

Table of Contents

Preface XIII

List of Symbols and Units XV

1	Foundations, Definitions and Concepts	1
1.1	Ions, Electrolytes and the Quantisation of Electrical Charge	1
1.2	Transition from Electronic to Ionic Conductivity in an Electrochemical Cell	3
1.3	Electrolysis Cells and Galvanic Cells: The Decomposition Potential and the Concept of EMF	4
1.4	Faraday's Laws	7
1.5	Systems of Units	9
2	Electrical Conductivity and Interionic Interactions	13
2.1	Fundamentals	13
2.1.1	The Concept of Electrolytic Conductivity	13
2.1.2	The Measurement of Electrolyte Conductance	14
2.1.3	The Conductivity	18
2.1.4	Numerical Values of Conductivity	19
2.2	Empirical Laws of Electrolyte Conductivity	21
2.2.1	The Concentration Dependence of the Conductivity	21
2.2.2	Molar and Equivalent Conductivities	22
2.2.3	Kohlrausch's Law and the Determination of the Limiting Conductivities of Strong Electrolytes	23
2.2.4	The Law of Independent Migration of Ions and the Determination of the Molar Conductivity of Weak Electrolytes	26
2.3	Ionic Mobility and Hittorf Transport	27
2.3.1	Transport Numbers and the Determination of Limiting Ionic Conductivities	28
2.3.2	Experimental Determination of Transport Numbers	29
2.3.3	Magnitudes of Transport Numbers and Limiting Ionic Conductivities	31
2.3.4	Hydration of Ions	32
2.3.5	The Enhanced Conductivity of the Proton, the Structure of the H_3O^+ Ion and the Hydration Number of the Proton	34

2.3.6	The Determination of Ionic Mobilities and Ionic Radii: Walden's Rule	36
2.4	The Theory of Electrolyte Conductivity: The Debye-Hückel-Onsager Theory of Dilute Electrolytes	38
2.4.1	Introduction to the Model: Ionic Cloud, Relaxation and Electrophoretic Effects	38
2.4.2	The Calculation of the Potential due to the Central Ion and its Ionic Cloud: Ionic Strength and Radius of the Ionic Cloud	39
2.4.3	The Debye-Onsager Equation for the Conductivity of Dilute Electrolyte Solutions	44
2.4.4	The Influence of Alternating Electric Fields and Strong Electric Fields on the Electrolyte Conductivity	46
2.5	The Concept of Activity from the Electrochemical Viewpoint	46
2.5.1	The Activity Coefficient	46
2.5.2	Calculation of the Concentration Dependence of the Activity Coefficient	48
2.5.3	Extensions to More Concentrated Electrolytes	51
2.6	The Properties of Weak Electrolytes	61
2.6.1	The Ostwald Dilution Law	61
2.6.2	The Dissociation Field Effect	63
2.7	The Concept of pH and the Idea of Buffer Solutions	64
2.8	Non-aqueous Solutions	66
2.8.1	Ion Solvation in Non-aqueous Solvents	67
2.8.2	Electrolytic Conductivity in Non-aqueous Solutions	68
2.8.3	The pH-Scale in Protonic Non-aqueous Solvents	70
2.9	Simple Applications of Conductivity Measurements	71
2.9.1	The Determination of the Ionic Product of Water	71
2.9.2	The Determination of the Solubility Product of a Slightly Soluble Salt	72
2.9.3	The Determination of the Heat of Solution of a Slightly Soluble Salt	72
2.9.4	The Determination of the Thermodynamic Dissociation Constant of a Weak Electrolyte	73
2.9.5	The Principle of Conductivity Titrations	73
3	Electrode Potentials and Double-Layer Structure at Phase Boundaries	77
3.1	Electrode Potentials and their Dependence on Concentration, Gas Pressure and Temperature	77
3.1.1	The EMF of Galvanic Cells and the Maximum Useful Energy from Chemical Reactions	77
3.1.2	The Origin of Electrode Potentials, Galvani Potential Difference and the Electrochemical Potential	78
3.1.3	Calculation of the Electrode Potential and the Equilibrium Galvani Potential Difference between a Metal and a Solution of its Ions – The Nernst Equation	81
3.1.4	The Nernst Equation for Redox Electrodes	82
3.1.5	The Nernst Equation for Gas-electrodes	83

