Contents

Preface xvii

	Symbols and Abbreviations xix
1	Introduction 1
1.1	General Considerations 1
1.1.1	The Transition from Electronic to Ionic Conduction 1
1.1.2	The Resistance of the Interface can be Infinite 2
1.1.3	Mass-Transport Limitation 2
1.1.4	The Capacitance at the Metal/Solution Interphase 4
1.2	Polarizable and Nonpolarizable Interfaces 4
1.2.1	Phenomenology 4
1.2.2	The Equivalent Circuit Representation 5
	Further Reading 7
2	The Potentials of Phases 9
2.1	The Driving Force 9
2.1.1	Definition of the Electrochemical Potential 9
2.1.2	Separability of the Chemical and the Electrical Terms 10
2.2	Two Cases of Special Interest 11
2.2.1	Equilibrium of a Species Between two Phases in Contact 11
2.2.2	Two Identical Phases not at Equilibrium 12
2.3	The Meaning of the Standard Hydrogen Electrode (SHE) Scale 13 Further Reading 15
3	Fundamental Measurements in Electrochemistry 17
3.1	Measurement of Current and Potential 17
3.1.1	The Cell Voltage is the Sum of Several Potential Differences 17
3.1.2	Use of a Nonpolarizable Counter Electrode 17
3.1.3	The Three-Electrode Setup 18
3.1.4	Residual jR _S Potential Drop in a Three-Electrode Cell 18
3.2	Cell Geometry and the Choice of the Reference Electrode 19
3.2.1	Types of Reference Electrodes 19
3.2.2	Use of an Auxiliary Reference Electrode for the Study of
	Fast Transients 20



3.2.3	Calculating the Uncompensated Solution Resistance for
	a few Simple Geometries 21
3.2.3.1	Planar Configuration 21
3.2.3.2	Cylindrical Configuration 21
3.2.3.3	Spherical Symmetry 22
3.2.4	Positioning the Reference Electrode 22
3.2.5	Edge Effects 24
	Further Reading 26
4	Electrode Kinetics: Some Basic Concepts 27
4.1	Relating Electrode Kinetics to Chemical Kinetics 27
4.1.1	The Relation of Current Density to Reaction Rate 27
4.1.2	The Relation of Potential to Energy of Activation 28
4.1.3	——————————————————————————————————————
4.1.3	Mass-Transport Limitation Versus Charge-Transfer Limitation 30
4.1.4	
	The Thickness of the Nernst Diffusion Layer 31
4.2 4.2.1	Methods of Measurement 33
	Potential Control Versus Current Control 33
4.2.2	The Need to Measure Fast Transients 35
4.2.3	Polarography and the Dropping Mercury Electrode (DME) 37
4.3	Rotating Electrodes 40
4.3.1	The Rotating Disk Electrode (RDE) 40
4.3.2	The Rotating Cone Electrode (RConeE) 44
4.3.3	The Rotating Ring Disk Electrode (RRDE) 45
	Further Reading 47
_	
5	Single-Step Electrode Reactions 49
5.1	The Overpotential, η 49
5.1.1	Definition and Physical Meaning of Overpotential 49
5.1.2	Types of Overpotential 51
5.2	Fundamental Equations of Electrode Kinetics 52
5.2.1	The Empirical Tafel Equation 52
5.2.2	The Transition-State Theory 53
5.2.3	The Equation for a Single-Step Electrode Reaction 54
5.2.4	Limiting Cases of the General Equation 56
5.3	The Symmetry Factor, β , in Electrode Kinetics 59
5.3.1	The Definition of β 59
5.3.2	The Numerical Value of β 60
5.4	The Marcus Theory of Charge Transfer 61
5.4.1	Outer-Sphere Electron Transfer 61
5.4.2	The Born–Oppenheimer Approximation 62
5.4.3	The Calculated Energy of Activation 63
5.4.4	The Value of β and its Potential Dependence 64
5.5	Inner-Sphere Charge Transfer 65
5.5.1	Metal Deposition 65
	Further Reading 66

