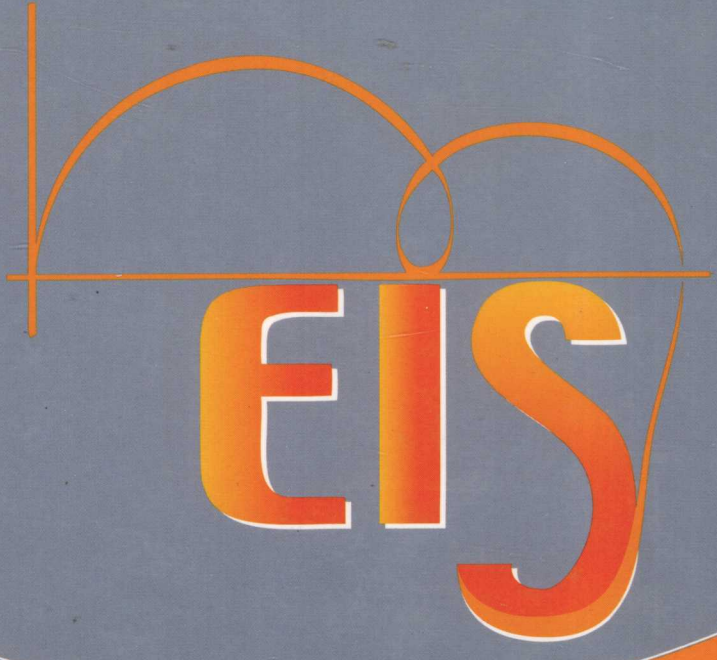
The Electrochemical Society Series

Electrochemical Impedance Spectroscopy

Mark E. Orazem & Bernard Tribollet



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ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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Preface

This book is intended for use both as a professional reference and as a textbook suitable for training new scientists and engineers. As a textbook, this work is suitable for graduate students in a variety of disciplines including electrochemistry, materials science, physics, electrical engineering, and chemical engineering. As these audiences have very different backgrounds, a portion of the book reviews material that may be known to some students but not to others. There are many short courses offered on impedance spectroscopy, but formal courses on the topic are rarely offered in university settings. Accordingly, this textbook is designed to accommodate both directed and independent learning.

Organization

The textbook has been prepared in seven parts:

Part I Background

This part provides material that may be covered selectively depending on the background of the students. The subjects covered include complex variables, differential equations, statistics, electrical circuits, electrochemistry, and instrumentation. The coverage of these topics is limited to what is needed to understand the core of the textbook, which is covered in the subsequent parts.

Part II Experimental Considerations

This part introduces methods used to measure impedance and other transfer functions. The chapters in this section are intended to provide an understanding of frequency-domain techniques and the approaches used by impedance instrumentation. This understanding provides a basis for evaluating and improving experimental design. The material covered in this section is integrated with the discussion of experimental errors and noise. The extension of impedance spectroscopy to other transfer-function techniques is developed in Part III.

Part III Process Models

This part demonstrates how deterministic models of impedance response can be developed from physical and kinetic descriptions. When possible, correspondence is drawn between hypothesized models and electrical circuit analogues. The treatment includes electrode kinetics, mass transfer, solid-state systems, time-constant dispersion, models accounting for two- and three-dimensional interfaces, generalized transfer functions, and a more specific example of a transfer-function technique in which the rotation speed of a disk electrode is modulated.

Part IV Interpretation Strategies

This part describes methods for interpretation of impedance data, ranging from graphical methods to complex nonlinear regression. The material covered in this section is integrated with the discussion of experimental errors and noise. 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 used for regression.

Part V Statistical Analysis

This part provides a conceptual understanding of stochastic, bias, and fitting errors in frequency-domain measurements. A major advantage of frequency-domain measurements is that real and imaginary parts of the response must be internally consistent. The expression of this consistency takes different forms that are known collectively as the Kramers-Kronig relations. The Kramers-Kronig relations and their application to spectroscopy measurements are described. Measurement models, used to assess the error structure, are described and compared with process models used to extract physical properties.

Part VI Overview

The final chapter in this book provides a philosophy for electrochemical impedance spectroscopy that integrates experimental observation, model development, and error analysis. This approach is differentiated from the usual sequential model development for given impedance spectra by its emphasis on obtaining supporting observations to guide model selection, use of error analysis to guide regression strategies and experimental design, and use of models to guide selection of new experiments. These concepts are illustrated with examples taken from the literature. This chapter is intended to illustrate that selection of models, even those based on physical principles, requires both error analysis and additional experimental verification.

