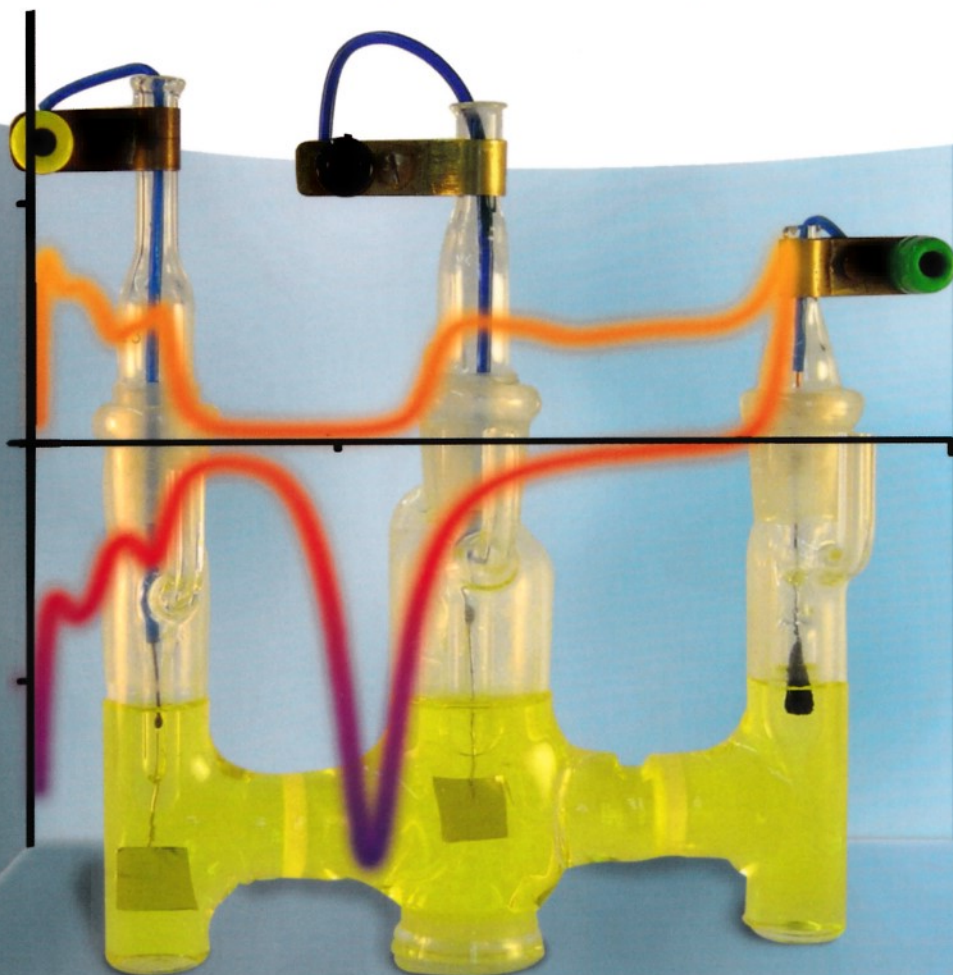


Rudolf Holze

# Experimental Electrochemistry

A Laboratory Textbook

Second, Completely Revised and Updated Edition



## Contents

<b>Preface to the Second Edition</b>	<i>ix</i>
<b>Preface to the First Edition</b>	<i>xi</i>
<b>Foreword to the Second Edition</b>	<i>xv</i>
<b>Symbols and Acronyms</b>	<i>xvii</i>

