## Contents

**Preface** ix  
**List of Symbols** xi  
**About the Companion Website** xv  

### 1. Introduction and Basic Principles 1  
*Charles W. Tobias*

1.1 Electrochemical Cells 1  
1.2 Characteristics of Electrochemical Reactions 2  
1.3 Importance of Electrochemical Systems 4  
1.4 Scientific Units, Constants, Conventions 5  
1.5 Faraday’s Law 6  
1.6 Faradaic Efficiency 8  
1.7 Current Density 9  
1.8 Potential and Ohm’s Law 9  
1.9 Electrochemical Systems: Example 10  
Closure 13  
Further Reading 13  
Problems 13  

### 2. Cell Potential and Thermodynamics 15  
*Wendell Mitchell Latimer*

2.1 Electrochemical Reactions 15  
2.2 Cell Potential 15  
2.3 Expression for Cell Potential 17  
2.4 Standard Potentials 18  
2.5 Effect of Temperature on Standard Potential 21  
2.6 Simplified Activity Correction 22  
2.7 Use of the Cell Potential 24  
2.8 Equilibrium Constants 25  
2.9 Pourbaix Diagrams 25  
2.10 Cells with a Liquid Junction 27  
2.11 Reference Electrodes 27  
2.12 Equilibrium at Electrode Interface 30  
2.13 Potential in Solution Due to Charge: Debye–Hückel Theory 31  
2.14 Activities and Activity Coefficients 33  
2.15 Estimation of Activity Coefficients 35  
Closure 36  
Further Reading 36  
Problems 36  

### 3. Electrochemical Kinetics 41  
*Alexander Naumovich Frumkin*

3.1 Double Layer 41  
3.2 Impact of Potential on Reaction Rate 42  
3.3 Use of the Butler–Volmer Kinetic Expression 46  
3.4 Reaction Fundamentals 49  
3.5 Simplified Forms of the Butler–Volmer Equation 50  
3.6 Direct Fitting of the Butler–Volmer Equation 52  
3.7 The Influence of Mass Transfer on the Reaction Rate 54  
3.8 Use of Kinetic Expressions in Full Cells 55  
3.9 Current Efficiency 58  
Closure 58  
Further Reading 59  
Problems 59  

### 4. Transport 63  
*Carl Wagner*

4.1 Fick’s Law 63  
4.2 Nernst–Planck Equation 63  
4.3 Conservation of Material 65  
4.4 Transference Numbers, Mobilities, and Migration 71
4.5 Convective Mass Transfer 75
4.6 Concentration Overpotential 79
4.7 Current Distribution 81
4.8 Membrane Transport 86
  Closure 87
  Further Reading 88
  Problems 88

5. Electrode Structures and Configurations 93

  John Newman

  5.1 Mathematical Description of Porous Electrodes 94
  5.2 Characterization of Porous Electrodes 96
  5.3 Impact of Porous Electrode on Transport 97
  5.4 Current Distributions in Porous Electrodes 98
  5.5 The Gas–Liquid Interface in Porous Electrodes 102
  5.6 Three-Phase Electrodes 103
  5.7 Electrodes with Flow 105
  Closure 108
  Further Reading 108
  Problems 108

6. Electroanalytical Techniques and Analysis of Electrochemical Systems 113

  Jaroslav Heyrovský

  6.1 Electrochemical Cells, Instrumentation, and Some Practical Issues 113
  6.2 Overview 115
  6.3 Step Change in Potential or Current for a Semi-Infinite Planar Electrode in a Stagnant Electrolyte 116
  6.4 Electrode Kinetics and Double-Layer Charging 118
  6.5 Cyclic Voltammetry 122
  6.6 Stripping Analyses 127
  6.7 Electrochemical Impedance 129
  6.8 Rotating Disk Electrodes 136
  6.9 IR Compensation 139
  6.10 Microelectrodes 141
  Closure 145
  Further Reading 145
  Problems 145

7. Battery Fundamentals 151

  John B. Goodenough

  7.1 Components of a Cell 151
  7.2 Classification of Batteries and Cell Chemistries 152
  7.3 Theoretical Capacity and State of Charge 156
  7.4 Cell Characteristics and Electrochemical Performance 158
  7.5 Ragone Plots 163
  7.6 Heat Generation 164
  7.7 Efficiency of Secondary Cells 166
  7.8 Charge Retention and Self-Discharge 167
  7.9 Capacity Fade in Secondary Cells 168
  Closure 169
  Further Reading 169
  Problems 169

8. Battery Applications: Cell and Battery Pack Design 175

  Esther Sans Takeuchi

  8.1 Introduction to Battery Design 175
  8.2 Battery Layout Using a Specific Cell Design 176
  8.3 Scaling of Cells to Adjust Capacity 178
  8.4 Electrode and Cell Design to Achieve Rate Capability 181
  8.5 Cell Construction 183
  8.6 Charging of Batteries 184
  8.7 Use of Resistance to Characterize Battery Performance 185
  8.8 Battery Management 186
  8.9 Thermal Management Systems 188
  8.10 Mechanical Considerations 190
  Closure 191
  Further Reading 191
  Problems 191


  Supramaniam Srinivasan

  9.1 Introduction 195
  9.2 Types of Fuel Cells 197
  9.3 Current–Voltage Characteristics and Polarizations 198
  9.4 Effect of Operating Conditions and Maximum Power 202
  9.5 Electrode Structure 205
  9.6 Proton-Exchange Membrane (PEM) Fuel Cells 206
  9.7 Solid Oxide Fuel Cells 211
  Closure 215
  Further Reading 215
  Problems 216