3.1.6	The Measurement of Electrode Potentials and Cell Voltages	84
3.1.7	Schematic Representation of Galvanic Cells	86
3.1.8	Calculation of Cell EMF's from Thermodynamic Data	88
3.1.9	The Temperature Dependence of the Cell Voltage	90
3.1.10	The Pressure Dependence of the Cell Voltage – Residual Current for the Electrolysis of Aqueous Solutions	91
3.1.11	Reference Electrodes and the Electrochemical Series	93
3.1.12	Reference Electrodes of the Second Kind	98
3.1.13	The Electrochemical Series in Non-aqueous Solvents	102
3.1.14	Reference Electrodes in Non-aqueous Systems and Usable Potential Ranges	104
3.2	Liquid-junction Potentials	105
3.2.1	The Origin of Liquid-junction Potentials	105
3.2.2	The Calculation of Diffusion Potentials	106
3.2.3	Concentration Cells with and without Transference	108
3.2.4	Henderson's Equation	109
3.2.5	The Elimination of Diffusion Potentials	111
3.3	Membrane Potentials	112
3.4	The Electrolyte Double-Layer and Electrokinetic Effects	115
3.4.1	Helmholtz and Diffuse Double Layer: the Zeta-Potential	116
3.4.2	Adsorption of Ions, Dipoles and Neutral Molecules – the Potential of Zero Charge	120
3.4.3	The Double-Layer Capacity	121
3.4.4	Some Data for Electrolytic Double Layers	123
3.4.5	Electrocapillarity	124
3.4.6	Electrokinetic Effects – Electrophoresis, Electro-osmosis, Dorn-effect and Streaming Potential	128
3.4.7	Theoretical Studies of the Double Layer	130
3.5	Potential and Phase Boundary Behaviour at Semiconductor Electrodes	133
3.5.1	Metallic Conductors. Semiconductors and Insulators	133
3.5.2	Electrochemical Equilibria on Semiconductor Electrodes	136
3.6	Simple Applications of Potential Difference Measurements	139
3.6.1	The Experimental Determination of Standard Potentials and Mean Activity Coefficients	139
3.6.2	Solubility Products of Slightly Soluble Salts	141
3.6.3	The Determination of the Ionic Product of Water	141
3.6.4	Dissociation Constants of Weak Acids	142
3.6.5	The Determination of the Thermodynamic State Functions ($\Delta_r G^0$, $\Delta_r H^0$ and $\Delta_r S^0$) and the Corresponding Equilibrium Constants for Chemical Reactions	144
3.6.6	pH Measurement with the Hydrogen Electrode	145
3.6.7	pH Measurement with the Glass Electrode	148
3.6.8	The Principle of Potentiometric Titrations	153

4	Electrical Potentials and Electrical Current	157
4.1	Cell Voltage and Electrode Potential during Current Flow: an Overview	157
4.1.1	The Concept of Overpotential	159
4.1.2	The Measurement of Overpotential; the Current-Potential Curve for a Single Electrode	160
4.2	The Electron-transfer Region of the Current-Potential Curve	162
4.2.1	Understanding the Origin of the Current-Potential Curve in the Electron- transfer-limited Region with the Help of the Arrhenius Equation	162
4.2.2	The Meaning of the Exchange Current Density j_0 and the Asymmetry Parameter β	166
4.2.3	The Concentration Dependence of the Exchange-current Density	169
4.2.4	Electrode Reactions with Consecutive Transfer of Several Electrons	170
4.2.5	Electron Transfer with Coupled Chemical Equilibria; the Electrochemical Reaction Order	173
4.2.6	Further Theoretical Considerations of Electron Transfer	179
4.2.7	Determination of Activation Parameters and the Temperature Dependence of Electrochemical Reactions	184
4.3	The Concentration Overpotential – The Effect of Transport of Material on the Current-Voltage Curve	185
4.3.1	The Relationship between the Concentration Overpotential and the Butler-Volmer Equation	186
4.3.2	Diffusion Overpotential and the Diffusion Layer	187
4.3.3	Current-Time Behaviour at Constant Potential and Constant Surface Concentration c^s	189
4.3.4	Potential-Time Behaviour at Constant Current: Galvanostatic Electrolysis	191
4.3.5	Transport by Convection, Rotating Electrodes	192
4.3.6	Mass Transport Through Migration – The Nernst-Planck Equation	199
4.3.7	Spherical Diffusion	200
4.3.8	Micro-electrodes	201
4.4	The Effect of Simultaneous Chemical Processes on the Current Voltage Curve	203
4.4.1	Reaction Overpotential, Reaction-limited Current and Reaction Layer Thickness	204
4.5	Adsorption Processes	207
4.5.1	Forms of Adsorption Isotherms	208
4.5.2	Adsorption Enthalpies and Pauling's Equation	211
4.5.3	Current-Potential Behaviour and Adsorption-limited Current	211
4.5.4	Dependence of Exchange Current Density on Adsorption Enthalpy, the Volcano Curve	212
4.6	Electrocrystallisation – Metal Deposition and Dissolution	213
4.6.1	Simple Model of Metal Deposition	214
4.6.2	Crystal Growth in the Presence of Screw Dislocations	218
4.6.3	Under-potential Deposition	219