<b>1</b>	<b>Introduction: An Overview of Practical Electrochemistry</b>	<b>1</b>
	Practical Hints	2
	Electrodes	3
	Measuring Instruments	6
	Electrochemical Cells	7
	Data Recording	9
<b>2</b>	<b>Electrochemistry in Equilibrium</b>	<b>11</b>
	Experiment 2.1: The Electrochemical Series	11
	Experiment 2.2: Standard Electrode Potentials and the Mean Activity Coefficient	15
	Experiment 2.3: pH Measurements and Potentiometrically Indicated Titrations	20
	Experiment 2.4: Redox Titrations (Cerimetry)	25
	Experiment 2.5: Differential Potentiometric Titration	27
	Experiment 2.6: Potentiometric Measurement of the Kinetics of the Oxidation of Oxalic Acid	30
	Experiment 2.7: Polarization and Decomposition Voltage	34
	Experiment 2.8: A Simple Relative Hydrogen Electrode	39
<b>3</b>	<b>Electrochemistry with Flowing Current</b>	<b>43</b>
	Experiment 3.1: Ion Movement in an Electric Field	44
	Experiment 3.2: Paper Electrophoresis	46
	Experiment 3.3: Charge Transport in Electrolyte Solution	47
	Experiment 3.4: Conductance Titration	51
	Experiment 3.5: Chemical Constitution and Electrolytic Conductance	54
	Experiment 3.6: Faraday's Law	56
	Experiment 3.7: Kinetics of Ester Saponification	58
	Experiment 3.8: Movement of Ions and Hittorf Transport Number	62

Experiment 3.9: Polarographic Investigation of the Electroreduction of Formaldehyde	68
Experiment 3.10: Galvanostatic Measurement of Stationary Current–Potential Curves	72
Experiment 3.11: Cyclic Voltammetry	75
Experiment 3.12: Slow Scan Cyclic Voltammetry	82
Experiment 3.13: Kinetic Investigations with Cyclic Voltammetry	86
Experiment 3.14: Numerical Simulation of Cyclic Voltammograms	90
Experiment 3.15: Cyclic Voltammetry with Microelectrodes	92
Experiment 3.16: Cyclic Voltammetry of Organic Molecules	96
Experiment 3.17: Cyclic Voltammetry in Nonaqueous Solutions	102
Experiment 3.18: Cyclic Voltammetry with Sequential Electrode Processes	104
Experiment 3.19: Cyclic Voltammetry of Aromatic Hydrocarbons	107
Experiment 3.20: Cyclic Voltammetry of Aniline and Polyaniline	110
Experiment 3.21: Galvanostatic Step Measurements	115
Experiment 3.22: Cyclic Voltammetry of a Supercapacitor Electrode	118
Experiment 3.23: Chronoamperometry	121
Experiment 3.24: Chronocoulometry	122
Experiment 3.25: Rotating Disk Electrode	124
Experiment 3.26: Rotating Ring-Disk Electrode	130
Experiment 3.27: Measurement of Electrode Impedances	133
Experiment 3.28: Corrosion Cells	136
Experiment 3.29: Aeration Cell	138
Experiment 3.30: Concentration Cell	139
Experiment 3.31: Salt Water Drop Experiment According to Evans	141
Experiment 3.32: Passivation and Activation of an Iron Surface	142
Experiment 3.33: Cyclic Voltammetry with Corroding Electrodes	143
Experiment 3.34: Tafel Plot of a Corroding Electrode	145
Experiment 3.35: Impedance of a Corroding Electrode	148
Experiment 3.36: Linear Polarization Resistance of a Corroding Electrode	150
Experiment 3.37: Oscillating Reactions	152
<b>4 Analytical Electrochemistry</b>	<b>155</b>
Experiment 4.1: Ion-Sensitive Electrode	156
Experiment 4.2: Potentiometrically Indicated Titrations	158
Experiment 4.3: Bipotentiometrically Indicated Titration	163
Experiment 4.4: Conductometrically Indicated Titration	165
Experiment 4.5: Electrogravimetry	167
Experiment 4.6: Coulometric Titration	170
Experiment 4.7: Amperometry	172
Experiment 4.8: Polarography (Fundamentals)	178
Experiment 4.9: Polarography (Advanced Methods)	182
Experiment 4.10: Anodic Stripping Voltammetry	183
Experiment 4.11: Abrasive Stripping Voltammetry	186
Experiment 4.12: Polarographic Analysis of Anions	189
Experiment 4.13: Tensammetry	191