Part VII Reference Material

The reference material includes an appendix on complex integration needed to follow the derivation of the Kramers-Kronig relations, a list of tables, a list of examples, a list of symbols, and a list of references.

Pedagogical Approach

The material is presented in a manner that facilitates sequential development of understanding and expertise either in a course or in self-study. Illustrative examples are interspersed throughout the text to show how the principles described are applied to common impedance problems. These examples are in the form of questions, followed by the solution to the question posed. The student can attempt to solve the problem before reading how the problem is solved. Homework problems, suitable either for self-study or for study under direction of an instructor, are developed for each chapter. Important equations and relations are collected in tables, which can be easily accessed. 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.

As can be found in any field, the notation used in the impedance spectroscopy literature is inconsistent. In treatments of diffusion impedance, for example, the symbol θ is used to denote the dimensionless oscillating concentration variable; whereas, the symbol θ used in kinetic studies denotes the fractional surface coverage by a reaction intermediate. Compromises were necessary to create a consistent notation for this book. For example, the dimensionless oscillating concentration variable was given the symbol θ, and γ was used to denote the the fractional surface coverage by a reaction intermediate. As discussed in Section 1.2.3, the book deviates from the IUPAC convention for the notation used to denote the imaginary number and the real and imaginary parts of impedance.

This book is intended to provide a background and training suitable for application of impedance spectroscopy to a broad range of applications, such as corrosion, biomedical devices, semiconductors and solid-state devices, sensors, batteries, fuel cells, electrochemical capacitors, dielectric measurements, coatings, electrochromic materials, analytical chemistry, and imaging. The emphasis is on generally applicable fundamentals rather than on detailed treatment of applications. The reader is referred to other sources for discussion of specific applications of impedance.[1–4]

Remember! 0.1 *The elephant at left is used to identify important concepts for each chapter. It is intended to remind the student of the parable of the blind men and the elephant.*

The active participation in related short courses demonstrates a rising interest in impedance spectroscopy. As discussed in the preliminary section on the history of the technique, the number of papers published that mention use of electrochemical impedance spectroscopy has increased dramatically over the past 10 years. Nevertheless, the question may be raised: *Why teach a full semester-long course on impedance spectroscopy? It is, after all, just an experimental technique.* 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.

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July, 2008

Acknowledgments

The authors met for the first time in 1981 in the research group of John Newman at the University of California, Berkeley. **Mark Orazem** was a graduate student, and **Bernard Tribollet** was a visiting scientist on sabbatical leave from the *Centre National de la Recherche Scientifique* (CNRS) in Paris. We have maintained a fruitful collaboration ever since and our careers, as well as the content of this book, build on the foundation we received from John. We owe an additional debt of gratitude to many persons, including:

- Our families, who have embraced our collaboration over the years
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While we have received help and support from many people, the remaining errors and omissions in this text are ours. We will gratefully receive corrections and suggestions from our readers to be implemented in future editions of this book.

The Blind Men and the Elephant

Impedance spectroscopy is a complicated area of research that has been subject to significant controversy. As we begin a study of this subject it is well to remember the Buddhist parable of the blind men and the elephant. American poet John Godfrey Saxe (1816–1887) based the following poem on the fable.[5]

The Blind Men and the Elephant

John Godfrey Saxe

It was six men of Indostan
To learning much inclined,
Who went to see the Elephant
(Though all of them were blind),
That each by observation
Might satisfy his mind.

The First approached the Elephant,
And happening to fall
Against his broad and sturdy side,
At once began to bawl:
God bless me! but the Elephant
Is very like a wall!

The Second, feeling of the tusk,
Cried, Ho! what have we here
So very round and smooth and sharp?
To me 'tis mighty clear
This wonder of an Elephant
Is very like a spear!

The Third approached the animal,
And happening to take
The squirming trunk within his hands,
Thus boldly up and spake:
I see, quoth he, the Elephant

Is very like a snake!

The Fourth reached out an eager hand,
And felt about the knee.
What most this wondrous beast is like
Is mighty plain, quoth he;
'Tis clear enough the Elephant
Is very like a tree!

The Fifth, who chanced to touch the ear,
Said: Een the blindest man
Can tell what this resembles most;
Deny the fact who can,
This marvel of an Elephant
Is very like a fan!?

