IMPEDANCE SPECTROSCOPY

EMPHASIZING SOLID MATERIALS AND SYSTEMS

Edited by

J. Ross Macdonald

Department of Physics and Astronomy
University of North Carolina
Chapel Hill, North Carolina

A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

NEW YORK CHICHESTER BRISBANE TORONTO SINGAPORE

CONTENTS

1. FUNDAMENTALS OF IMPEDANCE SPECTROSCOPY 1

J. Ross Macdonald and William B. Johnson

1.1. Background, Basic Definitions, and History 1

1.1.1. The Importance of Interfaces 1

1.1.2. The Basic Impedance Spectroscopy Experiment 2

1.1.3. Response to a Small-Signal Stimulus in the Frequency Domain 4

1.1.4. Impedance-Related Functions 6

1.1.5. Early History 8

1.2. Advantages and Limitations 8

1.2.1. Differences between Solid State and Aqueous Electrochemistry 11

1.3. Elementary Analysis of Impedance Spectra 12

1.3.1. Physical Models for Equivalent Circuit Elements 12

1.3.2. Simple RC Circuits 13

1.3.3. Analysis of Single Impedance Arcs 16

1.4. Selected Applications of IS 20

2. THEORY 27

2.1. The Electrical Analogs of Physical and Chemical Processes 27

Ian D. Raistrick

2.1.1. Introduction 27

2.1.2. The Electrical Properties of Bulk Homogeneous Phases 29

2.1.2.1. Introduction 29

2.1.2.2. Dielectric Relaxation in Materials with a Single Time Constant 30

2.1.2.3. Distributions of Relaxation Times 34

2.1.2.4. Conductivity and Diffusion in Electrolytes 43

2.1.2.5. Conductivity and Diffusion—A Statistical Description 45
2.1.2.6. Migration in the Absence of Concentration Gradients 47
2.1.2.7. Transport in Disordered Media 50
2.1.3. Mass and Charge Transport in the Presence of Concentration Gradients 56
2.1.3.1. Diffusion 56
2.1.3.2. Mixed Electronic–Ionic Conductors 61
2.1.3.3. Concentration Polarization 63
2.1.4. Interfaces and Boundary Conditions 64
2.1.4.1. Reversible and Irreversible Interfaces 64
2.1.4.2. Polarizable Electrodes 66
2.1.4.3. Adsorption at the Electrode–Electrolyte Interface 68
2.1.4.4. Charge Transfer at the Electrode–Electrolyte Interface 71
2.1.5. Grain Boundary Effects 75
2.1.6. Current Distribution, Porous and Rough Electrodes—the Effect of Geometry 78
2.1.6.1. Current Distribution Problems 78
2.1.6.2. Rough and Porous Electrodes 79

2.2. Physical and Electrochemical Models **84**
J. Ross Macdonald and Donald R. Franceschetti

2.2.1. The Modeling of Electrochemical Systems 84
2.2.2. Equivalent Circuits 85
2.2.2.1. Unification of Immittance Responses 85
2.2.2.2. Distributed Circuit Elements 87
Diffusion-Related Elements 87
The Constant Phase Element and Its Simple Combinations 90
2.2.2.3. Ambiguous Circuits 95
2.2.3. Modeling Results 99
2.2.3.1. Introduction 99
2.2.3.2. Supported Situations 101
Half-Cells 101
Full-Cell Results 103
Diffusion Effects 105
2.2.3.3. Unsupported Situations: Theoretical Models 107
Introduction 107
Boundary Conditions: Adsorption–Reaction Effects 107
DC Response 110

Adsorption–Reaction and Reaction–Diffusion Predictions 112
Theoretical Results for Various Cases of Interest 113
The Case of Charge of Only a Single-Sign Mobile 117
Some Results for More General and Realistic Situations 118
2.2.3.4. Unsupported Situations: Empirical and Semiempirical Models 121
Possible Circuit and Model Modifications 121
Further Empirical and Semiempirical Models 123
Fitting Ambiguity and a New Semiempirical Model 127

