Contents

 $\begin{array}{ll} \textbf{Preface} & XIII \\ \textbf{Abbreviations} & XV \\ \textbf{Symbols} & XVII \end{array}$

1	Introduction 1
1.1	General Considerations 1
1.1.1	The Current–Potential Relationship 1
1.1.2	The Resistance of the Interface Can Be Infinite 2
1.1.3	The Transition from Electronic to Ionic Conduction 3
1.1.4	Mass-Transport Limitation 3
1.1.5	The Capacitance at the Metal/Solution Interface 5
1.2	Polarizable and Nonpolarizable Interfaces 5
1.2.1	Phenomenology 5
1.2.2	The Equivalent Circuit Representation 6
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 12
2.2.1	Equilibrium of a Species Between Two Phases in Contact 12
2.2.2	Two Identical Phases Not at Equilibrium 13
2.3	The Meaning of the Standard Hydrogen Electrode (SHE) Scale 14
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 Non-Polarizable Counter Electrode 17
3.1.3	The Three-Electrode Measurement 18
3.1.4	Residual jR_S Potential Drop in a Three-Electrode Cell 19
3.2	Cell Geometry and the Choice of the Reference Electrode 20

VI	Contents	
	3.2.1	Types of Reference Electrodes 20
	3.2.2	Use of an Auxiliary Reference Electrode for the Study
		of Fast Transients 21
	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 22
	3.2.3.3	Spherical Symmetry 22
	3.2.4	Positioning the Reference Electrode 24
	3.2.5	Edge Effects 25
	4	Electrode Kinetics: Some Basic Concepts 29
	4.1	Relating Electrode Kinetics to Chemical Kinetics 29
	4.1.1	The Relation of Current Density to Reaction Rate 29
	4.1.2	The Relation of Potential to Energy of Activation 30
	4.1.3	Mass-Transport versus Charge-Transfer Limitation 32
	4.1.4	The Thickness of the Nernst Diffusion Layer 33
	4.2	Methods of Measurement 35
	4.2.1	Potential Control versus Current Control 35
	4.2.2	The Need to Measure Fast Transients 37
	4.2.3	Polarography and the Dropping-Mercury Electrode (DME) 40
	4.2.4	Application of the Stationary Dropping-Mercury Electrode
	4.3	for Kinetic Studies 43
	4.3.1	Rotating Electrodes 44 The Potating Digg Electrode (RDE) 44
	4.3.2	The Rotating Disc Electrode (RDE) 44 The Rotating Cone Electrode (RConeE) 49
	4.3.3	The Rotating Cone Electrode (RConeE) 49 The Rotating Ring–Disc Electrode (RRDE) 49
	4.3.4	Rotating Cylinder Electrode (RCylE) 51
	4.4	The Physical Meaning of Reversibility 52
		The Thysical Meaning of Reversionity 32
	5	Single-Step Electrode Reactions 55
	5.1	The Overpotential, η 55
	5.1.1	Definition and Physical Meaning of Overpotential 55
	5.1.2	Types of Overpotential 57
	5.2	Fundamental Equations of Electrode Kinetics 59
	5.2.1	The Empirical Tafel Equation 59
	5.2.2	Transition-State Theory 59
	5.2.3	The Equation for a Single-Step Electrode Reaction 61
	5.2.4	Limiting Cases of the General Equation 63
	5.3	The Symmetry Factor in Electrode Kinetics 66
	5.3.1	The Definition of β 66
	5.3.2	The Numerical Value of β 68
	5.4	The Marcus Theory of Charge Transfer 68
	5.4.1	Outer-Sphere Electron Transfer 68
	5.4.2	The Born–Oppenheimer Approximation 69

