Electrochemical Supercapacitors

Scientific Fundamentals and Technological Applications

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To my son, Dr. Adrian
and his sons, Alexander and the "Little B"

Foreword

The first model for the distribution of ions near the surface of a metal electrode was devised by Helmholtz in 1874. He envisaged two parallel sheets of charges of opposite sign located one on the metal surface and the other on the solution side, a few nanometers away, exactly as in the case of a parallel plate capacitor. The rigidity of such a model was allowed for by Gouy and Chapman independently, by considering that ions in solution are subject to thermal motion so that their distribution from the metal surface turns out diffuse. Stern recognized that ions in solution do not behave as point charges as in the Gouy–Chapman treatment, and let the center of the ion charges reside at some distance from the metal surface while the distribution was still governed by the Gouy–Chapman view. Finally, in 1947, D. C. Grahame transferred the knowledge of the structure of electrolyte solutions into the model of a metal/solution interface, by envisaging different planes of closest approach to the electrode surface depending on whether an ion is solvated or interacts directly with the solid wall. Thus, the Gouy–Chapman–Stern–Grahame model of the so-called *electrical double layer* was born, a model that is still qualitatively accepted, although theoreticians have introduced a number of new parameters of which people were not aware 50 years ago.

Irrespective of the structural details, it has long been accepted that a double layer exists at the electrode/electrolyte solution boundary, which governs adsorption phenomena and influences charge transfer reaction rates, and where electrostatic energy is stored as in a capacitor a few molecular diameters thick. Nevertheless, the existence of a double layer has always been inferred from indirect observations of related properties and quantities, but never directly probed, so much that it was compared to the Arab Phoenix: "Everybody says it exists, nobody knows where it is." This until recently, when it was realized that the energy stored per unit surface area of an electrode is noticeable per se and becomes technologically very interesting with the introduction of new materials with an exceptionally extended active surface: especially treated carbons, some transition metal oxides, electrosynthesized conducting polymers. The interfacial capacity is further increased if the purely capacitive charge is supplemented by a Faradaic charge related to bidimensional redox reactions or tridimensional intercalation processes.

"Supercapacitors" are devices that store electrical energy on the basis of the above phenomena and that can be discharged at a much higher rate than conventional batteries. They have aroused interest for various applications, including electric vehicles, in particular cars as well as trains. I should say that in spite of our awareness of the principles, supercapacitors have appeared on the scientific scene rather suddenly, or at least this has been the impression of those who have realized that something was happening at the technological level. Of the many examples we can produce of innovations developed in technology first and then "discovered" from a fundamental point of view, supercapacitors furnish an authoritative example of the reverse: a technological innovation pushed by fundamental knowledge.

The situation is now that fundamental researchers know everything of the electrical double layer but ignore its application to supercapacitors, while engineers know of supercapacitors but may ignore the fundamentals of their operation. This monograph comes at an opportune time to fill this gap, with a balanced presentation of fundamentals aimed at applications, and applications related to fundamental principles. B. E. Conway has worked for more than 50 years in almost all areas of electrochemistry, particularly interfacial electrochemistry. He is therefore a "veteran" in the field, being the first to realize the potentialities of some materials for their double layer energy.

This volume offers what cannot be found in any other work for its comprehensiveness, exhaustiveness, and focus. For the first time a highly theoretical topic, the electrical double layer at electrodes, is shown to manifest itself in highly technological applications. It is with a real sense of pride that electrochemists in the near future will press the accelerator in their electric car knowing that certain performances are possible only thanks to the discharge of the "so-called" (but is it indeed there?) *electrical double layer* of which technologists have long maintained "electrochemistry can do without it."

The content of this book is useful both for scientists working in fundamental research and technologists, in particular those interested in electrochemical energy conversion and chemistry and physics of electrified interfaces, as well as for engineers working in the field of electrochemical power sources and electrical energy storing devices. They will find the book an invaluable source of information and inspiration. For the way the topics are presented, people working in the area of materials chemistry and physics will find this book of great general interest in view of the typical dependence of the performance of supercapacitors on the structure of materials.

