

# Contents

## Part I Basic Electrochemistry

<b>I.1 The Electrical Double Layer and Its Structure</b> .....	3
Zbigniew Stojek	
I.1.1 Introduction .....	3
I.1.2 Double-Layer Models .....	5
I.1.3 Thickness of the Electric Double Layer .....	8
I.1.4 Recent Developments .....	8
References .....	8
<b>I.2 Thermodynamics of Electrochemical Reactions</b> .....	11
Fritz Scholz	
I.2.1 Introduction .....	11
I.2.2 The Standard Potential .....	12
I.2.3 The Formal Potential .....	19
I.2.4 Characteristic Potentials of Electroanalytical Techniques .....	22
I.2.5 Thermodynamics of the Transfer of Ions Between Two Phases .....	27
I.2.6 Thermodynamic Data Derived from Standard and Formal Potentials .....	30
References .....	31
<b>I.3 Kinetics of Electrochemical Reactions</b> .....	33
György Inzelt	
I.3.1 Introduction .....	33
I.3.2 Relationship Between the Current Density and Potential Under Steady-State Conditions .....	34
I.3.3 Current–Potential Transients .....	49
References .....	53

## Part II Electroanalytical Techniques

<b>II.1 Cyclic Voltammetry</b> .....	57
Frank Marken, Andreas Neudeck, and Alan M. Bond	
II.1.1 Introduction .....	57
II.1.2 Basic Principles .....	63
II.1.3 Effects Due to Capacitance and Resistance .....	71
II.1.4 Electrode Geometry, Size, and Convection Effects .....	74
II.1.5 Determination of Redox State and Number of Transferred Electrons .....	78
II.1.6 Heterogeneous Kinetics .....	81
II.1.7 Homogeneous Kinetics .....	87
II.1.8 Multi-phase Systems .....	98
References .....	102
<b>II.2 Pulse Voltammetry</b> .....	107
Zbigniew Stojek	
II.2.1 Introduction .....	107
II.2.2 Staircase Voltammetry .....	110
II.2.3 Normal Pulse Voltammetry .....	111
II.2.4 Reverse Pulse Voltammetry .....	115
II.2.5 Differential Pulse Voltammetry .....	117
References .....	119
<b>II.3 Square-Wave Voltammetry</b> .....	121
Milivoj Lovrić	
II.3.1 Introduction .....	121
II.3.2 Simple Reactions on Stationary Planar Electrodes .....	123
II.3.3 Simple Reactions on Stationary Spherical Electrodes and Microelectrodes .....	127
II.3.4 Reactions of Amalgam-Forming Metals on Thin Mercury Film Electrodes .....	128
II.3.5 Electrode Reactions Complicated by Adsorption of the Reactant and Product .....	129
II.3.6 Applications of Square-Wave Voltammetry .....	135
References .....	143
<b>II.4 Chronocoulometry</b> .....	147
György Inzelt	
II.4.1 Introduction .....	147
II.4.2 Fundamental Theoretical Considerations .....	148
II.4.3 Practical Problems .....	151
II.4.4 Double-Step Chronocoulometry .....	152

II.4.5	Effect of Heterogeneous Kinetics on Chronocoulometric Responses .....	155
	References .....	157
<b>II.5</b>	<b>Electrochemical Impedance Spectroscopy</b> .....	<b>159</b>
	Utz Retter and Heinz Lohse	
II.5.1	Introduction .....	159
II.5.2	Definitions, Basic Relations, the Kramers–Kronig Transforms .	159
II.5.3	Measuring Techniques .....	161
II.5.4	Representation of the Impedance Data .....	164
II.5.5	Equivalent Circuits .....	164
II.5.6	The Constant Phase Element .....	164
II.5.7	Complex Non-Linear Regression Least-Squares (CNRLS) for the Analysis of Impedance Data .....	165
II.5.8	Commercial Computer Programs for Modelling of Impedance Data .....	166
II.5.9	Charge Transfer at the Electrode – the Randles Model .....	166
II.5.10	Semi-infinite Hemispherical Diffusion for Faradaic Processes .	170
II.5.11	Diffusion of Particles in Finite-Length Regions – the Finite Warburg Impedance .....	171
II.5.12	Homogeneous or Heterogeneous Chemical Reaction as Rate-Determining Step .....	173
II.5.13	Porous Electrodes .....	173
II.5.14	Semiconductor Electrodes .....	173
II.5.15	Kinetics of Non-Faradaic Electrode Processes .....	174
II.5.16	References to Relevant Fields of Applications of EIS .....	176
	References .....	176
<b>II.6</b>	<b>UV/Vis/NIR Spectroelectrochemistry</b> .....	<b>179</b>
	Andreas Neudeck, Frank Marken, and Richard G. Compton	
II.6.1	Introduction – Why Couple Techniques? .....	179
II.6.2	Flowing Versus Stagnant Systems – Achieving Spatial, Temporal, and Mechanistic Resolution .....	182
II.6.3	UV/Vis/NIR Spectroelectrochemical Techniques .....	187
	References .....	198
<b>II.7</b>	<b>Stripping Voltammetry</b> .....	<b>201</b>
	Milivoj Lovrić	
II.7.1	Introduction .....	201
II.7.2	Overview of Preconcentration Methods .....	202
II.7.3	Stripping Voltammetry at Two Immiscible Liquid Electrolyte Solutions .....	216
II.7.4	General Features of Stripping Voltammetry .....	216
	References .....	218