The Sixth no sooner had begun
About the beast to grope,
Than, seizing on the swinging tail
That fell within his scope,
I see, quoth he, the Elephant
Is very like a rope!

And so these men of Indostan
Disputed loud and long,
Each in his own opinion
Exceeding stiff and strong,
Though each was partly in the right,
And all were in the wrong!

Moral:
So oft in theologic wars,
The disputants, I ween,
Rail on in utter ignorance
Of what each other mean,
And prate about an Elephant
Not one of them has seen!

The logo for the 2004 International Symposium on Impedance Spectroscopy, shown in Figure 1, was intended to evoke the lessons of the blind men and the elephant. The multiple loops resemble the Nyquist plots obtained in some cases for the impedance of corroding systems influenced by formation of surface films. The low-frequency inductive loop was deformed to evoke the image of the elephant's trunk, and the capacitive loops resemble the head and body of the elephant.

Impedance spectroscopy is, of course, not a religion, but an application of a frequency-domain measurement to a complex system that cannot be easily visu-

Figure 1: The logo for the 2004 International Symposium on Impedance Spectroscopy, held in Cocoa Beach, Florida.

alized. The quantities measured, e.g., current and potential for electrochemical or electronic systems and stress and strain for mechanical systems, are macroscopic values that represent the spatial average of individual events. These quantities are influenced by the desired physical properties, such as diffusivity, rate constants, and viscosity, but do not provide a direct measure of them.

Application of impedance spectroscopy is very much like feeling an elephant that we cannot see. Measurement of current and potential under a steady state yields some information concerning a given system. By adding frequency dependence to the macroscopic measurements, impedance spectroscopy expands the information that can be extracted from the measurements. Impedance measurements, however, are not sufficient. Additional observations are needed to gain confidence in the model identification.

History of Impedance Spectroscopy

Impedance spectroscopy is an electrochemical technique with broad applications that is growing in importance. As seen in Figure 2, the number of papers published in this area has doubled roughly every four or five years. In 2006, over 1,200 journal articles were published that mention the use of electrochemical impedance spectroscopy.

Timeline

By his application of Laplace transforms to the transient response of electrical circuits, Oliver Heaviside created the foundation for impedance spectroscopy. Heaviside coined the words *inductance*, *capacitance*, and *impedance* and introduced these concepts to the treatment of electrical circuits. His papers on the subject, published in *The Electrician* beginning in 1872, were compiled by Heaviside in book form in 1894.[6,7] From the perspective of the application to physical systems, however, the history of impedance spectroscopy begins in 1894 with the work of Nernst.[8]

Nernst applied the electrical bridge invented by Wheatstone[9,10] to the measurement of the dielectric constants for aqueous electrolytes and different organic fluids. Nernst's approach was soon employed by others for measurement of dielectric properties[11,12] and the resistance of galvanic cells.[13] Finkelstein[14] applied the technique to the analysis of the dielectric response of oxides. Warburg[15,16] developed expressions for the impedance response associated with the laws of diffusion, developed almost 50 years earlier by Fick,[17] and introduced the electrical circuit analogue for electrolytic systems in which the capacitance and resistance were functions of frequency. The concept of diffusion impedance was applied by Krüger to the capacitive response of mercury electrodes.[18]

In the 1920s, impedance was applied to biological systems, including the resistance and capacitance of cells of vegetables[19] and the dielectric response of blood suspensions.[20–22] Impedance was also applied to muscle fibers, skin tissues, and other biological membranes.[23,24] The capacitance of the cell membranes was found to be a function of frequency,[25] and Fricke observed a relationship between the frequency exponent of the impedance and the observed constant phase angle.[26] In 1941, brothers Cole and Cole showed that the frequency-dependent complex

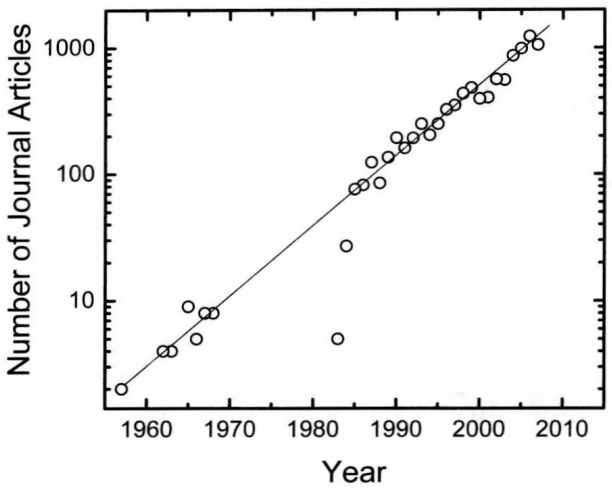

Figure 2: Number of journal articles on electrochemical impedance spectroscopy identified on October 3, 2007 using the Engineering Village search engine. The key words used were "(((impedance or admittance) and (Electrochemical)), Journal article only).

