Differential Impedance Analysis

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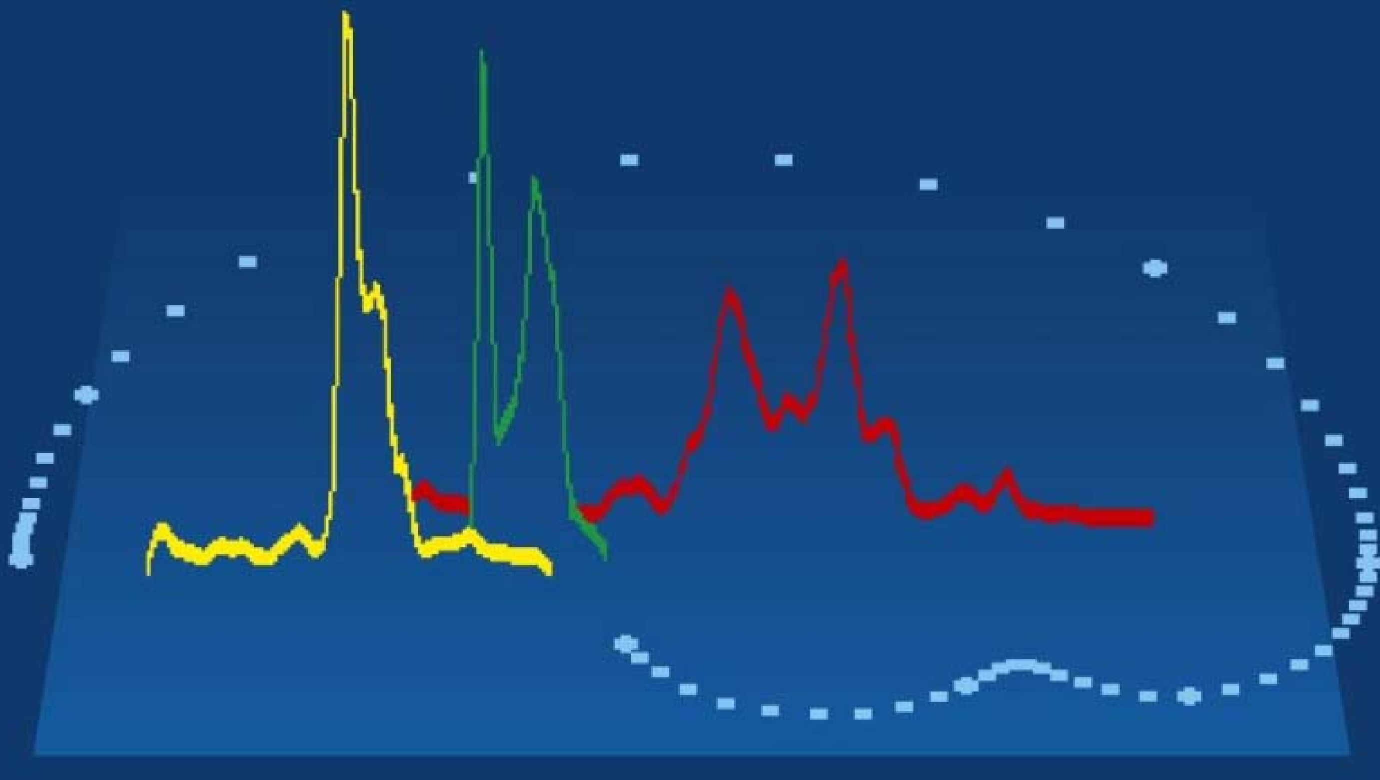

Marin Drinov Academic Publishing House

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Centre of Excellence *POEMES* series

Academic Publishing House M. Drinov

Sofia 2005

à notre maître

I. Epelboin

Preface

This book is a fusion of two parts. Part I is an introduction to the "classical" Impedance Spectroscopy. Part II contains the basics of the Differential Impedance Analysis (DIA) – a novel method for impedance data analysis, developed by the authors.

During the last decades the Electrochemical Impedance Spectroscopy has been elaborated as the most informative and powerful method for investigating electrochemical processes. Based on the principle of the Transfer Function, introduced earlier in the Technical Cybernetics, the Electrochemical Impedance Spectroscopy is a further development of that fundamental idea, applied to studies of non-linear electrochemical systems. The close relationship between the state space and the space of the parameters is an intrinsic property of these systems, however. As a result the necessity of a new specific theory appeared.

During those years of theoretical derivations, a new modern and powerful technique has also been developed. Based on the fundamental Fourier Transform and on other mathematical and software algorithms, the impedance measurement technique of our days is extremely sensitive, selective and adaptive. The best facilities of this type can cover more than 11 frequency decades and are capable of measuring resistances from micro-Ohms up to terra-Ohms and capacitances from pico-Farads up to kilo-Farads.

All these achievements – theoretical and technological, have determined the success of the Electrochemical Impedance Spectroscopy.

Chapter 1 introduces the main principles of the Electrochemical Impedance Spectroscopy including the basic working hypotheses necessary to ensure the consistence of the measured results with the developed theory.

Chapter 2 introduces the basics of the impedance modelling and interpretation – model structures and elements and their combinations. The list of the studied elements includes also the bounded constant phase element (BCP), developed by the authors. This element generalizes all other impedance elements. It can also be used for approximation of possible deviations from the classical description, taking into account the restrictions of the host matrix on the diffusion process, the inhomogeneities of the adsorption layer and of the charge transfer activity and others.

