussion, it should be apparent that the bipolar plate is a key component of a fuel-cell stack. As well as being a fairly intricate item to manufacture, the choice of material for its construction raises issues. For low-temperature fuel

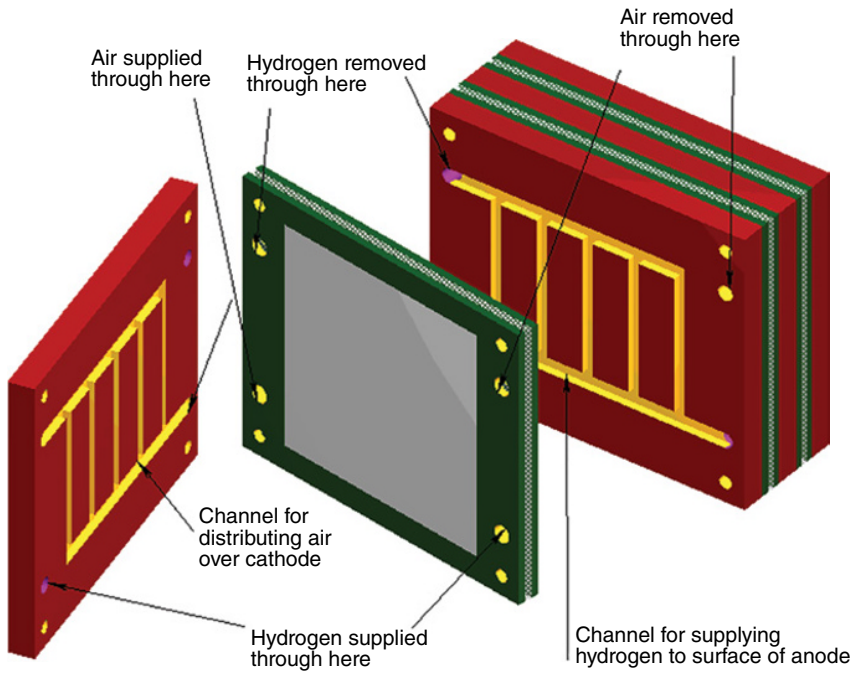


Figure 1.12 Internal manifolding. A more complex bipolar plate allows reactant gases to be fed to electrodes through internal tubes. (Source: Courtesy of Ballard Power Systems.)

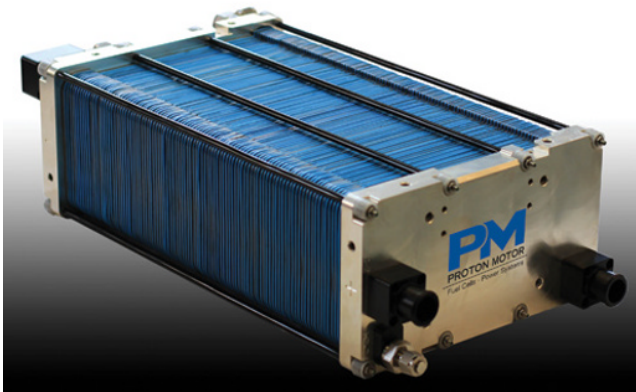


Figure 1.13 A 96-cell, water-cooled PEMFC stack that produces up to 8.4 kW and weighs 1.4 kg. (Source: Courtesy of Proton Motor GmbH.)

cells, graphite was one of the first materials to be employed, but it is difficult to work and brittle and, consequently, has now largely been replaced by various carbon composite materials. Stainless steel can also be used, but it will corrode in some types of fuel cell. Ceramic materials have found application in fuel cells that operate at high temperatures. The bipolar plate nearly always is a major contributor to the capital cost of a fuel cell.

1.6 Principal Technologies

Setting aside practical issues such as manufacturing and materials costs, the two fundamental technical problems with fuel cells are:

- The slow reaction rates, particularly for the oxygen reduction reaction, which lead to low levels of current and power.
- The fact that hydrogen is not a readily available fuel¹.

To address these problems, many different types of fuel cell have been developed and tested. The systems are usually distinguished by the electrolyte that is used and the operating temperature, though there are always other important differences as well. There are six principal types of fuel cell, namely:

- Low temperature (50–150°C): alkaline electrolyte (AFC), proton-exchange membrane (PEMFC), direct methanol (DMFC) and other liquid-fed fuel cells.
- Medium temperature (around 200°C): PAFC.
- High temperature (600–1000°C): molten carbonate (MCFC) and SOFC.

Some operational data on each type are given in Table 1.1. There are other less well-known types such as the direct borohydride (DBFC) and direct carbon fuel cells (DCFC); the former operates at low temperatures and the latter at high temperatures.

Table 1.1 Principal types of fuel cell.

Fuel cell type	Mobile ion	Operating temperature (°C)	Fuel	Applications and notes
Alkaline (AFC)	OH ⁻	50–200	Pure H ₂	Space vehicles, e.g., Apollo, Shuttle
Proton-exchange membrane (PEMFC)	H ⁺	30–100 + ^a	Pure H ₂	Vehicles and mobile applications, and for lower power CHP systems
Direct methanol (DMFC)	H ⁺	20–90	Methanol	Portable electronic systems of low power, running for long times
Phosphoric acid (PAFC)	H ⁺	~220	H ₂ , (low S, low CO, tolerant to CO ₂)	Large numbers of 200-kW CHP systems in use
Molten carbonate (MCFC)	CO ₃ ²⁻	~650	H ₂ , various hydrocarbon fuels (no S)	Medium- to large-scale CHP systems, up to MW capacity
Solid oxide (SOFC)	O ²⁻	500–1000	Impure H ₂ , variety of hydrocarbon fuels	All sizes of CHP systems, 2kW to multi MW

CHP, combined heat and power.

a) New electrolyte materials as described in Chapter 4 are enabling higher operating temperatures for the PEMFC.

