

Contents

<i>Preface</i>	vii
<i>About the Authors</i>	ix
1 Equilibrium Electrochemistry and the Nernst Equation	1
1.1 Chemical Equilibrium	1
1.2 Electrochemical Equilibrium: Introduction	5
1.3 Electrochemical Equilibrium: Electron Transfer at the Solution–Electrode Interface	9
1.4 Electrochemical Equilibrium: The Nernst Equation	11
1.5 Walther Hermann Nernst	17
1.6 Reference Electrodes and the Measurement of Electrode Potentials	19
1.7 The Hydrogen Electrode as a Reference Electrode	26
1.8 Standard Electrode Potentials and Formal Potentials	27
1.9 Formal Potentials and Experimental Voltammetry	30
1.10 Electrode Processes: Kinetics vs. Thermodynamics	32
References	34
2 Electrode Kinetics	37
2.1 Currents and Reaction Fluxes	37
2.2 Studying Electrode Kinetics Requires Three Electrodes	39
2.3 Butler–Volmer Kinetics	42
2.4 Standard Electrochemical Rate Constants and Formal Potentials	45
2.5 The Need for Supporting Electrolyte	48
2.6 The Tafel Law	48
2.7 Julius Tafel	50

2.8	Multistep Electron Transfer Processes	51
2.9	Tafel Analysis and the Hydrogen Evolution Reaction	54
2.10	B. Stanley Pons	59
2.11	Cold Fusion — The Musical!	60
2.12	Why Are Some Standard Electrochemical Rate Constants Large but Others Slow? The Marcus Theory of Electron Transfer: An Introduction	62
2.13	Marcus Theory: Taking It Further. Inner and Outer Sphere Electron Transfer	68
2.14	Marcus Theory: Taking It Further. Adiabatic and Non-Adiabatic Reactions	69
2.15	Marcus Theory: Taking It Further. Calculating the Gibbs Energy of Activation	72
2.16	Relationship between Marcus Theory and Butler–Volmer Kinetics	75
2.17	Marcus Theory and Experiment. Success!	77
2.18	Extending Marcus–Hush Theory: The Fermi–Dirac Distribution of Electrons. Symmetric versus Asymmetric Marcus–Hush Theory	77
	References	82
3	Diffusion	83
3.1	Fick’s First Law of Diffusion	83
3.2	Fick’s Second Law of Diffusion	85
3.3	The Molecular Basis of Fick’s Laws	87
3.4	How Did Fick Discover His Laws?	89
3.5	The Cottrell Equation: Solving Fick’s Second Law	94
3.6	The Cottrell Problem: The Case of Unequal Diffusion Coefficients	98
3.7	The Nernst Diffusion Layer	100
3.8	Mass Transfer versus Electrode Kinetics: Steady-State Current–Voltage Waveshapes	102
3.9	Mass Transport Corrected Tafel Relationships	106
	References	111
4	Cyclic Voltammetry at Macroelectrodes	113
4.1	Cyclic Voltammetry: The Experiment	113
4.2	Cyclic Voltammetry: Solving the Transport Equations	115
4.3	Cyclic Voltammetry: Reversible and Irreversible Kinetics	117

4.4	What Dictates 'Reversible' and 'Irreversible' Behaviour?	125
4.5	Reversible and Irreversible Behaviour: The Effect of Voltage Scan Rate	126
4.6	Reversible versus Irreversible Voltammetry: A Summary	132
4.7	The Measurement of Cyclic Voltammograms: Five Practical Considerations	133
4.8	The Effect of Unequal Diffusion Coefficients: $D_A \neq D_B$	137
4.9	Multiple Electron Transfer: Reversible Electrode Kinetics	140
4.10	Multiple Electron Transfer: Irreversible Electrode Kinetics	149
4.11	The Influence of pH on Cyclic Voltammetry	154
4.12	The Scheme of Squares	158
4.13	Simultaneous Two-Electron Transfer in Electrode Kinetics?	159
4.14	Reversible Voltammetry and Non-Unity Stoichiometry	162
	References	163
5	Voltammetry at Microelectrodes	165
5.1	The Cottrell Equation for a Spherical or Hemispherical Electrode	165
5.2	Potential Step Transients at Microdisc Electrodes	169
5.3	Microelectrodes Have Large Current Densities and Fast Response Times	171
5.4	Applications of Potential Step Chronoamperometry Using Microdisc Electrodes	173
5.5	Double Potential Step Microdisc Chronoamperometry Exploring the Diffusion Coefficient of Electrogenenerated Species	176
5.6	Cyclic and Linear Sweep Voltammetry Using Microdisc Electrodes	184
5.7	Steady-State Voltammetry at the Microdisc Electrode	194
5.8	Microelectrodes versus Macroelectrodes	195
5.9	Ultrafast Cyclic Voltammetry: Megavolts per Second Scan Rates	199
5.10	Ultrasmall Electrodes: Working at the Nanoscale	200
	References	203
6	Voltammetry at Heterogeneous Surfaces	205
6.1	Partially Blocked Electrodes	205
6.2	Microelectrode Arrays	220
6.3	Voltammetry at Highly Ordered Pyrolytic Graphite Electrodes	227

