

Contents

Preface *xi*

1 Introduction *1*

- 1.1 Brief History of Electrochemical Cells *2*
- 1.2 Configuration of Electrochemical Cells *3*
- 1.3 Half-Reactions in Electrochemical Cells *4*
- 1.4 Faradaic and Non-Faradaic Reactions *5*
- 1.5 Nernst Equation *6*
- 1.6 Overpotential and Reaction Rate *7*
- 1.7 Several Important Features of Electrochemical Cells *7*
- References *8*
- Problems *8*

2 Thermodynamics of Electrochemical Cells *9*

- 2.1 Open Electrochemical Cell Systems *9*
 - 2.1.1 Nernst Potential E_n of Galvanic Cells *10*
 - 2.1.2 Thermoneutral Potential E_{tn} of Electrolytic Cells *13*
 - 2.1.3 Thermodynamic Efficiency of Electrochemical Cells *15*
- 2.2 Closed Electrochemical Cell Systems *16*
 - 2.2.1 E_n of Batteries *16*
 - 2.2.2 Theoretical Energy Density of Battery Cells *17*
 - 2.2.3 Maximum Theoretical Charge Capacity of a Battery Cell *17*
 - 2.2.4 Round-Trip Efficiency of Battery Cell *18*
- 2.3 Temperature Dependence of E_n and E_{tn} *18*
- 2.4 Pressure Dependence of E_n and E_{tn} *20*
- 2.5 Thermal and Chemical Expansion Coefficients *22*
- 2.6 Heat Production and Consumption in Electrochemical Cells *23*
- 2.7 Gibbs Phase Rule in Electrochemical Cells *25*
- References *27*
- Problems *28*

3	Kinetics of Electrochemical Cells	29
3.1	Bulk Ionic Transport in Solid Inorganic Electrolytes (SIEs)	29
3.1.1	Ionic Conductivity	30
3.1.2	Extrinsic Ionic Conductors	31
3.1.3	Intrinsic Ionic Conductors	32
3.1.4	Random-Walk Theory	32
3.2	Ionic Transport in Solid Amorphous Electrolytes	34
3.3	Ionic Transport in Aqueous Solution Electrolytes	35
3.3.1	Basic Principles	35
3.3.2	Ideality versus Non-ideality	38
3.3.3	Walden's Law	40
3.4	Comparison of Aqueous and Non-Aqueous Electrolytes	41
3.5	Kinetics of Electrode Reactions	41
3.5.1	Generic Rate of Electrode Kinetics	41
3.5.2	Potential-Dependent Rate of Electrode Kinetics	42
3.5.2.1	Standard Rate Constant k^0	42
3.5.2.2	Exchange Current Density i_0	43
3.5.2.3	Butler-Volmer Formulation	43
3.5.2.4	Mass Transfer Involved Activation Polarization	44
	References	45
	Problems	45
4	Fuel Cells and Electrolytic Cells	47
4.1	Fuel Cells/Electrolytic Cells Basics	47
4.2	Voltage Losses in FCs and ECs	49
4.2.1	Ohmic Voltage Loss	49
4.2.2	Activation Polarization	50
4.2.3	Concentration Polarization	52
4.2.3.1	Air-Electrode	53
4.2.3.2	Fuel-Electrode	56
4.2.3.3	Effect of Pressure	58
4.2.3.4	Coupled Activation and Concentration Polarizations	58
4.3	Efficiencies of Fuel Cells and Electrolytic Cells	59
4.3.1	Efficiency of Fuel Cells	59
4.3.2	Efficiency of Electrolytic Cells	61
4.4	Fuel Cells with Acidic Electrolytes	61
4.4.1	PAFC	61
4.4.1.1	Electrode Reactions	62
4.4.1.2	Cell Components	62
4.4.2	PEMFC	62
4.4.2.1	Electrode Reactions	62
4.4.2.2	Cell Components	62
4.4.2.3	Water Management	63
4.4.3	Solid Acid Fuel Cells	64
4.4.3.1	Electrode Reactions	64

