Book Review

Electrochemical Impedance Spectroscopy

M. E. Orazem and B. Tribollet

reviewed by Jean Vereecken

Electrochemical impedance spectros-copy (EIS) has proven to be a very powerful method, used in several domains and with different purposes (study of a reaction mechanism, monitoring, assessment of a protection method, etc.) EIS is an electrochemical technique with a broad range of applications (corrosion, batteries and fuel cells, biomedical devices, semiconductors and solid-states devices, coatings, and more), thus its users are scientists and engineers with very different backgrounds.

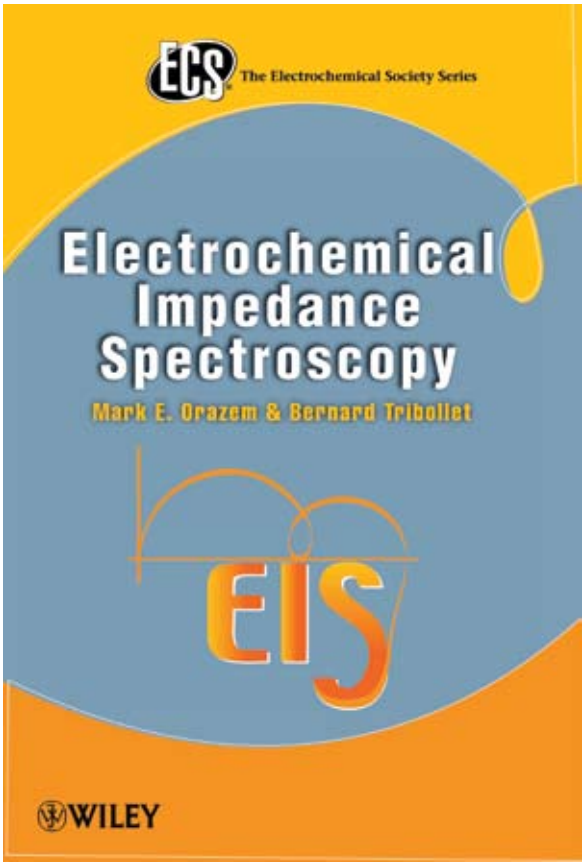
The number of papers published in this field has doubled roughly every four years. In 2006, over 1,200 articles were published that mention the use of EIS. Yet the methodology of the use of this technique is not always very rigorous and the interpretation of the data remains often very qualitative. Hence publication of this book has come at the right time.

The book is divided in seven parts. In order to deliver a basic and complete background, the first part provides material in different domains covering mathematics (complex variables, differential equations), statistics, and electrical circuits. Special attention is paid to electrochemistry, including the basics of thermodynamics, kinetics, and electrochemical instrumentation.

It should be emphasized that the authors make an effort to avoid confusion on the notations and symbols used in this different fields (electricity, chemistry, and electrochemistry: IUPAC conventions, for example). This coherent approach makes the reading and understanding of the book fluent, with the little drawback of having to convert the notations of references of the literature.

The second part is devoted to "Experimental Considerations" with the introduction of different methods providing the identification of electrochemical parameters. Starting with the steady-state polarization curves, the authors introduce the analysis in frequency domain, and comparing different measurement techniques, they conclude that each analysis method has its place in the experimental arsenal, summarizing their relative merits. The authors also consider relatively newer techniques such as LEIS (localized EIS), deploring their underutilization. This part also provides guidelines for the design of experimental cells, and the selection of appropriate impedance parameters and instrument controls (experimental errors and noise).

In the third part, the authors develop models for the impedance response from hypotheses involving different reaction sequences. The treatment includes electrode kinetics, mass transport, solid-state systems, time-constant dispersion, models accounting for two- and three-dimensional interfaces, porous electrodes, and oxide layers. The authors show (with many examples from the literature) that these models can be expressed in the mathematical formalism of electrical circuits. Chapter 13 is devoted to the oft-disputed meaning of the constant-phase-element (CPE), introduced as a convenient circuit element to account for dispersion of time constants. In Chapters 14 and 15, a generalized transfer function is presented as well as transfer-function techniques involving nonelectrical quantities (EHD).



It must be emphasized that this part of the book is illustrated by a great variety of examples from the literature, in order to explore the relationship between proposed mechanisms and the interfacial impedance response. It is obviously a pedagogical challenge to find an example for each mechanism, which might result in a loss of a general approach.