Milan, Italy Sergio Trasatti

Preface

Systems for electrochemical energy production originated with Volta's discovery in 1800 of "voltaic electricity" and were developed in various forms during the nineteenth century. Toward the end of that period, reversibly chargeable batteries for electrical energy storage and utilization became a major development in applied electrochemistry and during the present century have been improved to a high state of the art. They also represent a large fraction of the economic activity in industrial electrochemistry.

In relatively recent years, but originating with Becker's patent in 1957, a new type of electrochemically reversible energy storage system has been developed that uses the capacitance associated with charging and discharging of the double layer at electrode interfaces or, complementarily, the pseudocapacitance associated with electrosorption processes or surface redox reactions. In the first case, large interfacial capacities of many tens of farads per gram of active electrode material can be achieved at high-area carbon powders, fibers, or felts, while, in the second case, large pseudocapacitances can be developed at certain high-area oxides or conducting polymers where extents of Faradaic charge (Q) transfer are functionally related to the potential of the electrode (V), giving rise to a derivative corresponding to a capacitance dQ/dV.

These large specific-value capacitors, especially of the double-layer type, are perceived as electrical energy storage systems that can offer high power-density in discharge and recharge, and cycle lives on the order of 10^5 to 10^6, many times those of conventional batteries. A variety of uses of such electrochemical or so-called "supercapacitors" are now recognized and a new direction of power-source development, complementary to that of batteries, is well established.

An important aspect of this monograph is that it gives a comprehensive account of the electrochemical science and technology of these capacitor systems. An attempt is made to present a self-contained and unified treatment of the field, including essential details of the background science (e.g. of double-layer capacitance and the origins of pseudocapacitance, the electrolyte solutions used in electrochemical capacitors) as well as basic concepts of electrode kinetics and interfacial electrochemistry, dielectric polarization theory, porous electrodes, and conducting polymer materials that give rise to large specific capacitances. In this way, understanding and study of the material presented in this volume will not require frequent reference to other textbooks of physical chemistry or electrochemistry.

The text contains many illustrative diagrams and cross-references between chapters, and includes many literature references. For the convenience of the reader, three or four diagrams have been duplicated from one chapter or another to avoid the necessity of seeking earlier or later pages in the volume where cross-referenced material is cited.

The author's work in this field originated with a research contract between Continental Group Inc. and the University of Ottawa's Electrochemistry Group. We would like to acknowledge here the work carried out by Drs. H. Angerstein-Kozlowska, V. Birss, J. Wojtowicz, and Visiting Professor S. Hadzi-Jordanov (University of Skopje) with Mr. Dwight Craig (electrical engineer) of Continental Group in the period 1975 to 1981. More recently, new work in this field is being carried out at the University of Ottawa and is supported by the Natural Sciences and Engineering Research Council of Canada. For this work, acknowledgment is made to Dr. W. J. Pell and Mr. T. C. Liu.

Special thanks are due to Dr. B. V. Tilak of Occidental Chemical Corp., N.Y., for his critical reading of the manuscript before its submission for publication, and for his suggestions for additions and revisions. Appreciation is expressed to Dr. Tilak and Dr. S. Sarangapani (ICET Inc., Norwood, Mass.) for their detailed examination of Chapter 20 on technology development, and in particular for their suggestions for the best systematic organization of the manifold aspects of the subject treated in that chapter. Thanks are also due to Drs. S. Gottesfeld (Los Alamos National Laboratory) and J. Miller (J. M. Inc., Shaker Heights, Ohio) for reading the chapters on conducting-polymer capacitors and ac impedance, respectively. We are grateful to Dr. Miller for permission to reproduce some of his computer-generated graphs and data on ac impedance evaluation of capacitors.

The author is also most grateful to Drs. S. P. Wolsky and N. Marincic for their permission to draw on various diagrams and tables from the proceedings of papers presented at the seminars on electrochemical capacitors held at Deerfield Beach and Boca Raton, Fla, over the period 1991 to 1997, under the auspices of Florida Educational Seminars Inc. (abbreviated as FES in the text).