<b>5</b>	<b>Nontraditional Electrochemistry</b>	<b>197</b>
	Experiment 5.1: UV-Vis Spectroscopy	197
	Experiment 5.2: Surface-Enhanced Raman Spectroscopy	200
	Experiment 5.3: Surface-Enhanced Raman Spectroscopy of a Self-Assembled Monolayer	203
	Experiment 5.4: Infrared Spectroelectrochemistry	205
	Experiment 5.5: Electrochromism	207
	Experiment 5.6: Raman Spectroscopic Monitoring of Charge/Discharge of an Intrinsically Conducting Polyaniline Supercapacitor Electrode Material	209
<b>6</b>	<b>Electrochemical Energy Conversion and Storage</b>	<b>211</b>
	Experiment 6.1: Lead–Acid Accumulator	211
	Experiment 6.2: Discharge Behavior of Nickel–Cadmium Accumulators	216
	Experiment 6.3: Performance Data of a Fuel Cell	218
	Experiment 6.4: Charging Supercapacitors	221
	Experiment 6.5: Discharging Supercapacitors	224
	Experiment 6.6: Zinc–Air Cell	227
	Experiment 6.7: Lithium-Ion Battery	228
	Experiment 6.8: Low-Temperature Discharge Behavior of Nickel–Cadmium Accumulators	230
	Experiment 6.9: Discharge Behavior of Nickel–Cadmium Accumulators at Constant Load	233
	Experiment 6.10: Impedance of a Button Cell	234
	Experiment 6.11: Potentiostatic Polarization Curves	236
	Experiment 6.12: Galvanostatic Polarization Curves	237
<b>7</b>	<b>Electrochemical Production</b>	<b>241</b>
	Experiment 7.1: Cementation Reaction	241
	Experiment 7.2: Galvanic Copper Deposition	242
	Experiment 7.3: Electrochemical Oxidation of Aluminum	244
	Experiment 7.4: Kolbe Electrolysis of Acetic Acid	245
	Experiment 7.5: Electrolysis of Acetyl Acetone	247
	Experiment 7.6: Anodic Oxidation of Malonic Acid Diethylester	250
	Experiment 7.7: Indirect Anodic Dimerization of Acetoacetic Ester (3-Oxo-Butyric Acid Ethyl Ester)	251
	Experiment 7.8: Electrochemical Bromination of Acetone	253
	Experiment 7.9: Electrochemical Iodination of Ethanol	255
	Experiment 7.10: Electrochemical Production of Potassium Peroxodisulfate	257
	Experiment 7.11: Yield of Chlor-Alkali Electrolysis According to the Diaphragm Process	258
	<b>Appendix</b>	<b>261</b>
	<b>Index</b>	<b>263</b>

**S**howing how to apply the theoretical knowledge in practice, the one and only compilation of electrochemical experiments on the market now in a new edition.

Maintaining its didactic approach, this successful textbook provides clear and easy-to-follow instructions for carrying out the experiments, illustrating the most important principles and applications in modern electrochemistry, while pointing out the potential dangers and risks involved.

This second edition contains approximately 25% new material and 20 new experiments, many of which cover electrochemical energy conversion and storage as well as electrochemical equilibrium.

With a foreword by R. Daniel Little.



*Rudolf Holze is Full Professor of Physical Chemistry and Electrochemistry at the Institute of Chemistry at Chemnitz University of Technology. He finished his studies of chemistry at Bonn University with a diploma thesis on new cathode materials for lithium batteries. His doctoral thesis focused on impedance measurements at porous electrodes for energy conversion systems. As a postdoctoral fellow with E.B. Yeager at Case Western Reserve University, Cleveland, Ohio, USA, he studied transition metal complexes as electrocatalysts for fuel cells. Research interests include spectroelectrochemistry, electrochemical materials science (intrinsically conducting polymers, corrosion, functionalized electrode surfaces) and corrosion. He has written and edited eight books and more than 350 research papers and reviews. In editorial boards of various journals and as editor he is actively involved in scientific communication, including the organization of conferences and workshops.*