6.4	Electrochemically Heterogeneous Electrodes	231
6.5	Electrodes Covered with Porous Films	232
6.6	Voltammetric Particle Sizing	237
6.7	Scanning Electrochemical Microscopy (SECM)	240
	References	245

7 Cyclic Voltammetry: Coupled Homogeneous Kinetics and Adsorption 247

7.1	Homogeneous Coupled Reactions: Notation and Examples	247
7.2	Modifying Fick's Second Law to Allow for Chemical Reaction	249
7.3	Cyclic Voltammetry and the EC Reaction	250
7.4	How Do the Parameters K_1 and Λ Emerge?	254
7.5	Cyclic Voltammetry and the EC ₂ Reaction	257
7.6	Examples of EC and EC ₂ Processes	260
7.7	ECE Processes	269
7.8	ECE versus DISP	276
7.9	The CE Mechanism	279
7.10	The EC' (Catalytic) Mechanism	280
7.11	Adsorption	283
7.12	Voltammetric Studies of Droplets and Solid Particles	294
7.13	Enzyme Modified Electrodes	299
7.14	Characterising Diffusion: Linear versus Convergent versus Thin Layer	301
7.15	Homogeneous Coupled Kinetic and Reversible Electron Transfer: Tafel Slopes	304
	References	306

8 Hydrodynamic Electrodes 307

8.1	Convection	307
8.2	Modifying Fick's Laws to Allow for Convection	309
8.3	The Rotating Disc Electrode: An Introduction	310
8.4	The Rotating Disc Electrode: Theory	311
8.5	Osborne Reynolds (1842–1912)	315
8.6	The Rotating Disc Electrode: Further Theory	315
8.7	Chronoamperometry at the Rotating Disc Electrode: An Illustration of the Value of Simulation	322
8.8	The Rotating Disc and Coupled Homogeneous Kinetics	325

8.9	The Channel Electrode: An Introduction	328
8.10	The Channel Electrode: The Levich Equation Derived	331
8.11	Channel Flow Cells and Coupled Homogeneous Kinetics	332
8.12	Chronoamperometry at the Channel Electrode	338
8.13	The Channel Electrode Is Not 'Uniformly Accessible'	340
8.14	Channel Microelectrodes	341
8.15	Channel Microband Electrode Arrays for Mechanistic Electrochemistry	343
8.16	The High Speed Channel Electrode	347
8.17	Hydrodynamic Electrodes Based on Impinging Jets	350
8.18	Sonovoltammetry	351
	References	361
9	Voltammetry for Electroanalysis	363
9.1	Potential Step Voltammetric Techniques	363
9.2	Differential Pulse Voltammetry	364
9.3	Square Wave Voltammetry	366
9.4	Stripping Voltammetry	370
9.5	Sono-electroanalysis	377
9.6	Electrochemical Detection of Electrode Reactions' Intermediates and Products	383
	References	386
10	Voltammetry in Weakly Supported Media: Migration and Other Effects	387
10.1	Potentials and Fields in Fully Supported Voltammetry	387
10.2	The Distribution of Ions Around a Charged Electrode	390
10.3	The Electrode–Solution Interface: Beyond the Gouy–Chapman Theory	395
10.4	Double Layer Effect on Electrode Kinetics: Frumkin Effects	399
10.5	A.N. Frumkin (1895–1976)	401
10.6	Transport by Diffusion and by Migration	402
10.7	Measurement of Ion Mobilities	404
10.8	Liquid Junction Potentials	406
10.9	Chronoamperometry and Cyclic Voltammetry in Weakly Supported Media	409
	References	415

11 Voltammetry at the Nanoscale	417
11.1 Transport to Particles Supported on an Electrode	417
11.2 Electrochemical Heterogeneity at the Nanoscale	425
11.3 Nanoparticle Voltammetry: The Transport Changes as the Electrode Shrinks in Size	427
11.4 Altered Chemistry at the Nanoscale	437
11.5 The Electrochemical Study of Nanoparticles in Solution: 'Nano-impacts'	438
11.6 Identifying (Nano) Electrocatalysis	440
References	447
Appendix: Simulation of Electrode Processes	449
A.1 Fick's First and Second Laws	449
A.2 Boundary Conditions	450
A.3 Finite Difference Equations	450
A.4 Backward Implicit Method	451
A.5 Conclusion	453
References	453
<i>Index</i>	455