Finally, special thanks are due to Denise Angel, who typed, with great efficiency and accuracy, all the chapters of this volume in several drafts, exercising literacy and care that would be difficult to match. Grateful thanks are also due to Eva Szabo for drafting most of the diagrams.

Ottawa, Canada B. E. Conway

Contents

Chapter 1 Introduction and Historical Perspective

1.1. Historical Overview 1
1.2. Scope of the Monograph 8
References 9

Chapter 2 Similarities and Differences between Supercapacitors and Batteries for Storing Electrical Energy

2.1. Introduction 11
2.1.1. Energy Storage Systems 11
2.1.2. Modes of Electrical Energy Storage by Capacitors and Batteries 12
2.2. Faradaic and Non-Faradaic Processes 13
2.2.1. Non-Faradaic 14
2.2.2. Faradaic 14
2.3. Types of Capacitors and Types of Batteries 15
2.3.1. Distinguishable Systems 15
2.3.2. Cell Design and Equivalent Circuits 17
2.4. Differences of Densities of Charge Storage in Capacitors and Batteries 18
2.4.1. Electron Densities per Atom or Molecule . . . 18
2.4.2. Comparison of Energy Densities Attainable in Electrochemical Capacitors and Batteries 19
2.5. Comparison of Capacitor and Battery Charging Curves 20

2.6. Comparison of Charge and Discharge Behavior of Electrochemical Capacitors and Battery Cells Evaluated by Cyclic Voltammetry ... 22
2.7. Li Intercalation Electrodes—A Transition Behavior ... 25
2.8. Charging of a Nonideally Polarizable Capacitor Electrode ... 28
2.9. Comparative Summary of Properties of Electrochemical Capacitors and Batteries ... 29
References ... 31
General Reading References ... 31

Chapter 3 Energetics and Elements of the Kinetics of Electrode Processes
3.1. Introduction ... 33
3.2. Energetics of Electrode Processes ... 34
3.3. Energy Factors in Relation to Electrode Potential ... 37
3.4. Kinetics of Electrode Reactions at Metals ... 41
3.4.1. Currents and Rate Equations ... 41
3.4.2. Linearization of the Butler–Volmer Equation for Near-Equilibrium Conditions (low η) ... 45
3.5. Graphical Representation of the Exchange Current Density, i_o, and Behavior Near Equilibrium ... 46
3.6. Onset of Diffusion Control in the Kinetics of Electrode Processes ... 48
3.7. Kinetics when Steps Following an Initial Electron Transfer Are Rate Controlling ... 50
3.8. Double-Layer Effects in Electrode Kinetics ... 51
3.9. Electrical Response Functions Characterizing Capacitative Behavior of Electrodes ... 53
3.10. Instruments and Cells for Electrochemical Characterization of Capacitor Behavior ... 59
3.10.1. Cells and Reference Electrodes ... 59
3.10.2. Instruments ... 61
3.10.3. Two-Electrode Device Measurements ... 63
References ... 64
General Reading References ... 64

Chapter 4 Elements of Electrostatics Involved in Treatment of Double Layers and Ions at Capacitor Electrode Interphases
4.1. Introduction ... 67
4.2. Electrostatic Principles ... 68

4.2.1. Coulomb's Law: Electric Potential and Field, and the Significance of the Dielectric Constant 68
4.2.1.1. Units 68
4.2.1.2. Dielectric Constant 70
4.2.1.3. Electrostatic Potential, Field, and Force 71
4.2.1.4. Potential ϕ and Field **E** at an Ion . . 72
4.3. Lines of Force and Field Intensity—A Theorem 73
4.4. Capacity of a Condenser or Capacitor 74
4.5. Field Due to a Surface of Charges: Gauss's Relation 74
4.6. Poisson's Equation: Charges in a 3-Dimensional Medium 75
4.7. The Energy of a Charge 76
4.8. Electric Tension in a Dielectric in a Field 77
4.9. Electric Polarization Responses at the Molecular Level 78
4.9.1. Atoms and Molecules in Fields: Electronic Polarization 78
4.9.2. Interaction of a Permanent Dipole with a Field 79
4.9.2.1. Uniform Field 79
4.9.2.2. Nonuniform Field 79
4.9.2.3. Forces on a Quadrupole in a Field . . 80
4.10. Atoms and Molecules in Fields: Dielectric Properties and Dielectric Polarization 81
4.10.1. Dielectrics 81
4.10.2. Polarization of Solvent Molecules in Double-Layer and Ion Fields 81
4.10.3. Dipole Moments of Complex Molecules 82
4.11. Electric Polarization in Dielectrics 83
4.12. Energy and Entropy Stored by a Capacitor 83
References 86
General Reading References 86