- 4.4.3.2 Cell Components 65
- 4.5 Fuel Cells with Alkaline Electrolytes 65
 - 4.5.1 Liquid Alkaline FC 65
 - 4.5.1.1 Electrode Reactions 65
 - 4.5.1.2 Cell Components 65
 - 4.5.2 Anion-Exchange Membrane (AEM) FC 66
- 4.6 Fuel Cells with Molten Carbonate Electrolytes 66
 - 4.6.1 Electrode Reactions 67
 - 4.6.2 Components 67
 - 4.6.2.1 Electrolyte 67
 - 4.6.2.2 Electrolyte Matrix 67
 - 4.6.2.3 Cathode 68
 - 4.6.2.4 Fuel-Electrode (Anode) 69
 - 4.6.2.5 Interconnect 69
 - 4.6.2.6 Impurity Effect 69
- 4.7 Fuel Cells with Solid Oxide Electrolytes 69
 - 4.7.1 Electrode Reactions 70
 - 4.7.2 Components 70
 - 4.7.2.1 Oxide-Ion-Conducting Electrolytes 71
 - 4.7.2.2 Proton-Ion-Conducting Electrolytes 74
 - 4.7.2.3 Air-Electrodes 75
 - 4.7.2.4 Fuel-Electrodes 77
 - 4.7.2.5 Interconnects 78
- 4.8 Electrolytic Cells 80
 - 4.8.1 Co-Electrolysis of CO_2 and H_2O to Syngas 80
 - 4.8.2 Electrochemical CO_2 Reduction Reaction (CO_2RR) to Liquid Chemicals 81
 - 4.8.2.1 CO_2 to Methanol Conversion 83
 - 4.8.2.2 CO_2 to Formic Acid Conversion 83
 - 4.8.2.3 CO_2 to CO Conversion 84
 - 4.8.2.4 CO_2 to Methane Conversion 84
 - 4.8.2.5 CO_2 to Ethanol Conversion 85
 - 4.8.2.6 CO_2 to Ethylene Conversion 85
 - References 86
 - Problems 87
- 5 Batteries 89**
 - 5.1 Battery Basics 89
 - 5.1.1 Discharge Curve Shape and Gibbs Phase Rule 89
 - 5.1.2 Maximum Voltage and Energy Density of a Battery in General 91
 - 5.1.3 Maximum Voltage and Energy Density of a Binary Conversion-Type Battery 91
 - 5.1.4 Maximum Voltage and Energy Density of a Ternary Conversion-Type Battery 93
 - 5.1.5 C-rate 94

- 5.1.6 Electrochemical Stability Window of Electrolytes 95
- 5.2 Rechargeable Batteries with Aqueous Electrolytes 96
 - 5.2.1 Aqueous Batteries with Acidic Electrolytes 96
 - 5.2.1.1 Lead Acid Battery (LAB) 96
 - 5.2.1.2 All Vanadium Redox Flow Battery 98
 - 5.2.2 Batteries with Alkaline Electrolytes and Ni-Based Cathode 99
 - 5.2.2.1 Ni Cathode Chemistry 100
 - 5.2.2.2 “Memory” Effect of Ni-Cathode 101
 - 5.2.2.3 Ni–Cd Battery 101
 - 5.2.2.4 Ni–Zn Battery 102
 - 5.2.2.5 Ni–Fe Battery 103
 - 5.2.2.6 Ni-Metal Hydride (MH) Battery 103
 - 5.2.2.7 Alkaline Metal–Air Batteries 104
 - 5.2.2.8 Alkaline Redox Flow Batteries 105
 - 5.2.3 Batteries with Neutral Aqueous Electrolytes 106
- 5.3 Rechargeable Batteries with Organic Electrolytes 107
 - 5.3.1 Organic Electrolytes 108
 - 5.3.2 The “Rocking-Chair” Battery Concept 109
 - 5.3.3 Intercalation Chemistry 109
 - 5.3.3.1 Intercalation/Insertion Reaction 110
 - 5.3.3.2 What Determines the Potential of a Redox Couple? 111
 - 5.3.3.3 Terminology for Describing Structures of Intercalatable/Insertable Compounds 111
 - 5.3.4 Intercalatable/Insertable Electrodes 112
 - 5.3.4.1 Cathodes 112
 - 5.3.4.2 Anodes 113
 - 5.3.5 Conversion Electrodes 114
 - 5.3.5.1 Cathodes 115
 - 5.3.5.2 Anodes 115
 - 5.3.5.3 Beyond Li-ion Chemistry 116
- 5.4 Rechargeable Batteries with Solid Electrolytes 116
 - 5.4.1 Batteries with Oxide-Based Li-ion Conductors 117
 - 5.4.2 Batteries with Oxide-Based Na-Ion Conductors 118
 - 5.4.3 Battery with Oxide-Based Oxide-Ion Conductor 120
 - 5.4.3.1 Configuration and Working Principle 120
 - 5.4.3.2 Chemistry 121
 - 5.4.3.3 Performance Metrics of SOMARBs 122
 - 5.4.3.4 Kinetic Considerations of SOMARBs 123
- 5.5 Primary Batteries 124
 - 5.5.1 Batteries with Aqueous Alkaline Electrolytes 124
 - 5.5.1.1 Zn–MnO₂ 124
 - 5.5.1.2 Zn–Air 125
 - 5.5.2 Batteries with Organic Electrolytes and Li-Metal Anode 126
 - 5.5.2.1 Li–MnO₂ Battery 126
 - 5.5.2.2 Li–FeS₂ Battery 126