4.6.4	The Kinetics of Metal Dissolution and Metal Passivation	220
4.6.5	Electrochemical Materials Science and Electrochemical Surface Technology	222
4.7	Mixed Electrodes and Corrosion	225
4.7.1	Mechanism of Acid Corrosion	226
4.7.2	Oxygen Corrosion	227
4.7.3	Potential-pH Diagrams or Pourbaix Diagrams	227
4.7.4	Corrosion Protection	228
4.8	Current Flows on Semiconductor Electrodes	231
4.8.1	Photoeffects in Semiconductors	233
4.8.2	Photoelectrochemistry	234
4.8.3	Photogalvanic Cells	235
4.8.4	Solar Energy Harvesting	236
4.8.5	Detoxification using Photoelectrochemical Technology	240
4.9	Bioelectrochemistry	241
4.9.1	The Biochemistry of Glucose Oxidase as a Typical Redox Enzyme	242
4.9.2	The Electrochemistry of Selected Biochemical Species	244
5	Methods for the Study of the Electrode/Electrolyte Interface	251
5.1	The Measurement of Stationary Current-Potential Curves	251
5.1.1	The Potentiostat	252
5.1.2	Determination of Kinetic Data by Potential Step Methods	253
5.1.3	Measurements with Controlled Mass Transport	255
5.1.4	Stationary Measurement of Very Rapid Reactions with Turbulent Flow	257
5.2	Quasi-Stationary Methods	260
5.2.1	Cyclic Voltammetry: Studies of Electrode Films and Electrode Processes – Electrochemical Spectroscopy	260
5.2.2	AC Measurements	278
5.3	Electrochemical Methods for the Study of Electrode Films	291
5.3.1	Measurement of Charge Passed	292
5.3.2	Capacitance Measurements	294
5.4	Spectroelectrochemical and other Non-classical Methods	295
5.4.1	Introduction	295
5.4.2	Infra-Red Spectroelectrochemistry	297
5.4.3	Electron-spin Resonance	305
5.4.4	Electrochemical Mass Spectroscopy	309
5.4.5	Additional Methods of Importance	319
5.4.6	Scanning Microscope Techniques	321
5.5	Preparation of Nanostructures, Combination of STM and UHV-Transfer	326
5.5.1	Use of an STM-tip in SECM Experiments for the Preparation of Definite Nanostructure	326
5.5.2	Combination of STM and UHV Transfer	326
5.6	Optical Methods	328

5.6.1	Ellipsometry	329
5.6.2	XAS, SXS and XANES	334
6	Electrocatalysis and Reaction Mechanisms	339
6.1	On Electrocatalysis	339
6.2	The Hydrogen Electrode	341
6.2.1	Influence of Adsorbed Intermediates on <i>i</i> -V Curves	342
6.2.2	Influence of the pH-value of the Solution and the Catalyst Surface	344
6.2.3	Hydrogen Oxidation at Platinum and Chemisorbed Oxygen	345
6.3	The Oxygen Electrode	346
6.3.1	Investigation of the Oxygen Reduction Reaction with Rotating Ring-Disc Electrode	347
6.4	Methanol Oxidation	348
6.4.1	Parallel Pathways of Methanol Oxidation in Acid Electrolyte	350
6.4.2	Methanol Adsorption	350
6.4.3	Reaction Products and Adsorbed Intermediates of Methanol Oxidation	352
6.4.4	Effects of Surface Structure and Adsorbed Anions	354
6.4.5	On the Mechanism of Methanol Oxidation	355
6.4.6	Catalyst Promoters for Methanol Oxidation	356
6.5	Carbon Monoxide Oxidation at Platinum Surfaces	358
6.5.1	Identification of Surface Structures for CO Adsorbed on Pt(111)	358
6.5.2	Oxidation of CO in the Presence of Dissolved CO	359
6.5.3	The Oxidation of Carbon Monoxide: Langmuir-Hinshelwood Mechanism	361
6.5.4	CO Oxidation at Higher Overpotentials, Influence of Mass Transfer and Oxygen Coverage	363
6.6	Conversion of Chemical Energy of Ethanol into Electricity	364
6.7	Reaction Mechanisms in Electro-organic Chemistry	366
6.7.1	General Issues	366
6.7.2	Classification of Electrode Processes	367
6.7.3	Oxidation Processes: Potentials, Intermediates and End Products	369
6.7.4	Reduction Processes: Potentials, Intermediates and Products	371
6.7.5	Further Electroorganic Reactions and the Influence of the Electrode Surface	372
6.7.6	Electrochemical Polymerisation	373
6.8	Oscillations in Electrochemical Systems	375
7	Solid and Molten-salt Ionic Conductors as Electrolytes	381
7.1	Ionically Conducting Solids	381
7.1.1	Origins of Ionic Conductivity in Solids	381
7.1.2	Current/Voltage Measurements on Solid Electrodes	385
7.2	Solid Polymer Electrolytes (SPE's)	386
7.2.1	Current/Voltage Measurements with SPE's	388
7.2.2	Other Polymeric Membranes	388