3. MEASURING TECHNIQUES AND DATA ANALYSIS 133

3.1. Impedance Measurement Techniques 133
MICHAEL C. H. MCKUBRE AND DIGBY D. MACDONALD

3.1.1. Introduction 133
3.1.2. Frequency Domain Methods 134
3.1.2.1. Audio Frequency Bridges 134
High-Frequency Limitations 136
Low-Frequency Limitations 136
Limitations of Imposed Potential 137
3.1.2.2. Transformer Ratio Arm Bridges 137
High-Frequency Limitations 139
Low-Frequency Limitations 140
Limitations of Potential Control 140
3.1.2.3. Berberian–Cole Bridge 140
High-Frequency Limitations 142
Low-Frequency Limitations 143
Potential Control 143
3.1.2.4. Considerations of Potentiostatic Control 143
3.1.2.5. Oscilloscopic Methods for Direct Measurement 144
3.1.2.6. Phase-Sensitive Detection for Direct Measurement 147
3.1.2.7. Automated Frequency Response Analysis 148
3.1.2.8. Automated Impedance Analyzers 152
3.1.2.9. The Use of Kramers–Kronig Transforms 154
3.1.2.10. Spectrum Analyzers 157
3.1.3. Time Domain Methods 159
3.1.3.1. Introduction 159
3.1.3.2. Analog-to-Digital (A/D) Conversion 160

3.1.3.3. Computer Interfacing 165
3.1.3.4. Digital Signal Processing 168
3.1.4. Conclusions 173

3.2. Data Analysis 173
J. Ross Macdonald

3.2.1. Data Presentation and Adjustment 173
3.2.1.1. Previous Approaches 173
3.2.1.2. Three-dimensional Perspective Plotting 174
3.2.1.3. Treatment of Anomalies 177
3.2.2. Data Analysis Methods 179
3.2.2.1. Simple Methods 179
3.2.2.2. Complex Nonlinear Least Squares 180
3.2.2.3. Weighting 182
3.2.2.4. Which Impedance-Related Function to Fit? 183
3.2.2.5. The Question of "What to Fit" Revisited 183
3.2.2.6. Deconvolution Approaches 184
3.2.2.7. Examples of CNLS Fitting 185
3.2.2.8. Summary and Simple Characterization Example 188

4. APPLICATIONS OF IMPEDANCE SPECTROSCOPY 191

4.1. Characterization of Materials 191
N. Bonanos, B. C. H. Steele, and E. P. Butler

4.1.1. Microstructural Models for Impedance Spectra of Materials 191
4.1.1.1. Introduction 191
4.1.1.2. Layer Models 193
Blocking of Ions—Easy Paths 196
4.1.1.3. Effective Medium Models 198
The Maxwell–Wagner Models 198
The Fricke Model for Two-phase Dispersions 202
4.1.2. Experimental Techniques 205
4.1.2.1. Introduction 205
Considerations of Frequency and Impedance Range 205
4.1.2.2. Sample Preparation—Electrodes 206
Types of Electrodes 206
4.1.2.3. A Measurement System for IS of Materials 207
Principle of Operation 207
Test Procedures 210
Constructional Details 210

Performance and Errors 211
Measurement Rig 213
4.1.3. Interpretation of the Impedance Spectra of Materials 215
4.1.3.1. Introduction 215
Microstructural Aspects of Zirconia Ceramics 215
Bauerle's Circuit Equivalent 216
4.1.3.2. Characterization of Grain Boundaries by IS 217
Microstructure–Grain Boundary Property Correlations 218
Materials Lacking a Grain Boundary Impedance Arc 222
4.1.3.3. Characterization of Two-Phase Dispersions by IS 225
Extraction of Conductivities in an Alkali Halide System 226
Structure–Property Correlations in Polyphase Ceramics 227
4.1.3.4. Assessment of IS as a Characterization Technique 230
Effect of Grain Anisotropy in β-Alumina Ceramics 230
Effect of Conduction along Grain Boundaries 234
Conclusions 236

4.2. Solid State Devices **238**
WILLIAM B. JOHNSON AND WAYNE L. WORRELL
4.2.1. Electrolyte–Insulator–Semiconductor–(EIS) Sensors 239
4.2.2. Solid Electrolyte Chemical Sensors 247
4.2.3. Solid State Batteries 251
4.2.4. Photoelectrochemical Solar Cells 254

4.3. Corrosion of Materials **260**
DIGBY D. MACDONALD AND MICHAEL C. H. MCKUBRE
4.3.1. Introduction 260
4.3.2. Fundamentals 261
4.3.3. Measurement of Corrosion Rate 262
4.3.4. Harmonic Analysis 267
4.3.5. Kramers–Kronig Transforms 274
4.3.6. Corrosion Mechanisms 277
4.3.6.1. Active Dissolution 277
4.3.6.2. Active–Passive Transition 281
4.3.6.3. The Passive State 285
Metal–Film Interface 287

The Film 288
Film–Solution Interface 294
4.3.7. Equivalent Circuit Analysis 301
Coatings 306
4.3.8. Other Impedance Techniques 308
4.3.8.1. Electrochemical Hydrodynamic Impedance (EHI) 309
4.3.8.2. Fracture Transfer Function (FTF) 311
4.3.8.3. Electrochemical Mechanical Impedance 312

REFERENCES **317**

INDEX **341**