5.5.2.3	Li-CF _x Battery	127
5.5.2.4	Li-SO ₂ Battery	128
5.5.2.5	Li-SOCl ₂	129
5.5.2.6	Li-AgV ₂ O ₅	129
	References	129
	Problems	130
6	Capacitors	131
6.1	Capacitor Basics	131
6.1.1	Capacitance	131
6.1.2	Dielectrics	132
6.1.3	Capacitors in Electrical Circuits	134
6.1.4	Capacitance from CV and GCD	135
6.1.5	Capacitors for Electrical Energy Storage	136
6.2	Parallel-Plate Capacitors (PPCs)	137
6.3	Electrochemical Double-layer Capacitors (EDLCs)	139
6.4	Electrochemical Pseudocapacitors (ECPCs)	140
6.4.1	A Brief History of ECPCs	141
6.4.2	ECPC Materials	141
6.4.3	Types of ECPCs	141
6.4.4	Electrochemical Signatures of ECPCs	142
	References	143
	Problems	143
7	Basic Electrochemical Methods	145
7.1	Controlled Potential Methods	145
7.1.1	Constant Potential	146
7.1.2	Potential Sweep	147
7.1.2.1	Reversible Systems	148
7.1.2.2	Totally Irreversible Systems	149
7.1.2.3	Quasi-Reversible Systems	150
7.1.2.4	Cyclic Voltammetry	150
7.2	Controlled Current Methods	150
7.2.1	Constant Current	151
7.2.1.1	Reversible Electrode Reactions with Multi-electron Transfer	152
7.2.1.2	Totally Irreversible Electrode Process	152
7.2.1.3	Quasi-reversible Electrode Process	153
7.2.2	Coulometric Titration	153
7.3	Current Transient Method	154
7.3.1	Galvanic Current Interruption	154
7.3.2	Galvanic Intermittent Titration (GITT)	155
7.4	Electrochemical Impedance Spectroscopy	157
7.4.1	EIS Theory	158
7.4.2	Experimental Setup	161
7.5	Electrical Conductivity	162

x | Contents

7.6	Electrical Conductivity Relaxation (ECR) Method	164
7.7	Ion Transport Number of Electrolyte	166
7.7.1	The Hittorf Method	166
7.7.2	The Moving Boundary Method	167
7.7.3	Concentration Cell Method	169
7.7.4	Quartz Crystal Microbalance (QCM) Method	169
7.7.5	Evans–Vincent–Bruce Method	170
	References	172
	Problems	172

Appendix A Common Reference Electrodes and Potentials 175

A.1	Calomel Electrodes	175
A.2	Silver/Silver Chloride Electrodes	176
A.3	Converting Potentials Between Reference Electrodes	177

Appendix B Standard Electrode Potentials in Aqueous Solutions 179

Appendix C Current Functions for Charge Transfer Process 189

Appendix D Standard Gibbs Free Energy of Formation of Selected Compounds 193

Reference 241

Appendix E Standard Heat of Combustion of Common Fuels 243

Appendix F Commonly Used Physical Constants 255

Nomenclature 257

Index 269