5.4.3	The Calculated Energy of Activation 71
5.4.4	The Value of β and Its Potential Dependence 71
5.5	Time-Resolved Kinetics of Charge Transfer 72
5.5.1	Metal Deposition and Dissolution 72
6	Multi-Step Electrode Reactions 77
6.1	Mechanistic Criteria 77
6.1.1	The Transfer Coefficient, α , and Its Relation to the Symmetry Factor, β 77
6.1.2	Steady State and Quasi-Equilibrium 79
6.1.3	Calculation of the Tafel Slope 81
6.1.4	Reaction Orders in Electrode Kinetics 84
6.1.5	The Effect of pH on Reaction Rates 88
6.1.6	The Enthalpy of Activation 90
7	Specific Examples of Multi-Step Electrode Reactions 93
7.1	Experimental Considerations 93
7.1.1	Multiple Processes in Parallel 93
7.1.2	The Level of Impurity That Can Be Tolerated 94
7.2	The Hydrogen-Evolution Reaction 98
7.2.1	Hydrogen Evolution on Mercury 98
7.2.2	Hydrogen Evolution on Platinum 99
7.3	Hydrogen Storage and Hydrogen Embrittlement 102
7.3.1	Hydrogen Storage 102
7.3.2	Hydrogen Embrittlement 104
7.4	Possible Paths for the Oxygen-Evolution Reaction 105
7.5	The Role and Stability of Adsorbed Intermediates 108
7.6	Catalytic Activity: The Relative Importance of j_0 and $b=109$
7.7	Adsorption Energy and Catalytic Activity 110
7.8	Electrocatalytic Oxidation of Methanol 112
8	The Ionic Double-Layer Capacitance C _{dl} 113
8.1	Theories of Double-Layer Structure 113
8.1.1	Phenomenology 113
8.1.2	The Parallel-Plate Model of Helmholtz 115
8.1.3	The Diffuse-Double-Layer Theory of Gouy and Chapman 116
8.1.4	The Stern Model 118
8.1.5	The Role of the Solvent at the Interface 121
8.1.6	Simple Instrumentation for the Measurement of $C_{\rm dl}$ 123
9	Electrocapillarity 127
9.1	Thermodynamics 127
9.1.1	Adsorption and Surface Excess 127
9.1.2	The Gibbs Adsorption Isotherm 129
913	The Flectrocapillary Equation 130

VIII	Contents	
	9.2	Methods of Measurement and Some Results 132
	9.2.1	The Electrocapillary Electrometer 132
	9.2.2	Some Experimental Results 137
	9.2.2.1	The Adsorption of Ions 137
	9.2.2.2	Adsorption of Neutral Molecules 138
	10	Nanotechnology and Electrocatalysis 141
	10 1	,
	10.1	
	10.1.1	Introduction 141
	10.1.2	The Vapor Pressure of Small Droplets and the Melting Point of Solid Nanoparticles 142
	10.1.3	The Thermodynamic Stability and Thermal Mobility of Nanoparticles 144
	10.2	The Effect of Particle Size on Catalytic Activity 146
	10.2.1	Does a Higher Energy of Adsorption Indicate Higher Catalytic Activity? 146
	10.2.2	Nanoparticles Compared to Microelectrodes 147
	10.2.3	The Need for High Surface Area 148
		Internal distance in Floring de Boostions 151
	11	Intermediates in Electrode Reactions 151
	11.1	Adsorption Isotherms for Intermediates Formed by Charge Transfer 151
	11.1.1	General 151
	11.1.2	The Langmuir Isotherm and Its Limitations 151
	11.1.3	Relating Bulk Concentration to Surface Coverage 153
	11.1.4	Application of the Langmuir isotherm for Charge-Transfer Processes 153
	11.1.5	The Frumkin and Temkin Isotherms 155
	11.2	The Adsorption Pseudocapacitance C_{Φ} 157
	11.2.1	Formal Definition of C_{Φ} and Its Physical Significance 157
	11.2.2	The Equivalent Circuit Representation 159
	11.2.3	Calculation of C_{Φ} as a function of θ and $E=160$
	11.2.3.1	The Langmuir Isotherm 160
	11.2.3.2	The Frumkin Isotherm 161
	11.2.4	The Case of Negative Values of the Parameter f 163
	12	Underpotential Deposition and Single-Crystal Electrochemistry 165
	12.1	Underpotential Deposition (UPD) 165
	12.1.1	Definition and Phenomenology 165
	12.1.2	UPD on Single Crystals 169
	12.1.3	Underpotential Deposition of Halogen Atoms 171
	12.1.4	Underpotential Deposition of Atomic Oxygen and Hydrogen 172
	13	Electrosorption 175
	13.1	Phenomenology 175
		O/