<b>II.8</b>	<b>Electrochemical Studies of Solid Compounds and Materials</b> . . . . .	223
	Dirk A. Fiedler and Fritz Scholz	
II.8.1	Introduction . . . . .	223
II.8.2	Experimental . . . . .	223
II.8.3	Electrochemical Methods . . . . .	228
II.8.4	Combined Methods . . . . .	232
	References . . . . .	233
<b>II.9</b>	<b>Potentiometry</b> . . . . .	237
	Heike Kahlert	
II.9.1	Introduction . . . . .	237
II.9.2	Cell Voltage . . . . .	237
II.9.3	Indicator Electrodes and Their Potentials . . . . .	238
II.9.4	Interferences and Detection Limits in Potentiometric Measurements . . . . .	251
	References . . . . .	255
<b>II.10</b>	<b>Electrochemical Quartz Crystal Nanobalance</b> . . . . .	257
	György Inzelt	
II.10.1	Introduction . . . . .	257
II.10.2	Theory and Basic Principles of Operation . . . . .	258
II.10.3	Applications of EQCN: Selected Examples . . . . .	262
	References . . . . .	269
 <b>Part III Electrodes and Electrolytes</b>		
<b>III.1</b>	<b>Working Electrodes</b> . . . . .	273
	Šebojka Komorsky-Lovrić	
III.1.1	Introduction . . . . .	273
III.1.2	Electrode Materials . . . . .	275
III.1.3	Electrode Geometry . . . . .	280
III.1.4	Hydrodynamic Conditions . . . . .	282
III.1.5	Chemically Modified Electrodes . . . . .	286
	References . . . . .	288
<b>III.2</b>	<b>Reference Electrodes</b> . . . . .	291
	Heike Kahlert	
III.2.1	Introduction . . . . .	291
III.2.2	The Standard Hydrogen Electrode . . . . .	293
III.2.3	Electrodes of the Second Kind as Reference Electrodes . . . . .	294
III.2.4	pH-Based Reference Electrodes . . . . .	299
III.2.5	Inner Potential Standards . . . . .	300
III.2.6	Solid-State Reference Electrodes . . . . .	301
III.2.7	Pseudo Reference Electrodes . . . . .	302

III.2.8	Practical Problems .....	303
	References .....	308
<b>III.3</b>	<b>Electrolytes .....</b>	<b>309</b>
	Šebojka Komorsky-Lovrić	
III.3.1	Introduction .....	309
III.3.2	Ionic Transport .....	310
III.3.3	Ionic Solutions .....	317
	References .....	330
<b>III.4</b>	<b>Experimental Setup .....</b>	<b>331</b>
	Zbigniew Stojek	
III.4.1	Introduction .....	331
III.4.2	The Working Electrode .....	331
III.4.3	The Reference Electrode .....	332
III.4.4	The Counter Electrode .....	333
III.4.5	Instrumental Parameters and Wiring .....	333
III.4.6	Nonaqueous Media .....	334
III.4.7	Elimination of Electrical Noise .....	334
	References .....	335
 <b>Part IV Publications in Electrochemistry</b>		
<b>IV.1</b>	<b>Seminal Publications in Electrochemistry and Electroanalysis .....</b>	<b>339</b>
	Fritz Scholz, György Inzelt, and Zbigniew Stojek	
<b>IV.2</b>	<b>Books on Fundamental Electrochemistry and Electroanalytical Techniques .....</b>	<b>343</b>
	Fritz Scholz	
IV.2.1	Electrochemical Dictionaries, Encyclopedias, and Reference Books .....	343
IV.2.2	Books on General Electrochemistry .....	343
IV.2.3	Monographs on Special Techniques and Subjects .....	344
IV.2.4	Series Editions of Advances in Electrochemistry .....	345
IV.2.5	Electrochemical Journals .....	345
IV.2.6	Journals that Regularly Publish Papers on Electrochemistry and/or Electroanalysis .....	345
<b>Index</b>	.....	<b>347</b>



<http://www.springer.com/978-3-642-02914-1>

Electroanalytical Methods  
Guide to Experiments and Applications  
Scholz, F. (Ed.)  
2010, XXVII, 359 p., Hardcover  
ISBN: 978-3-642-02914-1