

Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a technique that probes energy storage and dissipation properties over a range of frequencies by measuring impedance (the opposition to the flow of alternating current in a complex system). The technique is applicable to almost any physicochemical system, and has been employed in a wide variety of areas such as testing fuel cells, studying biomolecular interactions, microstructural characterization, corrosion studies, biomedical devices, semiconductors, solid-state devices, sensors, batteries, electrochemical capacitors, dielectric measurements, coatings, electrochromic materials, analytical chemistry, imaging, electrochemical cells, mass-beam oscillators, and biological tissues.

Because of its broad applications, the field has been growing tremendously, and the number of articles published has doubled approximately every four or five years. In 2006, more than 1200 papers mentioning its use appeared in journals.

A symposium devoted to EIS was held in Bombannes (France) in 1989, and subsequent conferences were held every three years in Santa Barbara (California, 1992), Ysermonde (Belgium, 1995), Angra do Reis (Brazil, 1998), Marilleva (Italy, 2001), Cocoa Beach (Florida, 2004), and Argelès-sur-Mer (France, 2007). The 8th International Symposium on EIS is scheduled for June 6–11, 2010 in Algarve (Portugal). The proceedings of these symposia, published in *Electrochimica Acta*, provide unique triennial views of the state of the art of EIS.

Mark E. Orazem, Professor of Chemical Engineering at the University of Florida, Gainesville, who is a Fellow of the Electrochemical Society (ECS), President-elect of the International Society of Electrochemistry (ISE), and Associate Editor of the *Journal of the Electrochemical Society*, and was the organizer of the 6th International Symposium on EIS, teaches a short course on the subject for the ECS. Bernard Tribollet, Director of Research at the Centre National de la Recherche Scientifique (CNRS) and Associate Director of the Laboratoire Interfaces et Systèmes Electrochimiques at the Université Pierre et Marie Curie and a member of the ECS and ISE, teaches an annual short course on impedance spectroscopy.

This book by Orazem and Tribollet, the latest volume in Wiley's Electrochemical Society Series, emphasizes generally applicable fundamentals rather than providing a detailed treatment of applications. The reader will find discussions of specific applications among the references at the end of the book. It is intended as both a reference source and a textbook for training new scientists

and engineers. Although many short courses on impedance spectroscopy are available, formal courses on the technique are rare, and therefore the book has been written to accommodate both independent and formal university learning.

The book is divided into seven parts. On pages i–xxxi, a preface summarizing the book's contents is followed by a detailed chronological history of impedance spectroscopy, which ranges from Oliver Heaviside's work on the transient response of electrical circuits using Laplace transforms (1872) to recent research and techniques, and includes a valuable time-line table up to 1992.

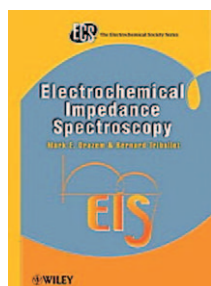
Part I: Background (Chapters 1–6) then deals with complex variables, differential equations, statistics, electrical circuits, electrochemistry, and electrochemical instrumentation. Students or readers may use this material selectively, depending on their backgrounds. Coverage is limited to that needed to understand the core of the textbook, which consists of the following parts.

Part II: Experimental Considerations (Chapters 7 and 8) introduces experimental methods used to measure impedance and other transfer functions. It considers frequency-domain techniques and approaches used in impedance instrumentation, and it provides a basis for evaluating and improving experimental design. The material is integrated with the discussion of experimental errors and noise.

Part III: Process Models (Chapters 9–15), the longest part, shows how deterministic models of impedance response can be developed from physical and kinetic descriptions. Hypothesized models are described and related to electrical circuit analogues. The topics include electrode kinetics, mass transfer, solid-state systems, time-constant dispersion, models accounting for two- and three-dimensional interfaces, and an example of a transfer-function technique in which the rotation speed of a disk electrode is modulated.

Part IV: Interpretation Strategies (Chapters 16–20) presents methods for interpreting impedance data, ranging from graphical methods to complex nonlinear regression. The material is integrated with the discussion of experimental errors and noise. It demonstrates that bias errors limit the frequency range that is useful for regression analysis and explains how the variance of stochastic errors is used to guide the weighting strategy employed for regression.

