Electrochemical Impedance Spectroscopy and its Applications

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All impedances are complex, but some are more complex than others.

Margaretha Sluyters-Rehbach

Preface

My first practical contact with electrochemical impedance spectroscopy (EIS) was during my postdoctoral training in the laboratory of Prof. Ron W. Fawcett at the University of Guelph, Ontario, Canada, in 1975. At that time I was using ac voltammetry on a dropping mercury electrode. Since then, the technique and equipment have evolved significantly. I was continually using EIS in subsequent years in the kinetics of the reduction of metal cations in nonaqueous solvents to determine the kinetics of hydrogen evolution, adsorption and absorption into metals, impedance of porous electrodes, and electrocatalytic reactions. After a series of seminars on the impedance spectroscopy in the laboratory of Prof. Brian Conway in Ottawa in 1994, he encouraged me to write a review in *Modern Aspects of Electrochemistry*, which was published in 1999. Prof. Conway has also asked me to write a second chapter in *Modern Aspects* on the impedance of hydrogen adsorption, absorption, and evolution (2002). Later, Prof. M. Schlesinger asked me to write yet another chapter on the impedance of porous electrodes (2009). This book originated from my previous reviews and lectures at various universities.

The purpose of this book is to present the concept of impedance, impedance of electrical and electrochemical systems, its limitations, and certain applications. The available books on EIS were written either by physicists or engineers, and I wanted to present it from the chemist's point of view. Some knowledge of electrochemistry is necessary to understand the developments of kinetic equations. I hope that it will be useful to students who are just starting to use this technique and to others already using it in their research. The book contains theory and applications, numerical examples shown in the text, and exercises with full solutions on the Internet.

First, electrical circuits containing resistances only are presented, followed by circuits containing R, C, and L elements in transient and ac conditions. To understand the concept of impedance, the notions of Laplace and Fourier transforms are presented and must be understood thoroughly. In this chapter, impedance plots are also presented, along with several examples for various circuits. Next, methods for determining impedances, including fast Fourier transform-based techniques, are discussed.

Based on that knowledge, the impedance of electrode processes in the presence of diffusion in various geometries and adsorption is mathematically developed. This leads to the general method of determining the impedances of complex mechanisms. As an illustration, the impedance of electrocatalytic reactions involving hydrogen adsorption, absorption, and evolution is presented.

The next two chapters deal with impedance dispersion at solid electrodes and the impedance of porous electrodes in the absence and presence of electroactive species.

It is difficult to present all applications of EIS; some applications (such as those to solid materials and PEM fuel cells, corrosion and passivity, batteries; see Sect. 1.3) may be found in available books. As examples, Mott-Schottky plots obtained for semiconductors, the impedance of coating and paints, and electrocatalysis of hydrogen adsorption, absorption and evolution were presented as they are well known in the electrochemical literature. Additionally, newer and developing applications such as the impedance of self-assembled monolayers, biological bilayers, and biosensors were also shown.

Finally, methods of verification of obtained impedances and the modeling of experimental data are discussed. The last two chapters deal with applications of nonlinear measurements and instrumental limitations.

Besides examples in the text, there are exercises at the end of certain chapters that can be solved using Excel, Maple, or Mathematica and more specialized programs such as ZView and KKtransform, with solutions on the Internet.

This book contains a comprehensive approach to impedance, but there exist more specialized books on impedance that should also be consulted; reading of the research literature cannot be avoided. One hour in the library may save one year of laboratory research.

Sherbrooke, Québec, Canada Andrzej Lasia

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