6	Multistep Electrode Reactions 67
6.1	Mechanistic Criteria 67
6.1.1	The Transfer Coefficient, α , and its Relation to the
	Symmetry Factor, β 67
6.1.2	Steady State and Quasi-Equilibrium 69
6.1.3	Calculation of the Tafel Slope 71
6.1.4	Reaction Orders in Electrode Kinetics 74
6.1.5	The Effect of pH on Reaction Rates 77
6.1.6	The Enthalpy of Activation 79
0.2.0	Further Reading 81
7	Specific Examples of Multistep Electrode Reactions 83
7.1	Experimental Considerations 83
7.1.1	Multiple Processes in Parallel 83
7.1.2	The Level of Impurity that can be Tolerated 84
7.2	The Hydrogen Evolution Reaction (HER) 87
7.2.1	Hydrogen Evolution on Mercury 87
7.2.2	Hydrogen Evolution on Platinum 89
7.3	Possible Paths for the Oxygen Evolution Reaction 91
7.4	The Role and Stability of Adsorbed Intermediates 94
7.5	Adsorption Energy and Catalytic Activity 95
	Further Reading 96
	-
8	The Electrical Double Layer (EDL) 97
8.1	Models of Structure of the EDL 97
8.1.1	Phenomenology 97
8.1.2	The Parallel-Plate Model of Helmholtz 99
8.1.3	The Diffuse Double Layer Model of Gouy and Chapman 100
8.1.4	The Stern Model 103
8.1.5	The Role of the Solvent at the Interphase 105
	Further Reading 107
_	T
9	Electrocapillary 109
9.1	Thermodynamics 109
9.1.1	Adsorption and Surface Excess 109
9.1.2	The Gibbs Adsorption Isotherm 111
9.1.3	The Electrocapillary Equation 112
9.2	Methods of Measurement and Some Results 114
9.2.1	The Electrocapillary Electrometer 114
9.2.2	Some Experimental Results 119
9.2.2.1	The Adsorption of Ions 119
9.2.2.2	Adsorption of Neutral Molecules 120
	Further Reading 122
10	Intermediates in Electrode Reactions 123
10 10 1	
10.1	Adsorption Isotherms for Intermediates Formed by
	Charge Transfer 123

10.1.1	General 123
10.1.2	The Langmuir Isotherm and its Limitations 123
10.1.3	Application of the Langmuir Isotherm for Charge-Transfer
	Processes 125
10.1.4	The Frumkin Adsorption Isotherms 126
10.2	The Adsorption Pseudocapacitance C_{ϕ} 127
10.2.1	Formal Definition of C_{ϕ} and its Physical Understanding 127
10.2.2	The Equivalent-Circuit Representation 129
10.2.3	Calculation of C_{ϕ} as a function of θ and E 130
	Further Reading 133
11	Underpotential Deposition and Single-Crystal
	Electrochemistry 135
11.1	Underpotential Deposition (UPD) 135
11.1.1	Definition and Phenomenology 135
11.1.2	UPD on Single Crystals 139
11.1.3	Underpotential Deposition of Atomic Oxygen and Hydrogen 141
	Further Reading 142
12	Electrosorption 145
12.1	Phenomenology 145
12.1.1	What is Electrosorption? 145
12.1.2	Electrosorption of Neutral Organic Molecules 147
12.1.3	The Potential of Zero Charge, E_{pzc} , and its Importance in
	Electrosorption 148
12.1.4	The Work Function and the Potential of Zero Charge 151
12.2	Adsorption Isotherms for Neutral Species 152
12.2.1	General Comments 152
12.2.2	The Parallel-Plate Model of Frumkin et al. 153
12.2.3	The Water Replacement Model of Bockris et al. 155
	Further Reading 157
13 ~	Fast Transients, the Time-Dependent Diffusion Equation,
	and Microelectrodes 159
13.1	The Need for Fast Transients 159
13.1.1	General 159
13.1.2	Small-Amplitude Transients 161
13.1.3	The Sluggish Response of the Electrochemical Interphase 162
13.1.4	How can the Slow Response of the Interphase be Overcome? 162
13.1.4.1	Galvanostatic Transients 162
13.1.4.2	The Double-Pulse Galvanostatic Method 163
13.1.4.3	The Coulostatic (Charge-Injection) Method 164
13.2	The Diffusion Equation 167
13.2.1	The Boundary Conditions of the Diffusion Equation 167
13.2.1.1	Potential Step, Reversible Case (Chrono-Amperometry) 168
13.2.1.2	Potential Step, High Overpotential Region
	(Chrono-Amperometry) 171