Chapter 3 describes the principal electrochemical impedance models. Commencing with the simplest model of ideally polarizable electrode, the list includes also one and two step reaction models and such ones with diffusion limitations. Their description contains the initial assumptions, the final impedance equation, as well as the impedance diagram. A generalization of the discussed model by introducing CPE and BCP for representing the existence of a given or unknown distribution of the model's parameters is also included.

Chapter 4 enriches the information of Chapter 3 in a more illustrative way. It is designed as a catalogue of models, presented with their complex-plane impedance images. Every single model is visualized with one or more figures, containing several diagrams corresponding to a selected variation of the parameters. Their values are chosen in such a way that gives the "ideal" diagram as well as the deformed diagrams, caused by the mixing of the parameters. The visual study of this catalogue could be very educative for understanding the diversity of the observed images. It could also be beneficial in the experimental practice, providing information necessary for the initial screening of the observed results. Some of the included diagrams have "strange" or very specific shapes – they are selected in order to find a similarity with some of the beautiful and most interesting experimental shapes reported in the literature by leading experts in the field.

Measured by powerful instruments, the experimental data are rich in information. They contain the main properties of the object, but also many of the fine details, concerning the processes inhomogeneity, the reaction geometry and their evolution. Thus every properly measured impedance diagram corresponds to the object's state and represents a specific fingerprint of its behaviour. The main point is to extract useful information from the experimental data and to understand it.

Two main approaches can meet this goal:

- Construction of a working hypothetical model, verification of its correspondence to the experimental data and identification of the model's parameters;
- Analysis of the experimental data as a specific fingerprint of the object and extraction of the model's structure and parameters from the data.

The principle of the Differential Impedance Analysis is different. It consists in the projection of the object's frequency behaviour into the space of the parameters of a simple model – an aperiodic inertial system, described by a first order differential equation. This operating model contains three elements and the resulting projection is a four dimensional one. Thus, the Differential Impedance Analysis could be treated as a next (secondary) transform, producing images of enriched dimensionality.

As a matter of fact, the Fourier Transform converts the initial two-dimensional space (potential – time) into a three dimensional projection (real and imaginary components and frequency). The DIA converts this 3-D image into a 4-D projection: additive, dissipative and absorption terms in respect to the frequency. Thus the DIA is a second step in the data analysis.

The procedure of consecutive transforms of the initial data from the time domain into the frequency domain and then into the parameters domain produces new images with enhanced analytical power and increased object's observability and identifiability.

It is worth to emphasize the fact that these transforms are unconditional. No initial hypotheses concerning the object's structure are necessary.

The DIA transform is based on a very simple mathematical equation corresponding to one first order Padé approximation, extended with a simple additive term. At the same time this equation corresponds to the First Cauer Form and meets the requirements for the model reduction. Thus a very large list of phenomena classes, including ladder and Voigt's electrochemical models, can be treated in this way.

The method of DIA involves also some additional steps of data processing. The 4-D set of data produced by the DIA is subject of a next transform – the Spectral Transform. It accumulates the similar values of the parameters in the resulting spectral peaks and thus emphasizes the most pronounced parameters values. At the same time the form and width of every spectral peak corresponds to the frequency distribution of the parameters. Thus, by the Spectral Transform, the DIA is able to treat also fuzzy data and to produce images of the fuzzy object's behaviour.

More or less, all real samples have distribution of their parameters. From this point of view, the DIA method is a useful and practically unique tool for analyzing real and unknown objects.

The second part of the book is an introduction into the DIA. Chapter 5 contains the basic mathematical derivations necessary for the understanding of the method.

Chapter 6 is a catalogue of the basic kinetic models with their DIA images – temporal projection (additive, dissipative and absorption terms and frequency) and parametric spectra. The examples are selected in such a way as to ensure maximum clarity and observability of the spectra.

In order to elucidate the practical application of the method, chapter 7 represents a number of examples with real samples. Beginning with the simple case of measured dummy cells, the list contains also more complicated examples taken from the authors' practice in investigating solid state and liquid objects and power sources as well.

The book concludes with a number of Annexes containing practical references and supporting information.

It is our pleasure to acknowledge with gratitude the financial support by the European Commission under contract NNE5/2002/18 “Portable and Emergency Energy Sources - POEMES”, that made possible the edition and the dissemination of the book.

We would like to acknowledge also the UNESCO UVO-ROSTE and the European Internet Centre for Impedance Spectroscopy for the fertile scientific atmosphere and professional contacts, which further promoted the idea for the generation of this monograph.

Our thanks for financial and organizational support are also directed to the Bulgarian Academy of Sciences and to the Academic Publishing House M. Drinov.

We also wish to express our gratitude:

To Prof. A. Popov and Prof. P. Andreev for numerous and supporting discussions;

To Ms. G. Raikova, for the exceptional skills that were needed to produce the figures;

To Ms. D. Nencheva, for devoting her energy and intelligence for the preparation of the text typesetting of the book;

To Prof. P. Zoltowski, Prof. M. Keddam, Prof. H. Takenouti, Prof. C. Gabrielli, Prof. T. Pajkossy for the numerous discussions and scientific collaboration;

To Prof. J. Kilner, Prof. C. Jullien and Prof. M. Viviani, for the active partnership;

To Prof. C. Brett and Prof. M. Orazem for the fruitful collaboration;

To many colleagues at the Bulgarian Academy of Sciences, for creating an optimal environment to study impedance.

Sofia, Bulgaria,

2005

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