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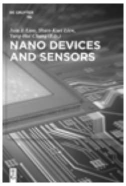

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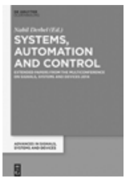

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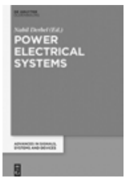

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Progress Reports on Impedance Spectroscopy

Measurements, Modeling, and Application

Edited by
Olfa Kanoun

DE GRUYTER
OLDENBOURG

Editor
Prof. Olfa Kanoun
Technische Universität Chemnitz
Faculty of Electrical Engineering and Information Technology
Reichenhainer Str. 70
09126 Chemnitz, Germany
Olfa.Kanoun@etit.tu-chemnitz.de

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Preface

Impedance spectroscopy is a widely used and powerful measurement method applied in many fields of science and technology such as electrochemistry, material science, biology and medicine. In spite of the apparently different scientific and application background in these fields, applications share the same measurement method in a system identification approach and profit from the possibility to use complex impedance over a wide frequency range and giving interesting opportunities for separating effects, for accurate measurements and for simultaneous measurements of different and even non-accessible quantities.

For electrochemical impedance spectroscopy (EIS) competency from several fields of science and technology is indispensable. Understanding electrochemical and physical phenomena is necessary for developing suitable models. Suitable measurement procedures should be developed taking specific requirements of the considered application into account. Signal processing methods are very important for extracting target information by suitable mathematical methods and algorithms. New trends are emerging rapidly involving special techniques for realizing fully automatic embedded solutions at low costs and requiring a deep overview of modern information technology.

The scientific dialogue between specialists of impedance spectroscopy, dealing with different fields of science, technology and application, is therefore particularly important to promote the adequate use of this powerful measurement method in both laboratory and in embedded solutions.

Since 2008, the International Workshop on Impedance Spectroscopy (IWIS) has been launched as a platform for promoting experience exchange and networking in the scientific and industrial field. Its aim is to serve for encouraging the sharing of experiences between scientists and to support new comers aiming to specialize in impedance spectroscopy. Since many years, the workshop has been gaining increasingly more acceptance in both scientific and industrial fields and addressing increasingly more fundamentals, but also diverse application fields of impedance spectroscopy. Many renowned scientists are contributing yearly to it and sharing their experience with scientists all around the world. By means of tutorials and special sessions, young scientists get a good overview of different fundamental sciences and technologies helping them to get expertise even in fields, which are still not in the focus of their background.

In 2013 the Circle of Experts of Impedance Spectroscopy (CEIS) was founded to promote exchange between experts and together with industry as interest group for promoting impedance spectroscopy all over the subfields related to fundamental and applications of impedance spectroscopy. The CEIS is the steering committee of the IWIS workshop supporting it and deciding about the yearly best paper and best poster award to recognize best contributions.

This peer reviewed book is the first edition in the series Progress Reports on Impedance Spectroscopy which has the aims to widen knowledge of scientists in this field by presenting selected and extended contributions from the International Workshop on Impedance Spectroscopy (IWIS'14 and IWIS'15). The series reports about new advances and different approaches in dealing with impedance spectroscopy, including theory, methods and applications. The book is therefore interesting for researcher and developers in the field of impedance spectroscopy.

I thank all contributors for the interesting contributions and the reviewers who supported by the decision about publication with their valuable comments.

Prof. Dr.-Ing. Olfa Kanoun

Contents

Part I: **Batteries**

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Florina Cuibus, Svetlozar Ivanov, Ulf Schwalbe, Marco Schilling and Andreas Bund

State-of-Charge and State-of-Health Estimation of Commercial $LiFePO_4$ Batteries by means of Impedance Spectroscopy

Abstract: Commercial $LiFePO_4$-type cells were characterized by electrochemical impedance spectroscopy to identify sensitive and reliable parameters suitable to diagnose the state of charge and state of health. On the basis of the proposed equivalent circuit, electrochemical parameters were extracted, and physical and chemical ageing phenomena were categorized and selected. It was observed that, after 2,000 cycles the charge transfer resistance increased approximately with 50% from the initial value, which indicates a decreasing of the exchange current density. The Warburg element showed a decrease of diffusion coefficient and lithium concentration due to the formation of solid electrolyte interface layer. The charge transfer resistance demonstrates more significant trend with ageing cycles and the results are consistent with experiment-based observations from the literature, which seems to be indicating the potential of the proposed model for battery age estimation.

Keywords: $LiFePO_4$ batteries, state of charge, state of health, electrochemical impedance spectroscopy

1 Introduction

The improvement of the storage system is one of the primary challenges for the development of modern electric vehicles. To fulfil the requirements for extended driving range, the storage systems need reliable high-energy batteries and an advanced battery management system (BMS) for efficient energy consumption optimization. The implementation of an efficient battery state-of-charge (SoC) and state-of-health (SoH) estimation is a central aspect for the development of BMS.

