

Contents

Preface — V

Part I: Basic concepts

1	Basic concepts — 3
1.1	Structure of interfaces — 3
1.1.1	Electrical double layer at interfaces: metal/electrolyte, semiconductor/electrolyte — 7
1.1.2	Electrochemical potential – potentials at interfaces: internal, surface, external potential — 15
1.1.2.1	Metal–solution interface at equilibrium: Nernst equilibrium potential — 18
1.1.2.2	Electron work function — 20
1.1.3	Charge transfer processes across the metal/electrolyte interface — 21
1.1.3.1	Basic concepts of nonequilibrium thermodynamics — 21
1.1.3.2	“Reversible” electrode processes — 27
1.1.3.3	“Irreversible” electrode processes: basic concepts of electrochemical kinetics — 32
1.1.3.4	Briefly on Marcus, Hush, Levich, Dogonadze (MHL) theory of electrode processes — 38
	Bibliography — 40
2	Selected electrochemical methods applied in analytical chemistry and material science — 41
2.1	Transient methods — 41
2.1.1	Capacitive current — 42
2.1.2	Faradaic current — 44
2.2	Electrochemical impedance spectroscopy — 48
2.2.1	Data presentation — 51
2.3	Electrochemical quartz crystal microbalance method — 58
	Bibliography — 62

Part II: Electrochemistry in material science – selected topics

3	Corrosion — 65
3.1	General remarks — 65
3.2	Corrosion – what does it mean? Mechanism of corrosion — 65

3.3	Characterization of corrosion: corrosion potential, corrosion current — 71
3.3.1	Stability of materials: potential/pH (Pourbaix) diagrams – the thermodynamic aspect — 72
3.3.2	Stability of materials: current–potential (Evans) diagrams – the kinetic aspect — 77
3.4	Evaluation of corrosion rate from electrochemical measurements — 80
3.4.1	Linear scan voltammetry — 80
3.4.2	Electrochemical impedance spectroscopy in corrosion — 82
3.5	Localized corrosion: pits, crevices, intergranular corrosion – oxygen reduction as accompanying cathodic reaction — 84
3.6	Hydrogen evolution as accompanying reaction – role in corrosion: embrittlement and cracking — 85
3.7	Protection against corrosion — 87
3.7.1	Electroplating — 89
	Bibliography — 91
4	Electrocatalysis — 93
4.1	General remarks — 93
4.2	How to compare the activity of catalysts in electrochemical reactions? — 95
4.3	Electrocatalysts — 96
4.3.1	Metals, alloys, and oxides — 97
4.3.2	Carbon catalysts and supports — 99
4.4	Catalyst activity — 100
4.4.1	Electron work function effect — 101
4.4.2	Adsorption impact — 101
4.4.3	Size effect — 104
4.5	Electrocatalysts in hydrogen–oxygen fuel cells — 106
4.5.1	Oxygen reduction reaction — 106
4.5.2	Hydrogen evolution and oxidation reactions — 109
	Bibliography — 111
5	Electrodeposition — 113
5.1	General remarks — 113
5.2	Electrocrystallization: nucleation and growth — 114
5.2.1	Critical size of nuclei — 116
5.2.2	Instantaneous and progressive nucleation — 117
5.2.3	Analytical approach to experimental data — 119

5.3	Deposit morphology —	123
5.4	Practical aspects of electrodeposition —	124
5.5	Electrodeposition of binary alloys and semiconductor compounds —	127
	Bibliography —	130
6	Underpotential deposition (UPD) —	133
6.1	General remarks —	133
6.2	Experimental examples – UPD features —	134
6.3	Underpotential deposits – catalytic properties —	137
	Bibliography —	139
7	Electrochemical methods in the formation of nanostructures —	141
7.1	General remarks —	141
7.2	Template-assisted electrodeposition of nanostructures —	142
7.2.1	Active template-assisted electrodeposition —	142
7.2.2	Restrictive template-assisted deposition —	143
7.2.2.1	Porous anodic alumina (PAA) matrices —	144
7.2.2.2	Porous anodic titanium dioxide matrices —	145
7.2.3	Concluding remarks —	145
7.3	Applications of nanostructured materials —	145
7.3.1	Catalysis —	147
7.3.2	Batteries: supercapacitors —	147
7.3.3	Photoelectrochemical devices: solar cells —	148
7.3.4	Biological applications: nanozymes —	148
	Bibliography —	149
8	Electrochemistry in energy conversion and storage —	153
8.1	Batteries —	153
8.1.1	Electrochemical cell – fundamentals —	153
8.1.2	Characteristics of batteries —	157
8.1.3	Classification of batteries and examples —	161
8.1.3.1	Primary batteries —	161
8.1.3.2	Secondary batteries —	162
8.1.3.3	Lithium batteries —	164
8.1.3.4	Fuel cells —	166
8.2	Supercapacitors —	169
8.2.1	General remarks —	169
8.2.2	Capacitor versus electrochemical cell/battery —	169
8.2.3	Working characteristics of supercapacitors —	175
	Bibliography —	177

9 Interfacing applied electrochemistry and biology — 179

- 9.1 General remarks — 179
- 9.2 Bioelectrocatalysis — 180
- 9.3 Biosensors — 185
- 9.4 Biofuel cells — 189
 - 9.4.1 Design and enzymes used in biofuel cells — 191
 - 9.4.1.1 Biocatalysts and design of biocathodes — 192
 - 9.4.1.2 Biocatalysts and design of bioanodes — 193
 - 9.4.2 Energy and power of the biofuel cells — 194
 - Bibliography — 198

Part III: Photoelectrochemistry in materials science – selected topics

10 Semiconductors electrochemistry and photoelectrochemistry: fundamentals — 205

- 10.1 Basic characteristics of semiconductors — 205
 - 10.1.1 Semiconductor under illumination — 208
 - 10.1.2 Recombination — 211
 - 10.1.3 Carriers and electric field — 212
- 10.2 Semiconductor–electrolyte interface — 213
 - 10.2.1 Model of semiconductor–electrolyte interface — 214
 - 10.2.2 Space charge layer — 215
 - 10.2.3 Polarization of semiconductor–electrolyte interface — 218
- 10.3 Fundamentals of electrochemical reactions on the SC electrode — 219
- 10.4 Photoeffects at/in semiconductor electrode in electrolyte — 227
- 10.5 Influence of surface states — 231
- 10.6 Corrosion, photocorrosion, and stability — 234
 - Bibliography — 239

11 Solar energy conversion in photoelectrochemical cells — 241

- 11.1 General remarks — 241
- 11.2 Efficiency and key parameters — 242
- 11.3 Photoelectrochemical cells: classification – principle of operation — 244
 - 11.3.1 Liquid photovoltaic cells — 245
 - 11.3.2 Dye-sensitized solar cells — 247
 - 11.3.3 Quantum dot-sensitized solar cells — 249
 - 11.3.4 Photoelectrosynthetic cells — 250
 - Bibliography — 256

12	Semiconductor particles in photocatalysis — 259
12.1	General remarks — 259
12.2	Size effect and dimensionality — 259
12.3	Photocatalytic degradation of organic/inorganic pollutants — 263
	Bibliography — 267

List of abbreviations — 269

List of symbols — 271

Index — 277

Contents

Part I: Basic concepts