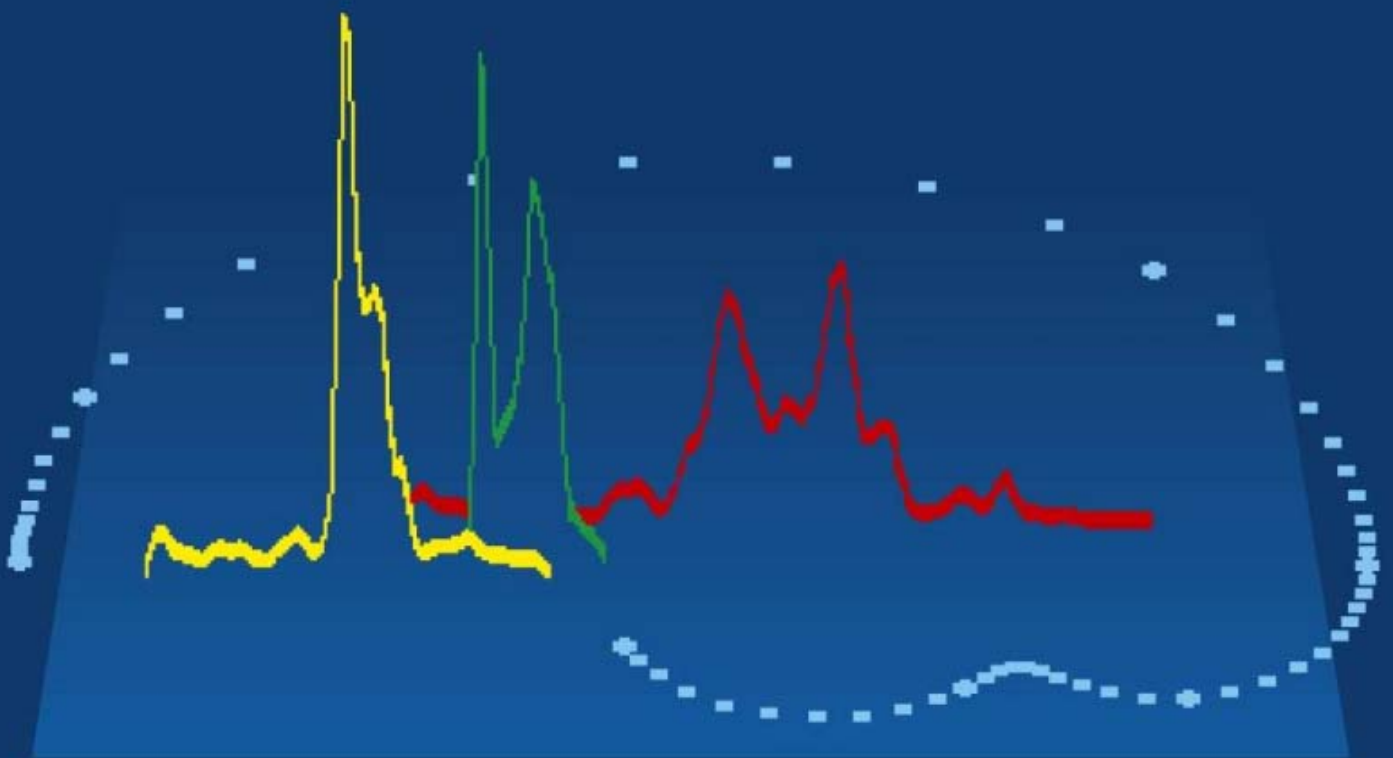


Differential Impedance Analysis

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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.

Preface

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 Caue 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.

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Contents

Preface	v
Introduction	1
Part I. FUNDAMENTALS OF THE ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY	5
Chapter 1. General Concepts	5
1.1. Basic Considerations	5
1.1.1. Principle of the Electrochemical Impedance Spectroscopy	5
1.1.2. Working Hypotheses	6
<i>Working Hypotheses Concerning the System Analysis</i>	6
<i>Working Hypotheses from an Electrochemical Point of View</i>	7
1.1.3. Trends in the Development of the Electrochemical Impedance Spectroscopy	8
1.2. Impedance Modelling and Identification	8
1.2.1. Theoretical Modelling and Identification	9
<i>Classical Modelling</i>	9
<i>Structural Modelling</i>	10
<i>Data Analysis</i>	15
1.2.2. Structural Identification Approach	22
1.3. Discussion	23
References	25
Chapter 2. Modelling Elements	29
2.1. Lumped Elements	29
2.1.1. Resistance	30
2.1.2. Capacitance	30
2.1.3. Inductance	31
2.2. Frequency Dependent Elements	32
2.2.1. Warburg Element	33
2.2.2. Constant Phase Element	34
2.3. Bounded Frequency Dependent Elements	35
2.3.1. Bounded Warburg Element	36
2.3.2. Bounded Constant Phase Element	37
2.3.3. Unloaded Constant Phase Element	38

