

# CONTENTS

## Preface

xi

## Abbreviations and Symbols

xiii

## 1 Fundamental Concepts

1

1.1 Why Electroanalysis?, 1

1.2 Faradaic Processes, 3

    1.2.1 Mass-Transport-Controlled Reactions, 4

        1.2.1.1 Potential-Step Experiment, 7

        1.2.1.2 Potential-Sweep Experiments, 9

    1.2.2 Reactions Controlled by the Rate of Electron Transfer, 12

        1.2.2.1 Activated Complex Theory, 16

1.3 Electrical Double Layer, 19

1.4 Electrocapillary Effect, 23

1.5 Supplementary Reading, 25

Problems, 27

References, 28

## 2 Study of Electrode Reactions and Interfacial Properties

29

2.1 Cyclic Voltammetry, 29

    2.1.1 Data Interpretation, 32

        2.1.1.1 Reversible Systems, 32

        2.1.1.2 Irreversible and Quasi-reversible Systems, 34

    2.1.2 Study of Reaction Mechanisms, 35

2.1.3 Study of Adsorption Processes, 37	
2.1.4 Quantitative Applications, 41	
<b>2.2 Spectroelectrochemistry, 42</b>	
2.2.1 Experimental Arrangement, 43	
2.2.2 Principles and Applications, 44	
2.2.3 Electrochemiluminescence, 47	
2.2.4 Optical Probing of Electrode–Solution Interfaces, 48	
<b>2.3 Scanning Probe Microscopy, 49</b>	
2.3.1 Scanning Tunneling Microscopy, 50	
2.3.2 Atomic Force Microscopy, 51	
2.3.3 Scanning Electrochemical Microscopy, 53	
<b>2.4 Electrochemical Quartz Crystal Microbalance, 57</b>	
<b>2.5 Impedance Spectroscopy, 58</b>	
Examples, 61	
Problems, 63	
References, 64	
<b>3 Controlled-Potential Techniques</b>	<b>67</b>
3.1 Chronoamperometry, 67	
3.2 Polarography, 69	
3.3 Pulse Voltammetry, 76	
3.3.1 Normal-Pulse Voltammetry, 76	
3.3.2 Differential-Pulse Voltammetry, 77	
3.3.3 Square-Wave Voltammetry, 80	
3.3.4 Staircase Voltammetry, 82	
3.4 AC Voltammetry, 84	
3.5 Stripping Analysis, 85	
3.5.1 Anodic Stripping Voltammetry, 86	
3.5.2 Potentiometric Stripping Analysis, 89	
3.5.3 Adsorptive Stripping Voltammetry and Potentiometry, 91	
3.5.4 Cathodic Stripping Voltammetry, 94	
3.5.5 Abrasive Stripping Voltammetry, 94	
3.5.6 Applications, 94	
3.6 Flow Analysis, 98	
3.6.1 Principles, 98	
3.6.2 Cell Design, 100	
3.6.3 Mass Transport and Current Response, 103	
3.6.4 Detection Modes, 105	
Examples, 108	
Problems, 111	
References, 112	
<b>4 Practical Considerations</b>	<b>115</b>
4.1 Electrochemical Cells, 115	
4.2 Solvents and Supporting Electrolytes, 117	