In Part IV, the authors describe the possible strategies for interpretation of impedance data, ranging from graphical methods to complex nonlinear regression. With different examples the authors show that the representation of impedance data (impedance format: impedance, admittance, complex capacity) has a great impact on the use of graphical methods to visualize and interpret data. In Chapter 16, the methods for representing impedance data are illustrated for two simple RC electrical circuits (blocking and active circuits). In Chapter 17, the graphical methods presented require no specific model of the system under evaluation. In Chapter 18, the graphical methods shown have a basis in a deterministic model for a given process (mass transport, reaction kinetics, Mott-Schottky plots). Chapter 19 provides an overview of issues associated with regression. Chapter 20 deals with a systematic approach to determine whether the mathematical models (described in Part III) provide a statistically adequate description of data. Bias errors are shown to limit the frequency range useful for regression analysis, and the variance of stochastic errors is used to guide the weighting strategy for regression.

Part V provides a conceptual understanding of stochastic, bias, and fitting errors in frequency-domain measurements. The Kramers-Kronig relations and their applications to EIS are described. Measurement models, used to assess the error structure, are described and compared with process models used to extract physical properties.

(continued on next page)

(continued from previous page)

The final chapter, entitled, "An Integrated Approach to Impedance Spectroscopy," provides an EIS philosophy that integrates experimental observation, model development, and error analysis. With the help of examples from the literature, the authors show how the model selection must be guided by additional supporting observations, how regression strategies and experimental design must be guided by error analysis, and how selection of new experiments can be supported by the use of models.

The book includes an appendix on complex integration, useful for the derivation of the Kramers-Kronig relations, and lists of tables, examples, symbols, and references.

This book can be recommended for scientists and engineers (young or senior) who are approaching EIS for the first time. It can be also considered as a state-of-the-art survey of the technique, with a wide range of references. This book is excellent not only for students (self-study material or as a textbook) in a variety of disciplines but also for teachers to organize their lecture in the field, as well as for researchers wishing to find information about experimental setups and conditions to obtain valid results.

The learning process is made easier by the insertion of questions, throughout the whole text, followed by their solutions. Problems, developed at the end of each chapter, are suitable either for a self-study process or for use by a teacher. Important concepts are identified and set aside at the bottom of pages as they appear in the text. Readily identifiable icons are used to distinguish examples and important concepts (the elephant, well known to the participants of EIS 2004).

About the Reviewer

Jean Vereecken wrote his PhD thesis in chemical engineering at the Université Libre de Bruxelles in 1969. He was a full professor at the Vrije Universiteit Brussel and Head of the Department Metallurgy, Electrochemistry, and Materials Science there until January 2007. He is now retired and is a professor emeritus. The research activities of the department are focused on surface engineering, and an important topic is the study of corrosion (mechanisms, protection, and monitoring). Prof. Vereecken was the chair of the Organizing Committee of the Third International Symposium on Electrochemical Impedance Spectroscopy in 1995, in Ysermonde (Belgium). During a period of instruction, in Paris in 1969, in the lab of I. Epelboin (now the lab of Cl. Deslouis, and where B. Tribollet is working), he developed a method of using EIS to study electrocrystallization of silver.

Paul Natishan, *President*

Fernando Garzon, *Vice-President*

Results of the 2009 Election of Officers and Slate of Officers for 2010

The ECS Tellers of Election have announced the results of the 2009 election of Society officers, with the following persons elected: President—Paul Natishan, U.S. Naval Research Laboratory; and Vice-President—Fernando Garzon, Los Alamos National Laboratory. The terms of William Brown (Vice-President), Esther Takeuchi (Vice-President), John Susko (Treasurer), and Johna Leddy (Secretary) were unaffected by this election.

At the Board of Directors meeting in San Francisco, California on May 28, 2009, members of the Board voted to approve the slate of candidates recommended by the ECS Nominating Committee. The slate of candidates for the next election of ECS officers, to be held in January-February 2010, include: for President—William D. Brown; for Vice-President (one to be elected)—Dennie T. Mah and Tetsuya Osaka; for Treasurer (one to be elected)—Christina Bock and E. Jennings Taylor. Full biographies and candidate statements will appear in the winter 2009 issue of *Interface*.