

Contents

Preface *xvii*

Symbols and Abbreviations *xix*

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

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	Mass-Transport Limitation Versus Charge-Transfer Limitation	30
4.1.4	The Thickness of the Nernst Diffusion Layer	31
4.2	Methods of Measurement	33
4.2.1	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
	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
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
10.1	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 <i>Work Function</i> 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 the Solution	182
14.1.3	Studies of Oxidation or Reduction of Species Adsorbed on 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
15	Electrochemical Impedance Spectroscopy (EIS)	195
15.1	Introduction	195
15.2	Graphical Representations	200
15.3	The Effect of Diffusion Limitation – The Warburg 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
20.3.3	The Direct Methanol Fuel Cell (DMFC)	415
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
--------------	------------