13.2.1.3	Current Step (Chronopotentiometry) 172
13.3	Microelectrodes 174
13.3.1	The Unique Features of Microelectrodes 174
13.3.2	Enhancement of Diffusion at a Microelectrode 175
13.3.3	Reduction of the Solution Resistance 176
13.3.4	The Choice between Single Microelectrodes and
	Large Ensembles 176
	Further Reading 178
14	Linear Potential Sweep and Cyclic Voltammetry 181
14.1	Three Types of Linear Potential Sweep 181
14.1.1	Very Slow Sweeps 181
14.1.2	Studies of Oxidation or Reduction of Species in the Bulk of
17.1.2	the Solution 182
14.1.3	Studies of Oxidation or Reduction of Species Adsorbed on
11.1.0	the Surface 182
14.1.4	Double-Layer Charging Currents 183
14.1.5	The Form of the Current–Potential Relationship 185
14.2	Solution of the Diffusion Equations 186
14.2.1	The Reversible Region 186
14.2.2	The High-Overpotential Region 187
14.3	Uses and Limitations of the Linear Potential Sweep Method 188
14.4	Cyclic Voltammetry for Monolayer Adsorption 190
14.4.1	Reversible Region 190
14.4.2	The High-Overpotential Region 192
	Further Reading 193
	6
15	Electrochemical Impedance Spectroscopy (EIS) 195
15.1	Introduction 195
15.2	Graphical Representations 200
15.3	The Effect of Diffusion Limitation – The Warburg
-515	Impedance 203
15.4	Advantages, Disadvantages, and Applications of EIS 206
	Further Reading 211
	- ····································
16	The Electrochemical Quartz Crystal Microbalance
	(EQCM) 213
16.1	Fundamental Properties of the EQCM 213
16.1.1	Introduction 213
16.1.2	The EQCM 214
16.1.3	The Effect of Viscosity 217
16.1.4	Immersion in a Liquid 218
16.1.5	Scales of Roughness 218
16.2	Impedance Analysis of the EQCM 219
16.2.1	The Extended Equation for the Frequency Shift 219
16.2.2	Other Factors Influencing the Frequency Shift 220

16.3	Uses of the EQCM as a Microsensor 220
16.3.1	Advantages and Limitations 220
16.3.2	Some Applications of the EQCM 222
	Further Reading 225
17	Corrosion 227
17.1	The Definition of Corrosion 227
17.2	Corrosion Costs 230
17.3	Thermodynamics of Corrosion 232
17.3.1	Introduction and Important Terms 232
17.3.2	Electrode Potentials and the Standard Electromotive Force (EMF)
	Series 236
17.3.3	The Dependence of Free Energy on the Equilibrium Constant and
	Cell Potential 241
17.3.4	The Nernst Equation 241
17.3.5	The Potential-pH (Pourbaix) Diagrams 242
17.4	Kinetics of Corrosion 252
17.4.1	Introduction and Important Terms 252
17.4.2	Two Limiting Cases of the Butler-Volmer Equation: Tafel
	Extrapolation and Polarization Resistance 255
17.4.3	Corrosion Rate 257
17.4.4	The Mixed-Potential Theory and the Evans Diagrams 257
17.4.5	Passivation and its Breakdown 264
17.5	Corrosion Measurements 270
17.5.1	Non-Electrochemical Tests 270
17.5.2	Electrochemical Tests 272
17.5.2.1	Open-Circuit Potential (OCP) Measurements 272
17.5.2.2	Polarization Tests 273
17.5.2.3	Linear Polarization Resistance (LPR) 277
17.5.2.4	Zero-Resistance Ammetry (ZRA) 277
17.5.2.5	Electrochemical Noise (EN) Measurements 278
17.5.2.6	Electrochemical Hydrogen Permeation Tests 279
17.5.3	Complementary Surface-Sensitive Analytical Characterization
	Techniques 284
17.6	Forms of Corrosion 286
17.6.1	Uniform (General) Corrosion 286
17.6.2	Localized Corrosion 289
17.6.2.1	Crevice Corrosion 289
17.6.2.2	Filiform Corrosion 291
17.6.2.3	Pitting Corrosion 291
17.6.3	Intergranular Corrosion 293
17.6.3.1	Sensitization 293
17.6.3.2	Exfoliation 294
17.6.4	Dealloying 295
17.6.5	Galvanic (Bimetallic) Corrosion 295
17.6.6	Environmentally Induced Cracking (EIC)/Environment-Assisted
	Cracking (EAC) 297