dielectric constant can be represented as a depressed semicircle in a complex admittance plane plot and suggested a formula, consistent with Fricke's law,[26] now known as a *constant-phase element*.[27]

In 1940, Frumkin[28] explored the relationships among the double-layer structure on mercury electrodes, the capacitance measured by use of a Wheatstone bridge, and the surface tension, following the theoretical underpinnings of the Lippmann equation. Grahame[29,30] expanded this treatment of the mercury electrode, providing a fundamental understanding of the structure of the electrical double layer. Dolin and Ershler applied the concept of an equivalent circuit to electrochemical kinetics for which the circuit elements were independent of frequency.[31] Randles developed an equivalent circuit for an ideally polarized mercury electrode that accounted for the kinetics of adsorption reactions.[32]

In the early 1950s, impedance began to be applied to more complicated reaction systems.[33–35] In subsequent years, Epelboin and Loric addressed the role of reaction intermediates in causing low-frequency inductive loops,[36] de Levie developed transmission line models for the impedance response of porous and rough electrodes,[37] and Newman showed that the nonuniform current and potential distribution of disk electrodes can result in high-frequency time-constant dispersion.[38] Levart and Schuhmann[39] developed a model for the diffusion impedance of a rotating disk that accounted for the influence of homogeneous chemical reactions. Kinetic models accounting for reaction intermediates were addressed in greater detail in publications by Armstrong et al.[40] and Epelboin et al.[41]

Nonlinear complex regression techniques, developed in the early 1970s,[42,43] were applied to impedance data by Macdonald et al.[44,45] and Boukamp.[46] The regression approaches were based on use of equivalent electrical circuits, which

became the predominant method for interpretation of impedance data. The experimental investigations turned increasingly toward those associated with technical applications, such as electrodeposition and corrosion.[47–49] Gabrielli et al. introduced the concept of a generalized transfer function for impedance spectroscopy.[50–52] During this time, the Kramers-Kronig relations, developed in the late 1920s,[53,54] were applied for the validation of electrochemical impedance data.[55] Agarwal et al.[56] described an approach that eliminated problems associated with direct integration of the Kramers-Kronig integral equations and accounted explicitly for stochastic errors in the impedance measurement.

Several authors have described methods for generalized deconvolution of impedance data.[57,58] Stoynov and co-workers developed a robust method in which calculation of the local derivatives of the impedance with respect to frequency allows visualization of the distribution of time constants for a given spectrum without *a-priori* assumption of a distribution function.[59,60] Stoynov and Savova-Stoynov described a graphical method of estimating instantaneous impedance projections from consecutive series of impedance diagrams obtained during the time of system evolution.[61]

A conference dedicated to the development of electrochemical impedance spectroscopy techniques was initiated in 1989 in Bombannes, France. The subsequent meetings, held every three years, took place in California (1992), Belgium (1995), Brazil (1998), Italy (2001), Florida (2004), and France (2007). The special issues associated with these conferences provide unique triennial snapshots of the state of impedance research.[62–67] One driving concern reflected in these volumes is the heterogeneity of electrode surfaces and the correspondence to the use and misuse of constant phase elements. Local impedance spectroscopy, developed by Lillard et al.,[68] may prove to be a useful method for understanding this relationship.

Areas of Investigation

A historical perspective on impedance spectroscopy is presented in Table 1. A brief listing of advances in this field cannot be comprehensive, and many important contributions are not mentioned. The reader may wish to explore other historical perspectives, such as that provided by Macdonald.[69] Chapters written by Sluyters-Rehbach and Sluyters[70] and by Lasia[71] provide excellent overviews of the field. Nevertheless, Table 1 provides a useful guide to the trends in areas related to electrochemical impedance spectroscopy. These areas include the types of systems investigated, the instrumentation used to make the measurements, including changes in the accessible frequency range, the methods used to represent the resulting data, and the methods used to interpret the data in terms of quantitative properties of the system.