¹ Although hydrogen is preferred for most types of fuel cell, other fuels can be used for some technologies. For example, methanol is employed in the direct methanol fuel cell (DMFC) and carbon as the fuel in the direct carbon fuel cell (DCFC).

To date, the PEMFC has proved to be the most successful commercially. The electrolyte is a solid polymer, in which protons are mobile. The chemistry is the same as that shown Figure 1.3 for an acid-electrolyte system. The PEMFC runs at relatively low temperatures, so the problem of slow reaction rates is addressed by using sophisticated catalysts and electrodes. Platinum has been the preferred catalyst. It is an expensive metal but, through improvements in materials, only minute amounts are now required. Consequently, in modern PEMFC designs, the platinum makes a relatively small contribution to the total cost of the fuel-cell system. More recent research suggests that in some cases platinum can be eliminated from the catalyst. Further discussion of the PEMFC is given in Chapter 4. The PEMFC has to be fuelled with hydrogen of high purity, and methods for meeting this requirement are discussed in Chapter 10.

The DMFC is a variant of the PEMFC. The technology differs from the PEMFC only in that methanol in its native liquid form is used as fuel. Other liquid fuels such as ethanol and formic acid may also be viable for some applications. Unfortunately, most of these liquid-fuelled cells produce very low levels of power, but, even with this limitation, there are many potential applications for such devices in the rapidly growing area of portable electronics devices. Such cells, for the foreseeable future at least, will remain low-power units and will therefore suit applications that require slow and steady consumption of electricity over long periods.

As mentioned earlier, an AFC system was chosen for the Apollo and Space Shuttle orbiter craft. The problem of slow reaction rate was overcome by using highly porous electrodes, with a platinum catalyst, and sometimes by operating at quite high pressures. Although some historically important AFCs have been run at about 200°C, the systems usually operate below 100°C. Unfortunately, the AFC is susceptible to poisoning by the carbon dioxide in the atmosphere. Thus the air and fuel supplies must be free from this gas, or else pure oxygen and hydrogen must be supplied.

The PAFC was the first type of fuel cell to reach commercialization and the technology enjoyed a reasonable degree of widespread terrestrial use in the period 1980–2000. Many 200-kW systems, manufactured by the International Fuel Cells Corporation, were installed in the United States and Europe. Other systems were produced by Japanese companies. In the PAFC, porous electrodes, platinum catalysts and a moderately high temperature (~220°C) help to boost the reaction rate to a reasonable level. Such PAFC systems were fuelled with natural gas, which is converted to hydrogen within the fuel-cell system by steam reforming. The required equipment for steam reforming unfortunately adds considerably to the costs, complexity and size of the fuel-cell system. Nevertheless, PAFC systems have demonstrated good performance in the field, for instance, units have run for periods in excess of 12 months without any maintenance that has required shutdown or human intervention. A typical installation of a 400 kW PAFC system is shown in Figure 1.14.

The most common form of SOFC operates in the region of 600–1000°C. These high temperatures permit high reaction rates to be achieved without the need for expensive platinum catalysts. At these elevated temperatures, fuels such as natural gas can be used directly (internally reformed) within the fuel cell without the need for a separate processing unit. The SOFC thus addresses the aforementioned key problems (viz. slow reaction rates and hydrogen supply) and takes full advantage of the inherent simplicity of the fuel-cell concept. Nevertheless, SOFCs are made from thin ceramic materials that are difficult to handle and therefore are expensive to manufacture. In addition,



Figure 1.14 Phosphoric acid fuel cell for stationary power-plant applications (Source: Creative commons – Courtesy of UTC.)

a large amount of extra equipment is needed to make a full SOFC system, e.g., air and fuel preheaters, heat-exchangers and pumps. Also the cooling system is more complex than for low-temperature fuel cells. Care also has to be taken during start-up and shutdown of SOFC systems, on account of the intrinsic fragile nature of the ceramic materials in the stacks.

The MCFC has an interesting and distinguishing feature in that it requires carbon dioxide to be fed to the positive electrode, as well as oxygen. This is usually achieved by recycling some of the exhaust gas from the anode to the cathode inlet. The high temperature means that a good reaction rate is achieved with a comparatively inexpensive catalyst — nickel. Like the SOFC, an MCFC system can be fuelled directly with gases, such as methane and coal gas (a mixture of hydrogen and carbon monoxide), without the need for an external reformer. This advantage for the MCFC is somewhat offset, however, by the nature of the electrolyte, namely, a hot and corrosive molten mixture of lithium, potassium and sodium carbonates.

1.7 Mechanically Rechargeable Batteries and Other Fuel Cells

At the start of this book, a fuel cell was defined as an electrochemical device that converts a fuel to electrical energy (and heat) continuously, as long as reactants are supplied to its electrodes. The implication is that neither the electrodes nor the electrolyte is consumed by operation of the cell. Of course, in all fuel cells the electrodes and