17.6.6.1	Hydrogen Embrittlement (HE) 297
17.6.6.2	Hydrogen-Induced Blistering 299
17.6.6.3	Hydrogen Attack 299
17.6.6.4	Stress Corrosion Cracking (SCC) 300
17.6.6.5	Corrosion Fatigue (CF) 303
17.6.7	Erosion Corrosion 304
17.6.8	Microbiological Corrosion (MIC) 305
17.7	Corrosion Protection 308
17.7.1	Cathodic Protection 308
17.7.1.1	Cathodic Protection with Sacrificial Anodes 308
17.7.1.2	Impressed-Current Cathodic Protection (ICCP) 310
17.7.2	Anodic Protection 312
17.7.3	Corrosion Inhibitors 313
17.7.4	Coatings 315
17.7.5	Other Mitigation Practices 320
	Further Reading 321
18	Electrochemical Deposition 323
18.1	Electroplating 323
18.1.1	Introduction 323
18.1.2	The Fundamental Equations of Electroplating 324
18.1.3	Practical Aspects of Metal Deposition 325
18.1.4	Hydrogen Evolution as a Side Reaction 326
18.1.5	Plating of Noble Metals 327
18.1.6	Current Distribution in Electroplating 328
18.1.6.1	Uniformity of Current Distribution 328
18.1.6.2	The Faradaic Resistance (R_F) and the Solution Resistance (R_S) 328
18.1.6.3	The Dimensionless Wagner Number 329
18.1.6.4	Kinetically Limited Current Density 333
18.1.7	Throwing Power 334
18.1.7.1	Macro Throwing Power 334
18.1.7.2	Micro Throwing Power 334
18.1.8	The Use of Additives 336
18.1.9	The Microstructure of Electrodeposits and the Evolution of
	Intrinsic Stresses 339
18.1.10	Pulse Plating 341
18.1.11	Plating from Nonaqueous Solutions 343
18.1.11.1	Statement of the Problem 343
18.1.11.2	Methods of Plating Al 345
18.1.12	Electroplating of Alloys 346
18.1.12.1	General Observations 346
18.1.12.2	Some Specific Examples 349
18.1.13	The Mechanism of Charge Transfer in Metal Deposition 351
18.1.13.1	Metal Ions Crossing the Interphase Carry the Charge Across it 351
18.2	Electroless Deposition of Metals 352
18.2.1	Some Fundamental Aspects of Electroless Plating of Metals and Alloys 352

18.2.2	The Activation Process 353
18.2.3	The Reducing Agent 353
18.2.4	The Complexing Agent 354
18.2.5	The Mechanism of Electroless Deposition 354
18.2.6	Advantages and Disadvantages of Electroless Plating Compared to
	Electroplating 357
18.3	Electrophoretic Deposition (EPD) 358
	Further Reading 361
*	
19	Electrochemical Nanotechnology 363
19.1	Introduction 363
19.2	Nanoparticles and Catalysis 363
19.2.1	Surfaces and Interfaces 364
19.2.2	The Vapor Pressure of Small Droplets and the Melting Point of
	Solid NPs 365
19.2.3	The Thermodynamic Stability and Thermal Mobility of NPs 368
19.2.4	Catalysts 368
19.2.5	The Effect of Particle Size on Catalytic Activity 369
19.2.6	Nanoparticles Compared to Microelectrodes 370
19.2.7	The Need for High Surface Area 371
19.3	Electrochemical Printing 372
19.3.1	Electrochemical Printing Processes 373
19.3.2	Nanoelectrochemistry Using Micro- and
	Nano-Electrodes/Pipettes 379
	Further Reading 384
20	Energy Conversion and Storage 387
20.1	Introduction 387
20.2	Batteries 388
20.2.1	Classes of Batteries 388
20.2.2	The Theoretical Limit of Energy per Unit Weight 390
20.2.3	How is the Quality of a Battery Defined? 391
20.2.4	Primary Batteries 392
20.2.4.1	Why Do We Need Primary Batteries? 392
20.2.4.2	The Leclanché and the Alkaline Batteries 392
20.2.4.3	The Li-Thionyl Chloride Battery 393
20.2.4.4	The Lithium-Iodine Solid-State Battery 395
20.2.5	Secondary Batteries 396
20.2.5.1	Self-Discharge and Specific Energy 396
20.2.5.2	Battery Stacks Versus Single Cells 396
20.2.5.3	Some Common Types of Secondary Batteries 397
20.2.5.4	The Li-ion Battery 402
20.2.5.5	Metal-Air Batteries 408
20.2.6	Batteries-Driven Electric Vehicles 409
20.2.7	The Polarity of Batteries 410
20.3	Fuel Cells 412
20.3.1	The Specific Energy of Fuel Cells 412

20.3.2	The Phosphoric Acid Fuel Cell (PAFC) 412
	The Direct Methanol Fuel Cell (DMFC) 415
20.3.3	· · · · · · · · · · · · · · · · · · ·
20.3.4	The Proton Exchange Membrane Fuel Cell (PEMFC) 418
20.3.5	The Alkaline Fuel Cell (AFC) 420
20.3.6	High-Temperature Fuel Cells 421
20.3.6.1	The Solid Oxide Fuel Cell (SOFC) 421
20.3.6.2	The Molten Carbonate Fuel Cell (MCFC) 422
20.3.7	Porous Gas Diffusion Electrodes 423
20.3.8	Fuel-Cell-Driven Vehicles 426
20.3.9	Criticism of the Fuel Cells Technology 427
20.4	Supercapacitors 428
20.4.1	Electrostatic Considerations 428
20.4.2	The Energy Stored in a Capacitor 429
20.4.3	The Essence of Supercapacitors 430
20.4.4	Advantages of Supercapacitors 432
20.4.5	Barriers for Supercapacitors 435
20.4.6	Applications of Supercapacitors 435
20.5	Hydrogen Storage 436
	Further Reading 443

Index 445