Contents

2.4. Simple Combinations of Elements	39
2.4.1. Resistance and Capacitance	40
<i>Connection in Series</i>	40
<i>Connection in Parallel</i>	40
2.4.2. Resistance and Time-Constant	41
2.4.3. Resistance and Bounded Warburg	42
2.5. Discussion	43
References	44
Chapter 3. Basic Electrochemical Models	45
3.1. Models without Diffusion Limitations	45
3.1.1. Ideally Polarizable Electrode	45
3.1.2. Polarizable Electrode	47
3.1.3. Faradaic Reaction Involving one Adsorbed Species	49
3.1.4. Faradaic Reaction Involving two Adsorbed Species	53
3.1.5. Adsorption	55
3.2. Models with Diffusion Limitations	56
3.2.1. Randles Model	56
3.2.2. Bounded Randles Model	58
3.3. Generalized Models	59
3.3.1. Modified Polarizable Electrode with Capacitive CPE	59
3.3.2. Modification of the Faradaic Resistance	60
3.3.3. Modified Adsorption Model	61
3.3.4. Modified Randles Model	62
3.4. Models with Voigt's Structure	63
3.4.1. Granular Homogeneous Bulk with Partially Blocking Electrodes	63
3.4.2. Granular Homogeneous Bulk with Blocking Electrodes	65
3.5. Discussion	66
References	67
Chapter 4. Catalogue of Impedance Models	69
4.1. Simple Combinations of Elements	70
4.2. Study of CPE and BCP	74
4.3. Basic Electrochemical Models with Ladder Structure	78
4.4. Models with Voigt's Structure	88

4.5. Models with Maxwell's Structure	91
4.6. Models Deformed by a Presence of Parasitic Inductance or Capacitance	93
Part II. DIFFERENTIAL IMPEDANCE ANALYSIS	95
Chapter 5. Theory of the Differential Impedance Analysis	95
5.1. Principle of the Scanning Local Analysis	95
5.2. Local Operating Model	97
5.3. Parametric Identification of the LOM	99
5.4. Parametric Analysis	100
5.4.1. Temporal Analysis	100
5.4.2. Spectral Analysis	102
5.5. Secondary Differential Impedance Analysis	105
5.5.1. Differential Temporal Analysis	105
5.5.2. Differential Spectral Analysis	106
5.5.3. Recognition of CPE Dispersion	107
5.6. DIA Identification of Models Including CPE	111
5.6.1. DIA of Bounded Constant Phase Element	111
<i>Temporal Analysis</i>	111
<i>Secondary DIA</i>	111
5.6.2. DIA of Randles Model	113
<i>Temporal Analysis</i>	113
<i>Secondary DIA</i>	115
5.6.3. DIA of Modified Randles Model	116
<i>Temporal Analysis</i>	116
<i>Secondary DIA</i>	116
5.6.4. DIA of a Modified Time-constant Model with Capacitive CPE	118
<i>Temporal Analysis</i>	118
<i>Secondary DIA</i>	120
5.7. Discussion	120
References	123
Chapter 6. DIA Images of Basic Kinetic Models - Catalogue	125
6.1. Warburg Element	128
6.2. Constant Phase Element	130
6.3. Bounded Warburg Element	132
6.4. Bounded Constant Phase Element	134

Contents

6.5. Polarizable Electrode	136
6.6. Modified Polarizable Electrode with Capacitive CPE – Example 1	138
6.7. Modified Polarizable Electrode with Capacitive CPE - Example 2	140
6.8. Polarizable Electrode with Modified Faradaic Resistance of CPE Type – Example 1	142
6.9. Polarizable Electrode with Modified Faradaic Resistance of CPE Type – Example 2	144
6.10. Polarizable Electrode with Modified Faradaic Resistance of CPE Type – Example 3	146
6.11. Two Step Reaction – Example 1	148
6.12. Two Step Reaction – Example 2	150
6.13. Two Step Reaction – Example 3	152
6.14. Three Step Reaction	154
6.15. Randles Model	156
6.16. Modified Randles Model	158
6.17. Modified Bounded Randles Model	160
6.18. Modified Adsorption Model – Example 1	162
6.19. Modified Adsorption Model – Example 2	164
Chapter 7. Applications of the DIA	167
7.1. Supporting Procedures in the Differential Impedance Analysis	167
7.1.1. Temporal Analysis in a Linear Scale	167
7.1.2. Zoomed Spectral Transform	170
7.1.3. Frequency Segmentation	170
7.2. DIA Selectivity	171
7.2.1. Example on Two Time-constant Model with Ladder Structure	171
<i>Experimental Conditions</i>	171
<i>Results with Pure Synthetic Data</i>	172
<i>Results with Noisy Data</i>	174
7.2.2. Comparative Analysis of Models with Similar Impedance Behaviour	177
7.3. Examples of Real Samples	180
7.3.1. DIA of Yttrium Iron Garnet Single Crystal	180
<i>Experimental</i>	180
<i>Results Obtained by DIA</i>	181
7.3.2. DIA of Yttria Stabilized Zirconia	182
<i>Experimental</i>	182
<i>Results Obtained by DIA</i>	183
7.3.3. DIA of the Negative Plate of Lead/acid Battery	190
<i>Experimental</i>	190
<i>Results Obtained by DIA</i>	190
7.3.4. DIA of Motor Oils	192
<i>Experimental</i>	192
<i>Results Obtained by DIA</i>	192
7.4. Discussion	195
References	196

Annexes	199
A1. Basic Mathematical Operations with Complex Numbers	199
A2. Structural Elements	201
A3. Models Description	202
A4. Impedance Data Plotting	203
A5. Data Exchange Formats /DEF/	207
A6. Abbreviations	214
A7. List of Symbols	217
A8. Index	221