## CONTENTS

4.3 Oxygen Removal, 118	Electrode Immobilization, 118
4.4 Instrumentation, 119	Instrumentation, 119
4.5 Working Electrodes, 123	Working Electrodes, 123
4.5.1 Mercury Electrodes, 123	Mercury Electrodes, 123
4.5.2 Solid Electrodes, 127	Solid Electrodes, 127
4.5.2.1 Rotating Disk and Rotating Ring Disk Electrodes, 128	Rotating Disk and Rotating Ring Disk Electrodes, 128
4.5.2.2 Carbon Electrodes, 130	Carbon Electrodes, 130
4.5.2.2.1 Glassy Carbon Electrodes, 131	Glassy Carbon Electrodes, 131
4.5.2.2.2 Carbon Paste Electrodes, 131	Carbon Paste Electrodes, 131
4.5.2.2.3 Carbon Fiber Electrodes, 133	Carbon Fiber Electrodes, 133
4.5.2.2.4 Diamond Electrodes, 133	Diamond Electrodes, 133
4.5.2.3 Metal Electrodes, 134	Metal Electrodes, 134
4.5.3 Chemically Modified Electrodes, 136	Chemically Modified Electrodes, 136
4.5.3.1 Self-Assembled Monolayers, 136	Self-Assembled Monolayers, 136
4.5.3.2 Carbon-Nanotube-Modified Electrodes, 139	Carbon-Nanotube-Modified Electrodes, 139
4.5.3.3 Sol-gel Encapsulation of Reactive Species, 139	Sol-gel Encapsulation of Reactive Species, 139
4.5.3.4 Electrocatalytically Modified Electrodes, 140	Electrocatalytically Modified Electrodes, 140
4.5.3.5 Preconcentrating Electrodes, 141	Preconcentrating Electrodes, 141
4.5.3.6 Permselective Coatings, 143	Permselective Coatings, 143
4.5.3.7 Conducting Polymers, 146	Conducting Polymers, 146
4.5.4 Microelectrodes, 149	Microelectrodes, 149
4.5.4.1 Diffusion at Microelectrodes, 151	Diffusion at Microelectrodes, 151
4.5.4.2 Microelectrode Configurations, 152	Microelectrode Configurations, 152
4.5.4.3 Composite Electrodes, 154	Composite Electrodes, 154
Examples, 158	
Problems, 158	
References, 159	

**5 Potentiometry 165**

5.1 Principles of Potentiometric Measurements, 165	
5.2 Ion-Selective Electrodes, 173	
5.2.1 Glass Electrodes, 173	
5.2.1.1 pH Electrodes, 173	
5.2.1.2 Glass Electrodes for Other Cations, 177	
5.2.2 Liquid Membrane Electrodes, 177	
5.2.2.1 Ion Exchanger Electrodes, 179	
5.2.2.2 Neutral Carrier Electrodes, 182	
5.2.3 Solid-State Electrodes, 185	
5.2.4 Coated-Wire Electrodes and Solid-State Electrodes Without an Internal Filling Solution, 188	
5.3 On-line, On-site, and In Vivo Potentiometric Measurements, 190	
Examples, 194	
Problems, 196	
References, 197	

**6 Electrochemical Sensors**

201

- 6.1 Electrochemical Biosensors, 202
  - 6.1.1 Enzyme-Based Electrodes, 202
    - 6.1.1.1 Practical and Theoretical Considerations, 202
    - 6.1.1.2 Enzyme Electrodes of Analytical Significance, 208
      - 6.1.1.2.1 Glucose Sensors, 208
      - 6.1.1.2.2 Ethanol Electrodes, 212
      - 6.1.1.2.3 Urea Electrodes, 213
      - 6.1.1.2.4 Toxin (Enzyme Inhibition) Biosensors, 215
    - 6.1.1.3 Tissue and Bacteria Electrodes, 215
  - 6.1.2 Affinity Biosensors, 216
    - 6.1.2.1 Immunosensors, 216
    - 6.1.2.2 DNA Hybridization Biosensors, 218
      - 6.1.2.2.1 Background and Principles, 218
      - 6.1.2.2.2 Electrical Transduction of DNA Hybridization, 219
      - 6.1.2.2.3 Other Electrochemical DNA Biosensors, 221
    - 6.1.2.3 Receptor-Based Sensors, 222
    - 6.1.2.4 Electrochemical Sensors Based on Molecularly Imprinted Polymers, 224
  - 6.2 Gas Sensors, 224
    - 6.2.1 Carbon Dioxide Sensors, 225
    - 6.2.2 Oxygen Electrodes, 226
  - 6.3 Solid-State Devices, 227
    - 6.3.1 Ion-Selective Field Effect Transistors, 227
    - 6.3.2 Microfabrication of Solid-State Sensor Assemblies, 229
    - 6.3.3 Microfabrication Techniques, 229
    - 6.3.4 Micromachined Analytical Microsystems, 232
  - 6.4 Sensor Arrays, 234
    - Examples, 237
    - Problems, 238
    - References, 239

**Index**

245