Battery ageing responsible for the cell impedance increase and power decay and energy decay origins from multiple and complex mechanisms [1]. Material properties, as well as storage and cycling conditions, have an impact on battery lifetime performance SoC and SoH. Therefore, prompt and reliable SoC and SoH determination, independent on the cycling current and operational history, is highly favourable. The

Florina Cuibus, Svetlozar Ivanov and Andreas Bund, Electrochemistry and Electroplating Group, Ilmenau University of Technology, 98693 Ilmenau, Germany
Ulf Schwalbe and Marco Schilling, Industrial Electronics Group, Ilmenau University of Technology, 98693 Ilmenau, Germany

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SoC, battery instability and ageing phenomena can be investigated non-destructively by means of electrochemical impedance spectroscopy (EIS) [2–4]. EIS is an established method for analysis of electrochemical systems and is considered a valuable tool to detect changes in mass transport properties, double-layer capacitance, ohmic resistance and reaction kinetics during battery operation and ageing. Furthermore, to the extensive use of this method add the properties of the cell (capacity, voltage), although the advantages of EIS method, the determination of electrical parameters of the individual electrode materials in commercial batteries, remain challenging. The implementation of EIS method (quick and online) or the determination of SoC and SoH for the BMS becomes as well challenging. The advantages of the EIS technique are that, the method does not have a pre-history and is sensitive enough for electrical parameter extraction. Therefore, an efficient estimation of SoC and SoH will improve the performance of the battery, developing better BMS. However, the SoC and SoH estimation is generally limited, as for example by other conventional methods like coulomb counting, which is not able to give the resistance, a crucial parameter for ageing diagnosis. In order to have an online and broad diagnosis, the resistance of material and electrolyte can be determined via EIS by an appropriate model extracted. Furthermore, EIS remains the most promising non-destructive method even if less practical application for battery characterization was employed. The capability of EIS measurements was already studied by Mingant et al. [5] by developing a diagnosis tool for SoC and SoH characterization. A lifetime model proposed by Omar et al. [6] provides a clear view regarding the change of the internal resistance and capacity fade at different conditions. On the basis of the parameters' evolution, a cycle life model was developed, which was proposed for the development of an accurate estimation of SoH. A series of EIS measurements performed in galvanostatic mode showed that the SoC and SoH have an influence on EIS. Good reviews of the available methods for SoC estimation are presented in [7, 8]. A large number of different types of Li-ion batteries (LiBs) existing on the market have advantages and disadvantages related to cost, performance, safety and cycle life. Considering safety and production cost, one of the suitable cell types is the $LiFePO_4$/graphite cell [9, 10]. The $LiFePO_4$ (LFP) cathode material received attention because of its long cycle and calendar life, low price and good thermal stability. Further advantages like fast kinetics (high power), low thermal heat exchange, stable structure, low price and non-toxicity, used for electrical cars, are the reasons why the LFP battery was chosen for this study.

The primary aim of this study is to characterize commercial LFP-type cells using EIS. Key aspects are SoH and SoC analysis by interpretation of the EIS spectral data, targeting identification of sensitive and reliable parameters, suitable for expressing SoC and SoH battery diagnostics. To perform specific ageing tests, physical and chemical ageing phenomena were categorized and selected. Further aim is to find appropriate scalable electrical parameters for simultaneous evaluation of SoC and SoH.

2 Experimental Set-up

Commercial 18650 cells (A123 Systems cylindrical) with a nominal capacity of 1.1 Ah and an LFP-based positive electrode were employed for all the measurements. The nominal voltage is 3.3 V and voltage limits are 3.6 and 2 V. The measurements were carried out using a BioLogic Potentiostat/Galvanostat (type VSP, France). To test the influence of various factors on the ageing of a commercial LFP cell, a test procedure shown in Fig. 1 was chosen. Concomitantly the SoC and SoH parameters based on EIS measurements were extracted and further modelled to predict the ageing of the battery.

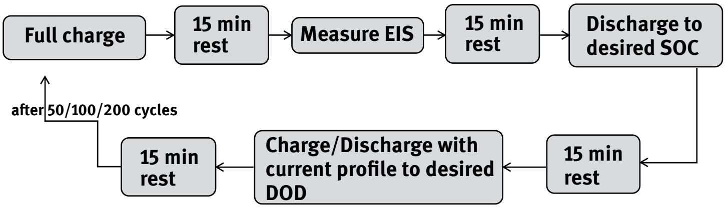

Fig. 1. Test procedure employed for SoC and SoH determination by means of EIS.

The first row describes the experimental procedure for SoC data acquisition by means of EIS. The procedure consists of EIS measurements, resting time, charge–discharge cycling current and discharge profile. The resting time of 15 minutes was experimentally determined. Experiments have shown that a resting time of 15 minutes is sufficient to have minimal influence on the capacity and parameter determination in the SoC range of interest. A charging current of 1.5 A and a discharging current of 1 A were chosen and represent the recommended charging–discharging current profile from the data sheet of the cells [11]. The cells were charged and discharged with 100% depth of discharge (DoD), which represents 3.6 V, the end-of-charge voltage, and 2 V, the cut-off voltage. EIS was measured at different SoC and SoH at OCP (I = 0 A) and a current amplitude of 50 mA. The EIS spectra were recorded between the frequency range 100 kHz and 10 mHz. The EIS test procedure is in Fig. 2 described.

EIS was performed for each cell at successive discharge intervals until a 2-V cut-off voltage was reached. The SoC of each cell was calculated on the basis of nominal voltage of the cell. In this study, the galvanostatic charge–discharge cycling of cells was conducted using a BioLogic Potentiostat/Galvanostat (type VSP, France) at room temperature (about 25°). The settings of voltage range and current density were chosen in correlation with the desired DoD.