13.1.1	What is Electrosorption? 175
13.1.2	Electrosorption of Neutral Organic Molecules 177
13.1.3	The Potential of Zero Charge, E_z , and Its Importance
	in Electrosorption 178
13.1.4	The Work Function and the Potential of Zero Charge 181
13.2	Methods of Measurement and Some Experimental Results 182
13.2.1	Electrosorption on Solid Electrodes 182
13.2.2	The Radiotracer Methods 185
13.2.3	Methods Based on the Change in Bulk Concentration 185
13.2.4	The Lipkowski Method 186
13.3	Adsorption Isotherms for Neutral Species 188
13.3.1	General Comments 188
13.3.2	The Parallel-Plate Model of Frumkin 189
13.3.3	The Water-Replacement Model of Bockris, Devanathan and Muller 191
14	Experimental Techniques 195
14.1	Fast Transients 195
14.1.1	The Need for Fast Transients 195
14.1.2	Small-Amplitude Transients 197
14.1.3	The Sluggish Response of the Electrochemical Interface 199
14.1.4	How can the Slow Response of the Interface be Overcome? 199
14.1.4.1	Galvanostatic Transient 199
14.1.4.2	The Double-Pulse Galvanostatic Method 200
14.1.4.3	The Coulostatic (Charge-Injection) Method 201
14.2	The Time-Dependent Diffusion Equation 204
14.2.1	The Boundary Conditions of the Diffusion Equation 204
14.2.1.1	Potential Step, Reversible Case (Chrono-amperometry) 205
14.2.1.2	Potential Step, High Overpotential Region (Chrono-amperometry) 208
14.2.1.3	Current Step (Chronopotentiometry) 209
14.2.2	Open-Circuit-Decay Transients 211
14.3	Microelectrodes 213
14.3.1	The Unique Features of Microelectrodes 213
14.3.2	Enhancement of Diffusion at a Microelectrode 214
14.3.3	Reduction of Solution Resistance 215
14.3.4	The Choice Between Single Microelectrodes or Ensembles of Thousands
	of Microelectrodes 216
14.3.5	Shapes of Microelectrodes and Ensembles 219
15	Experimental Techniques (2) 221
15.1	Linear Potential Sweep and Cyclic Voltammetry 221
15.1.1	Three Types of Linear Potential Sweep 221
15.1.2	Double-Layer-Charging Currents 223
15.1.3	The Form of the Current–Potential Relationship 225
15.2	Solution of the Diffusion Equations 226
15 2 1	Peversible Pegion 227

х	Contents	
	15.2.2	High-Overpotential Region 228
	15.3	Uses and Limitations of LPS and CV 229
	15.4	Cyclic Voltammetry for Monolayer Adsorption 232
	15.4.1	Reversible region 232
	15.4.2	High-Overpotential Region 235
	16	Experimental Techniques (3) 237
	16.1	Electrochemical Impedance Spectroscopy (EIS) 237
	16.1.1	Introduction 237
	16.1.2	Graphical Representations 241
	16.2	The Effect of Diffusion Limitation 244
	16.2.1	The Warburg Impedance is a Constant-Phase Element 244
	16.2.2	Some Experimental Results 248
	17	The Electrochemical Quartz Crystal Microbalance 253
	17.1	Fundamental Properties 253
	17.1.1	Introduction 253
	17.1.2	The Fundamental Equations of the QCM 254
	17.1.3	The Effect of Viscosity 255
	17.1.4	Immersion in a Liquid 256
	17.1.5	Scales of Roughness 256
	17.2	Impedance Analysis of the EQCM 258
	17.2.1	The Extended Equation for the Frequency Shift 258
	17.2.2	Other Factors Influencing the Frequency Shift 258
	17.2.3	Analysis of the Mechanical Impedance Spectrum 259
	17.3	Use of the EQCM as a Microsensor 262
	17.3.1	Some Applications of the EQCM 262
	17.3.2	Plating of a Metal on a Foreign Substrate 263
	18	Corrosion 265
	18.1	Scope and Economics of Corrosion 265
	18.1.1	Introduction 265
	18.1.2	The Fundamental Electrochemistry of Corrosion 266
	18.1.3	Micropolarization Measurements 271
	18.2	Potential-pH Diagrams 273
	18.2.1	Some Examples of Potential-pH Diagrams 273
	18.2.2	Passivation and Its Breakdown 280
	18.2.3	Localized Corrosion 283
	18.2.3.1	Pitting Corrosion 283
	18.2.3.2	Crevice Corrosion 285
	18.3	Corrosion Protection 286
	18.3.1	Bimetallic (Galvanic) Corrosion 286
	18.3.2	Cathodic Protection 288
	18.3.3	Anodic Protection 290
	18.3.4	Coatings and Inhibitors 291