Chapter 5 Behavior of Dielectrics in Capacitors and Theories of Dielectric Polarization
5.1. Introduction 87
5.2. Definitions and Relation of Capacitance to Dielectric Constant of the Dielectric Medium 88
5.3. Electric Polarization of Dielectrics in a Field 91
5.4. Formal Electrostatic Theory of Dielectrics 92

5.5. Dielectric Behavior Due to Induced, Distortional Polarization ... 98
5.6. Dielectric Polarization in a Simple Condensed Phase ... 98
5.7. Dielectric Polarization in a System of Noninteracting but Orientable Dipoles ... 99
5.8. Dielectric Polarization of Strongly Interacting Dipoles (High Dielectric Constant Solvents) ... 100
5.9. Dielectric Behavior of the Solvent in the Double Layer ... 102
References ... 104

Chapter 6 The Double Layer at Capacitor Electrode Interfaces: Its Structure and Capacitance
6.1. Introduction ... 105
6.2. Models and Structures of the Double Layer ... 108
6.3. Two-Dimensional Density of Charges in the Double Layer ... 114
6.4. Ionic Charge Density and Interionic Distances on the Solution Side of the Double Layer ... 116
6.5. Electron-Density Variation: "Jellium" Model ... 117
6.6. Electric Field across the Double Layer ... 119
6.7. Double-Layer Capacitance and the Ideally Polarizable Electrode ... 121
6.8. Equivalent Circuit Representation of Double-Layer Electrical Behavior ... 123
References ... 124

Chapter 7 Theoretical Treatment and Modeling of the Double Layer at Electrode Interfaces
7.1. Early Models ... 125
7.2. Treatment of the Diffuse Layer ... 127
7.3. Capacitance of the Diffuse Part of the Double Layer ... 129
7.4. Ion Adsorption and the Treatment of the Compact or Helmholtz Layer ... 133
7.4.1. Stern's Treatment ... 133
7.4.2. Quasi-Chemical Aspect of Anion Adsorption 135
7.5. The Solvent as Dielectric of the Double-Layer Capacitor ... 136
7.5.1. General ... 136
7.5.2. Types of Solvents that Constitute the Double-Layer Interphase ... 137

7.5.3. Dielectric Constant in the Double-Layer Interphase . . . 138
7.5.4. Electrostatic Polarization of Water as Solvent in the Double Layer . . . 139
7.5.5. Molecular-Level Treatments of Solvent Dipole Orientation at Charged Interfaces . . . 141
7.5.5.1. Two-State Dipole Orientation Treatments . . . 141
7.5.5.2. Cluster Models for Water Adsorption and Orientation . . . 143
7.5.6. H-Bonded Lattice Models . . . 148
7.5.7. Spontaneous Orientation of Water at Electrode Surfaces Due to Chemisorption . . . 149
7.5.8. Solvent Adsorption Capacitance at Solid Metals . . . 151
7.5.9. Recent Modeling Calculations . . . 152
7.6. The Metal Electron Contribution to Double-Layer Capacitance . . . 156
7.6.1. Origin of the Metal Contribution . . . 156
7.6.2. Profile of Electron Density at Electrode Surfaces . . . 157
7.7. The Potential Profile across the Diffuse Layer . . . 160
7.8. The Double Layer in Pores of a Porous Capacitor Electrode . . . 161
References . . . 165
General Reading References . . . 168