7.3	Ionically-conducting Melts	392
7.3.1	Conductivity	392
7.3.2	Current-Voltage Studies	393
7.3.3	Further Applications of High-temperature Melts	394
7.3.4	Room Temperature Melts	395
8	Industrial Electrochemical Processes	397
8.1	Introduction and Fundamentals	397
8.1.1	Special Features of Electrochemical Processes	397
8.1.2	Classical Cell Designs and the Space-Time Yield	399
8.1.3	Morphology of Electrocatalysts	401
8.1.4	The Activation Overpotential	403
8.2	The Electrochemical Preparation of Chlorine and NaOH	404
8.2.1	Electrode Reactions during the Electrolysis of Aqueous NaCl	404
8.2.2	The Diaphragm Cell	405
8.2.3	The Amalgam Cell	406
8.2.4	The Membrane Process	408
8.2.5	Membrane Processes using an Oxygen Cathode	410
8.3	The Electrochemical Extraction and Purification of Metals	414
8.3.1	Extraction from Aqueous Solution	414
8.3.2	Metal Purification in Aqueous Solution	415
8.3.3	Molten Salt Electrolysis	417
8.4	Special Preparation Methods for Inorganic Chemicals	418
8.4.1	Hypochlorite, Chlorate and Perchlorate	418
8.4.2	Hydrogen Peroxide and Peroxodisulphate	419
8.4.3	Classical Water Electrolysis	420
8.4.4	Modern Water Electrolysis and Hydrogen Technology	420
8.5	Electro-organic Synthesis	422
8.5.1	An Overview of Processes and Specific Features	422
8.5.2	Adiponitrile – The Monsanto Process	424
8.6	Modern Cell Designs	425
8.7	Future Possibilities for Electrocatalysis	428
8.7.1	Electrochemical Modification of Catalytic Activity in Heterogeneous Chemical Reactions – The NEMCA Effect	429
8.8	Component Separation Methods	431
8.8.1	Treatment of Waste Water	431
8.8.2	Electrodialysis	433
8.8.3	Electrophoresis	434
8.8.4	Electrochemical Separation Procedures in the Nuclear Industry	435
9	Galvanic Cells	439
9.1	Basics	440
9.2	Properties, Components and Characteristics of Batteries	441
9.2.1	Function and Construction of Lead-Acid Batteries	441
9.2.2	Function and Construction of Leclanché Cells	442

9.2.3	Electrolyte and Self-discharge	444
9.2.4	Open-circuit Voltage, Specific Capacity and Energy Density	444
9.2.5	Current-Voltage Characteristics, Power Density and Power-density/Energy-density Diagrams	446
9.2.6.	Battery Discharge Characteristics	447
9.2.7	Charge Characteristics, Current and Energy Yield and Cycle Number	448
9.2.8	Cost of Electrical Energy and of Installed Battery Power	449
9.3	Secondary Systems	450
9.3.1	Conventional Secondary Batteries	450
9.3.2	New Developments	452
9.3.3	Summary of Data for Secondary Battery Systems	461
9.4	Primary Systems other than Leclanché Batteries	464
9.4.1	Alkaline-Manganese Cells	464
9.4.2	The Zinc-Mercury Oxide Battery	465
9.4.3	Lithium Primary Batteries	466
9.4.4	Electrode and Battery Characteristics for Primary Systems	466
9.5	Fuel Cells	468
9.5.1	Fuel Cells with Gaseous Fuels	469
9.5.2	Modern Developments	472
9.5.3	Fuel Cells with Liquid Fuels	481
9.6	Primary and Secondary Air Batteries	483
9.6.1.	Metal-Air Primary Batteries	484
9.6.2.	Metal-Air Secondary Systems	485
9.7	Efficiency of Batteries and Fuel Cells	486
9.8	Super-capacitors	487
10	Analytical Applications	491
10.1	Titration Processes using Electrochemical Indicators	491
10.2	Electro-analytical Methods	494
10.2.1	Polarography and Voltammetry	494
10.2.2	Further Methods - Coulometry, Electrogravimetry and Chronopotentiometry	502
10.3	Electrochemical Sensors	505
10.3.1	Conductivity and pH Measurement	505
10.3.2	Redox Electrodes	506
10.3.3	Ion-sensitive Electrodes	506
10.3.4	Sensors for the Analysis of Gases	510
	Subject Index	521