Experimental Systems

The early applications of what we now know as impedance spectroscopy were to the dielectric properties of fluids and metal oxides. Impedance measurements performed on mercury electrodes emphasized development of a fundamental understanding of the interface between the electrode and the electrolyte. The mercury drop electrodes were ideal for this purpose because they provided a uniform and easily refreshed interface that could be considered to be ideally polarizable over a broad range of potential. The impedance technique was used to identify an interfacial capacitance that could be compared to the theories for diffuse electrical double layers. In the 1920s, considerable effort was placed on biological systems, including the dielectric properties of blood and the impedance response of cell membranes. In the 1950s, impedance began to be used for studies of anodic dissolution. One may identify a trend from ideal surfaces suitable for fundamental studies to ones associated with technical materials. Impedance became useful for studying processes such as corrosion, deposition of films, and other electrochemical reactions. It became clear that the solid electrode surfaces were not uniform, and this complicated interpretation of impedance spectra in terms of meaningful physical properties. Recently, local impedance spectroscopy has emerged as a means of studying heterogeneous electrode surfaces.

Measurement Techniques

Early experimental techniques relied on use of Wheatstone bridges. The bridge is based on a nulling technique that requires manipulation of an adjustable resistor and capacitor at each frequency to obtain an effective frequency-dependent resistance and capacitance of the cell, from which can be derived an impedance. In time, the mechanical signal generator was replaced by an electronic signal generator, but the frequency range remained limited to acoustic frequencies (kHz to Hz). The ability to record time-domain signals on an oscilloscope enabled measurement to subacoustic frequencies (on the order of mHz). Subsequent development of digital signal analysis allowed automated recording of impedance spectra. These techniques are described in Chapter 7. Development of microelectrodes enabled local measurement of current density and local impedance spectra. These techniques are also described in Chapter 7.

A parallel development has taken place for related transfer-function methods. For electrochemical systems, impedance spectroscopy, which relies on measurement of current and potential, provides the general system response. As described in Chapters 14 and 15, transfer-function methods allow the experimentalist to isolate the portion of the response associated with specific inputs or outputs.

Impedance Representation

The methods used to plot impedance data began with plots of effective resistance and capacitance, reflecting the use of bridges for measurement. These plots gave

way to Nyquist and Bode plots, which remain the traditional means of representing impedance data. More recently, authors have promoted the use of Bode plots corrected for Ohmic resistance and the use of logarithmic plots of the imaginary impedance as a function of frequency. As described in Chapter 17, such plots provide limited yet quantitative interpretation of impedance spectra.

Mathematical Analysis

The impedance response associated with diffusion in an infinite domain and in a solid film was developed in the very early twentieth century. Similarly quantitative models were developed in the 1940s for the capacitive behavior of the double layer. In the middle of the twentieth century, models were being developed that accounted for heterogeneous reactions and adsorbed intermediates. In the 1960s and 1970s, such models were being generalized to account for homogeneous reactions and reactions on porous electrodes. The development of quantitative models is presented in Part III.

These models provided a quantitative relationship between physicochemical parameters and impedance response, but the application of interpretation strategies did not keep pace with the model development. Interpretation was based on graphical examination of plotted data. In simple cases, plots could be used directly as described in Chapter 18. For more complicated cases, simulations could be compared graphically to data to reveal qualitative agreement.

Nonlinear regression analysis, described in Chapters 19 and 20, was developed for impedance spectroscopy in the early 1970s. The models were cast in the form of electrical circuits with mathematical formulas added to account for the diffusion impedance associated with simplified geometries.

There were significant difficulties associated with fitting models to impedance data. The electrochemical systems frequently did not conform to the assumptions made in the models, especially those associated with electrode uniformity. Constant-phase elements (CPEs), described in Chapter 13, were introduced as a convenient general circuit element that was said to account for distributions of time constants. The meaning of the CPE for specific systems was often disputed.

In addition, the variance of impedance measurements depends strongly on frequency, and this variation needs to be addressed by the regression strategies employed. An assumed dependence of the variance of the impedance measurement on impedance values was employed in early stages of regression analysis, and this gave rise to some controversy over what assumed error structure was most appropriate. An experimental approach using measurement models, described in Chapter 21, was later developed, which eliminated the need for assumed error structures.

The long time required to make impedance measurements in the acoustic to subacoustic frequency range caused the resulting impedance to be influenced by changes in the system properties during the course of the measurement. The Kramers-Kronig relations, described in Chapter 22, were employed to determine