Chapter 8 Behavior of the Double Layer in Nonaqueous Electrolytes and Nonaqueous Electrolyte Capacitors
8.1. Introduction . . . 169
8.2. Fundamental Aspects of Double-Layer Capacitance Behavior in Nonaqueous Solvent Media . . . 170
8.3. Comparative Double-Layer Capacitance Behavior in Several Nonaqueous Solutions . . . 176
8.4. General Outlook . . . 180
References . . . 180

Chapter 9 The Double Layer and Surface Functionalities at Carbon
9.1. Introduction . . . 183
9.1.1. Historical . . . 183
9.1.2. Carbon Materials for Electrochemical Capacitors . . . 185

9.2. Surface Properties and Functionalities of Carbon Materials 186
9.3. Double-Layer Capacitance of Carbon Materials. 193
9.4. Oxidation of Carbon 196
9.5. Surface Specificity of Double-Layer Capacitance Behavior at Carbon and Metals 198
9.6. Double-Layer Capacitance at Edge and Basal Planes of Graphite 199
9.7. Materials Science Aspects of Carbon Materials for Conditioned Double-Layer Capacitors 203
9.7.1. Heat and Chemical Treatments of Carbon Materials for Capacitors 203
9.7.2. Research Requirements for Carbon Materials in Electrochemical Capacitors 208
9.7.3. Electron Spin Resonance Characterization of Free Radicals at Carbon Surfaces 209
9.8. Interaction of Oxygen with Carbon Surfaces 212
9.9. Electronic Work Function and Surface Potentials of Carbon Surfaces 213
9.10. Intercalation Effects 217
References 219
General Reading References 220

Chapter 10 Electrochemical Capacitors Based on Pseudocapacitance
10.1. Origins of Pseudocapacitance 221
10.2. Theoretical Treatments of Pseudocapacitance (C_ϕ) . . 224
10.2.1. Types of Treatment 224
10.2.2. Electrosorption Isotherm Treatment of Pseudocapacitance: A Thermodynamic Approach 224
10.3. Kinetic Theory of Pseudocapacitance 236
10.3.1. Electrode Kinetics under Linearly Time-Variant Potential 236
10.3.2. Evaluation of Characteristic Peak Current and Peak Potential Quantities 239
10.3.3. Transition between Reversibility and Irreversibility 241
10.3.4. Relation to Behavior under dc Charge and Discharge Conditions 243
10.4. Potential Ranges of Significant Pseudocapacitances 246

10.5. Origin of Redox and Intercalation Pseudocapacitances 248
10.6. Pseudocapacitance Associated with Specific Adsorption of Anions and the Phenomenon of Partial Charge Transfer 253
10.7. Pseudocapacitance Behavior at High-Area Carbon Materials 255
10.8. Procedures for Distinguishing Pseudocapacitance (C_ϕ) from Double-Layer Capacitance (C_{dl}) 255
References 256
General Reading References 257

Chapter 11 The Electrochemical Behavior of Ruthenium Oxide (RuO_2) as a Material for Electrochemical Capacitors
11.1. Historical Aspects 259
11.2. Introduction 264
11.3. Formation of RuO_2 Films that Have Capacitative Properties 265
11.4. The Transition from Monolayer to Multilayer Electrochemical Formation of RuO_2 267
11.5. States and Chemical Constitution of Electrochemically and Thermochemically Formed RuO_2 for Capacitors 270
11.6. Mechanism of Charging and Discharging RuO_2 276
11.7. Oxidation States Involved in Voltammetry of RuO_2 and IrO_2 Electrodes 277
11.7.1. Oxidation States and Redox Mechanisms . . 277
11.7.2. Charging in Inner and Outer Surface Regions of RuO_2 Films 279
11.8. Conclusions on Mechanisms of Charging RuO_2 Capacitor Materials 282
11.9. Weight Changes on Charge and Discharge 284
11.10. dc and ac Response Behavior of RuO_2 Electrochemical Capacitor Electrodes 285
11.11. Other Oxide Films Exhibiting Redox Pseudocapacitance Behavior 286
11.12. Surface Analysis and Structure of RuO_2–TiO_2 Films 290
11.13. Impedance Behavior of RuO_2–TiO_2 Composite Electrodes 292
11.14. Use and Behavior of IrO_2 293