19	Electroplating 293
19.1	General Observations 293
19.1.1	Introduction 293
19.1.2	The Fundamental Equations of Electroplating 294
19.1.3	Practical Aspects of Metal Deposition 295
19.1.4	Hydrogen Evolution as a Side Reaction 296
19.1.5	Plating of Noble Metals 296
19.2	Current Distribution in Plating 297
19.2.1	Uniformity of Current Distribution 297
19.2.2	The Faradaic Resistance, R_F and the Solution Resistance, R_S 298
19.2.3	The Dimensionless Wagner Number, W _a 298
19.2.4	Kinetically Limited Current Density 302
19.3	Throwing Power 303
19.3.1	Macro-Throwing Power 303
19.3.2	Micro-Throwing Power 304
19.3.3	The Use of Additives 305
19.4	Plating from Nonaqueous Solutions 307
19.4.1	Statement of the Problem 307
19.4.2	Methods of Plating of Aluminum 308
19.5	Electroplating of Alloys 310
19.5.1	General Observations 310
19.5.2	Some Specific Examples 312
19.6	Electroless Deposition of Metals 313
19.6.1	Some Fundamental Aspects of Electroless Plating
	of Metals and Alloys 313
19.6.2	Advantage and Disadvantages Compared to Electroplating 315
19.7	The Mechanism of Charge Transfer in Metal Deposition 316
19.7.1	Metal Deposition is an Unexpectedly Fast Reaction 316
19.7.2	What Carries the Charge Across the Interface During Metal
	Deposition? 317
19.7.3	Microscopic Reversibility and the Anodic Dissolution of Metals 318
19.7.4	Reductio Ad Absurdum 319
19.7.5	Migration of the Ion Across the Double Layer 320
19.7.6	The Mechanism of Ion Transfer 321
19.7.7	The Symmetry Factor, β 322
19.7.8	The Exchange-Current Density, j_0 324
19.7.9	Why Are Some Electrode Reactions Fast? 325
20	Energy Conversion and Storage 329
20.1	Batteries and Fuel Cells 329
20.1.1	Classes of Batteries 329
20.1.1.1	Primary Batteries 329
20.1.1.2	Rechargeable Batteries 330
20.1.1.3	Fuel Cells 331
20.1.2	The Theoretical Limit of Energy Per Unit Weight 332

XII	Contents
	20.1.2

20.1.3	How Is the Quality of a Battery Defined? 333
20.2	Primary Batteries 333
20.2.1	Why Do We Need Primary Batteries? 333
20.2.2	The Leclanché and the Alkaline Batteries 334
20.2.3	The Li-Thionyl Chloride Battery 335
20.2.4	The Lithium-Iodine Solid State Battery 338
20.3	Secondary Batteries 338
20.3.1	Self-Discharge and Cycle Life 338
20.3.2	Battery Stacks versus Single Cells 339
20.3.3	Some Common Types of Secondary Batteries 339
20.3.3.1	The Lead-Acid Battery 339
20.3.3.2	The Nickel-Cadmium Battery 341
20.3.3.3	The Nickel-Metal Hydride Battery (NiMH) 343
20.3.4	The Li-Ion Battery 344
20.4	Fuel Cells 346
20.4.1	The Energy Density of Fuel Cells 346
20.4.1.1	The Hydrogen-Oxygen Fuel Cell 346
20.4.2	Fuel Cells Using Hydrocarbons – the Phosphoric Acid
	Fuel Cell (PAFC) 346
20.4.3	The Direct Methanol Fuel Cell (DMFC) 348
20.4.3.1	The Anode 349
20.4.3.2	The Polymer Electrolyte Membrane (PEM) 350
20.4.3.3	The Reduction of Molecular Oxygen at the Cathode 351
20.4.4	High-Temperature Fuel Cells 352
20.4.4.1	The High-Temperature Solid-Oxide (HTSO) Fuel Cell 353
20.4.4.2	The Molten Carbonate Fuel Cell 353
20.4.5	Why Do We Need a Fuel Cell? 354
20.5	Porous Gas Diffusion Electrodes 356
20.6	The Polarity of Batteries 358
20.7	Super-Capacitors 358
20.7.1	Electrostatic Considerations 358
20.7.2	The Energy Stored in a Capacitor 360
20.7.3	The Advantage of Electrochemical Super-Capacitors 361
2074	Hybrid Super-Capacitors 361

Index 363