Part V: Statistical Analysis (Chapters 21 and 22) deals with stochastic, bias, and fitting errors in frequency-domain measurements. An important advantage of frequency-domain measurements is that real and imaginary parts of the response must be internally consistent, and the expression of this consistency takes different forms known collectively as the Kramers–Kronig relationships, which



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are described along with their application to spectroscopic measurements. Measurement models that are used to assess the error structure are described and compared with process models used to extract physical properties.

Part VI: Overview (Chapter 23), the shortest part, gives a philosophy for EIS that integrates experimental observation, model development, and error analysis. The authors' approach differs from the usual sequential approach to developing models for given impedance spectra by emphasizing the advantages of obtaining supporting observations to guide model selection, the use of error analysis to guide regression strategies and experimental design, and the use of models to guide selection of new experiments. They illustrate this approach by citing examples from the scientific literature. This final chapter of the book illustrates that selection of models, even those based on physical principles, requires both error analysis and additional experimental verification.

Part VII: Reference Material includes an appendix on complex integration methods that are required for understanding the derivation of the Kramers–Kronig relationships, as well as lists of tables, examples, and symbols. The 297 references, some as recent as 2007, include books, articles, and dissertations, many by the authors themselves. The index (six double-column pages) provides a user-friendly means of finding specific information. Meticulously numbered mathematical equations, tables, figures, and diagrams appear throughout the text to clarify the material.

The authors present the subject in a manner that facilitates the sequential development of understanding and expertise, either in a formal course or in self-study. Throughout the book, illustrative examples in the form of questions followed by answers demonstrate how the principles that have been described can be applied to problems. In this way the student can try to solve the problems before reading the answers. Also, homework problems, suited for self-study or study under the supervision of an instructor, are given in each chapter. Important equations and relationships are identified and collected in easily accessible tables. An easily recognized icon—an elephant—appears frequently at the bottom of a page where a critical concept is first mentioned, to remind the student that it should be remembered. The elephant also serves to remind the reader of the parable of the blind wise men and the elephant, which is quoted in the introductory section to emphasize the philosophy that impedance spectroscopy cannot be used as a stand-alone technique.

Another book on the subject, *Impedance Spectroscopy: Emphasizing Solid Materials and Systems*, edited by J. R. Macdonald (John Wiley & Sons, New York, 1987), and its successor, *Impe-*


dance Spectroscopy: Theory, Experiment, and Applications, edited by E. Barsoukov and J. R. Macdonald (Wiley-Interscience, New York, 2005), are excellent research monographs. However, as I have emphasized, the work by Orazem and Tribollet is a textbook, which deals with fundamentals in greater detail, provides less material on applications, but also includes a variety of pedagogical aids. Scientific professionals will probably want to have both volumes on their bookshelves, but the work by Orazem and Tribollet is better suited for students and beginners in the use of impedance spectroscopy. In short, the books are complementary rather than competitive.

While admitting that impedance spectroscopy is “just an experimental technique”, Orazem and Tribollet justify the need for a full semester-long course on impedance spectroscopy by stating: “In our view, impedance spectroscopy represents the confluence of a significant number of disciplines, and successful training in the use and interpretation of impedance requires a coherent education in the application of each of these disciplines to the subject. In addition to learning about impedance spectroscopy, the student will gain a better understanding of a general philosophy of scientific inquiry” (p. xviii).

I agree with their view, and I am pleased to recommend their book to professionals and graduate students in a variety of disciplines such as electrochemistry, materials science, physics, and electrical and chemical engineering, and to others concerned with the topics that I cited in the first paragraph of this review.

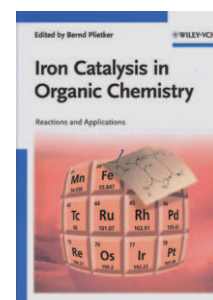
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Iron Catalysis in Organic Chemistry

Iron, as the most abundant transition metal on the face of our earth, plays a pivotal role in biological electron transfer and redox processes. However, the organic chemists' toolkit contains only a handful of well-established iron catalysis methodologies. Under the editorial supervision of Bernd Plietker (University of Stuttgart), an excellent monograph on *Iron Catalysis in Organic Chemistry* has come to fruition. It is the clear ambition of this work to familiarize the catalysis community with the advantages and adventures that lie within the realm of



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