11.15. Comparative Oxide Film Behavior at Transition Metal Electrodes . . . 293
References . . . 295
General Reading References . . . 297

Chapter 12 Capacitance Behavior of Films of Conducting, Electrochemically Reactive Polymers
12.1. Introduction and General Electrochemical Behavior 299
12.2. Chemistry of the Polymerization Processes . . . 304
12.3. General Behavior in Relation to Pseudocapacitance . . . 312
12.4. Forms of Cyclic Voltammograms for Conducting Polymers . . . 314
12.5. Classification of Capacitor Systems Based on Conducting Polymer Active Materials . . . 320
12.6. Complementary Studies Using Other Procedures . . . 322
12.7. Ellipsometric Studies of Conducting Polymer Film Growth and Redox Pseudocapacitative Behavior . . . 327
12.8. Other Developments on Conducting Polymer Capacitors . . . 331
References . . . 332
General Reading References and Tabulations . . . 334

Chapter 13 The Electrolyte Factor in Supercapacitor Design and Performance: Conductivity, Ion Pairing and Solvation
13.1. Introduction . . . 335
13.2. Factors Determining the Conductance of Electrolyte Solutions . . . 337
13.3. Electrolyte Conductance and Dissociation . . . 338
13.4. Mobility of the Free (Dissociated) Ions . . . 343
13.5. Role of the Dielectric Constant and Donicity of the Solvent in Dissociation and Ion Pairing . . . 344
13.6. Favored Electrolyte–Solvent Systems . . . 345
13.6.1. Aqueous Media . . . 345
13.6.2. Nonaqueous Media . . . 347
13.6.3. Molten Electrolytes . . . 350
13.7. Properties of Solvents and Solutions for Nonaqueous Electrochemical Capacitor Electrolytes . . . 351
13.8. Relation of Electrolyte Conductivity to Electrochemically Available Surface Area and Power Performance of Porous Electrode Supercapacitors . . . 360

13.9. Separation of Cations and Anions on Charge and Its Effect on the Electrolyte's Local Conductivity..... 361
13.10. The Ion Solvation Factor..................... 362
13.11. Compilations of Solution Properties............. 365
13.12. Appendix: Selection of Experimental Data on Properties of Electrolyte Solutions in Nonaqueous Solvents and Their Mixtures.................. 366
13.12.1. Summary Tables..................... 366
13.12.2. Some Graphically Represented Data from the Literature....................... 366
13.12.3. Selected Tabulations.................. 366
13.12.4. Conductivities...................... 373
References............................... 374
General Reading References.................. 375

Chapter 14 Electrochemical Behavior at Porous Electrodes; Applications to Capacitors
14.1. Introduction............................... 377
14.2. Charging and Frequency Response of RC Networks 380
14.3. General Theory of Electrochemical Behavior of Porous Electrodes.......................... 383
14.3.1. System Requirements.................. 383
14.3.2. The de Levie Model and its Treatment..... 383
14.3.3. Configuration of Double Layers in Porous Electrodes........................... 403
14.4. Porous Electrode Interfaces as Fractal Surfaces..... 405
14.5. Atom Densities in Surfaces and Bulk of Fine Particles................................. 406
14.6. Pore Size and Pore-Size Distribution............. 408
14.7. Real Area and Double-Layer Capacitance......... 411
14.8. Electro-osmotic Effects in Porous Electrodes....... 415
References............................... 416

Chapter 15 Energy Density and Power Density of Electrical Energy Storage Devices
15.1. Ragone Plots of Power Density vs. Energy Density.. 417
15.2. Energy Density and Power Density, and Their Relationship................................ 421
15.2.1. General Considerations................ 421
15.2.2. Power Density...................... 425
15.2.3. Relation to Energy Density............. 427
15.2.4. Power and Energy Density Relationships for Capacitors........................... 433

15.2.5. Power Density Rating of a Capacitor....... 436
15.3. Power Limitation Due to Concentration Polarization 440
15.4. Relation between C-Rate Specification and Power Density.................................. 443
15.4.1. Formal Definition..................... 443
15.4.2. Significance of C-Rate in Battery and Capacitor Discharge.................... 444
15.5. Optimization of Energy Density and Power Density 448
15.5.1. Capacitor–Battery Hybrid Systems....... 448
15.5.2. Condition for Maximum Power Delivery .. 452
15.5.3. Test Modes.......................... 456
15.5.4. Constant Power Discharge Regime for a Capacitor............................ 459
15.5.5. Effects of Temperature................. 462
15.6. The Entropy Component of the Energy Held by a Charged Capacitor.......................... 463
15.7. Energy Density of Electrolytic Capacitors 464
15.8. Some Application Aspects of Power-Density Factors 468
15.9. Energy Storage by Flywheel Systems............ 474
References 475

Chapter 16 AC Impedance Behavior of Electrochemical Capacitors and Other Electrochemical Systems
16.1. Introduction 479
16.2. Elementary Introductory Principles Concerning Impedance Behavior 486
16.2.1. Alternating Current and Voltage Relationships 486
16.2.2. Root-mean-square and Average Currents in ac Studies 489
16.3. Origin of the Semicircular Form of Complex-Plane Plots for Z'' vs. Z' over a Range of Frequencies 491
16.3.1. Impedance Relationships as a Function of Frequency 491
16.3.2. Time Constant and Characteristic Frequency ω_r 496
16.4. Significance of RC Time Constants 497
16.4.1. Transient Currents and Voltages 497
16.4.2. Formal Significance of the RC Product as a Time Constant....................... 501
16.5. Measurement Techniques 502

16.5.1. AC Bridges 502
16.5.2. Lissajous Figures 503
16.5.3. Phase-Sensitive Detection Using Lock-in Amplifiers 504
16.5.4. Digital Frequency-Response Analyzers (Solartron and Other Instruments) 505
16.6. Kinetic and Mechanistic Approach to Interpretation of Impedance Behavior of Electrochemical Systems 506
16.6.1. Procedures and Role of Diffusion Control . . . 506
16.6.2. Principles of the Kinetic Analysis Method . . 509
16.6.3. Example of the Kinetic Analysis of ac Behavior of the Cathodic H_2 Evolution Reaction 510
16.6.4. Relation to Linear-Sweep Modulation and Cyclic Voltammetry 513
16.6.4.1. Methodology 513
16.6.4.2. Response-Current Behavior 513
16.6.4.3. Relation between Response Currents in Cyclic Voltammetry and Alternating Voltage Modulation 515
16.6.5. Impedance of a Pseudocapacitance 518
References 524

Chapter 17 Treatments of Impedance Behavior of Various Circuits and Modeling of Double-Layer Capacitor Frequency Response
17.1. Introduction and Types of Equivalent Circuits 525
17.2. Equivalent Series Resistance 528
17.2.1. Significance of esr 528
17.2.2. Impedance Limits for Some Commercial Capacitors Due to esr 530
17.3. Impedance Behavior of Selected Equivalent Circuit Models 532
17.4. Discharge of a Capacitor with esr into a Load Resistance, R_L 538
17.5. Simulation of Porous Electrode Frequency Response by Multielement RC Equivalent Circuits 547
17.6. Impedance Behavior of a Redox Pseudocapacitance . . 549
17.7. Electrochemistry at Porous Electrodes 555
References 556

Chapter 18 Self-Discharge of Electrochemical Capacitors in Relation to that at Batteries
18.1. Introduction 557
18.2. Practical Phenomenology of Self-Discharge 557
18.3. Self-Discharge Mechanisms 559
18.4. Methodologies for Self-Discharge Measurements 561
18.5. Self-Discharge by Activation-Controlled Faradaic Processes 562
18.6. Slope Parameters for Decline of Potential on Self-Discharge 567
18.7. Comparison with a Regular Capacitor Discharging through an Ohmic Leakage Resistance 568
18.8. Self-Discharge under Diffusion Control 569
18.9. Charging of a Nonideally Polarizable Electrode 573
18.10. Self-Discharge of Double-Layer-Type Supercapacitor Devices 574
18.11. Time-Dependent Redistribution of Charge in Nonuniformly Charged Porous Electrodes 575
18.12. Temperature Effects on Self-Discharge 578
18.13. Self-Discharge of a Pseudocapacitance 579
18.14. Examples of Experimental Measurements on Self-Discharge of Carbon Capacitors and Carbon Fiber Electrodes 582
18.14.1. Introduction 582
18.14.2. Potential Decay (Self-Discharge) and Recovery in Terms of a Faradaic Process 583
18.14.3. Self-Discharge Behavior of a Commercial Capacitor 584
18.15. Self-Discharge and Potential Recovery Behavior at an RuO_2 Electrode 586
18.15.1. Background 586
18.15.2. Potential Decay (Self-Discharge) and Recovery in Relation to Charge and Discharge Curves 587
18.15.3. Model for Potential Recovery 591
18.15.4. Quasi-Reversible Potentials of RuO_2 after Self-Discharge 592
18.16. Self-Discharge in a Stack 595
References 595

Chapter 19 Practical Aspects of Preparation and Evaluation of Electrochemical Capacitors
19.1. Introduction 597
19.2. Preparation of Electrodes for Small Aqueous Carbon-Based Capacitors for Testing Materials..... 598
19.3. Preparation of RuO_x Capacitor Electrodes 599
19.4. Preparation of RuO_x Capacitors with a Polymer Electrolyte Membrane (U.S. Patent 5,136,477) 600
19.5. Assembly of Capacitors........................ 600
19.6. Experimental Evaluation of Electrochemical Capacitors 602
19.6.1. Cyclic Voltammetry.................... 602
19.6.2. Impedance Measurements 602
19.6.3. Constant Current Charge or Discharge 603
19.6.4. Constant Potential Charge or Discharge 605
19.6.5. Constant Power Charge or Discharge 605
19.6.6. Leakage Current and Self-Discharge Behavior 605
19.7. Other Test Procedures 606
References 606

Chapter 20 Technology Development
20.1. Introduction 609
20.2. Development of the Technology of Electrochemical Capacitors 610
20.2.1. Classes of Capacitors 610
20.3. Summaries of Device Developments and Technology Advances 612
20.4. Materials Requirements........................ 613
20.4.1. Electrodes 613
20.4.2. Carbon Electrode Materials 615
20.4.3. Activation Procedures for Carbon Particles and Fibers.................. 615
20.4.4. Oxide, Redox-Pseudocapacitance Systems 618
20.4.5. Conducting-Polymer Electrodes 618
20.4.6. Electrolyte Systems 618
20.4.7. Practical Design Aspects 620
20.4.8. Capacitor Stacking 620
20.4.9. Bipolar Electrode Arrangements 622
20.4.10. Current Distribution in Capacitor Devices 623
20.4.11. Scale-up Factors 625
20.5. State of the Art............................ 627

20.5.1. Electrode Development 627
20.5.2. Ruthenium Oxide Materials 634
20.5.3. Other Embodiments 635
20.6. Self-Discharge: Phenomenological Aspects 641
20.7. Thermal Management 643
20.8. Other Variables that Affect Capacitor Performance 644
20.8.1. Temperature Dependence of Capacitance and Capacitor Performance 644
20.8.2. Constant Current versus Constant Potential Charging Modes 648
20.8.3. Rate Effects on Charge or Discharge 649
20.9. Safety and Health Hazards in the Use of Electrochemical Capacitors 649
20.10. Recent Advances in the Use of Materials 651
20.11. Usage Basis 655
20.12. Commercial Development and Testing 658
20.13. Capacitor–Battery Hybrid Application for Electric Vehicle Drive Systems 663
20.14. Market Aspects 666
20.14.1. Electrochemical Capacitors in the Capacitor Market 666
20.14.2. Market Status and Future Opportunities .. 667
20.15. Technology Summary Based on Patent Literature .. 667
20.16. Energy Storage by High-Voltage Electrostatic Capacitors 668
20.17. Concluding Summary 670
20.18. Appendix on Information Sources 671
References 673
General Reading References 674

Chapter 21 Patent Survey 675

Index 685

Electrochemical Supercapacitors

Scientific Fundamentals and Technological Applications