


Analytical
Electrochemistry 2nd Ed

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ANALYTICAL ELECTROCHEMISTRY

SECOND EDITION

Dedicated to the memory of my parents, Elka and Moshe Wang

PREFACE

The goal of this textbook is to cover the full scope of modern electroanalytical techniques and devices. The main emphasis is on electroanalysis, rather than physical electrochemistry. The objective is to provide a sound understanding of the fundamentals of electrode reactions and of the principles of electrochemical methods, and to demonstrate their potential for solving real-life analytical problems. Given the impressive progress in electroanalytical chemistry, and its growing impact on analytical chemistry, this work offers also an up-to-date, easy-to-read presentation of recent advances including new methodologies, sensors, detectors, and microsystems. The book is suitable for a graduate-level course in electroanalytical chemistry or as a supplement to a high-level undergraduate course in instrumental analysis. It should also be very useful to those considering the use of electroanalysis in their laboratories.

The material is presented in six roughly equal chapters. The first chapter is devoted to fundamental aspects of electrode reactions and the structure of the interfacial region. Chapter 2 discusses the study of electrode reactions and high-resolution surface characterization. Chapter 3 gives an overview of finite-current controlled-potential techniques. Chapter 4 describes the electrochemical instrumentation and electrode materials (including new modified and microelectrodes). Chapter 5 deals with the principles of potentiometric measurements and various classes of ion-selective electrodes, while Chapter 6 is devoted to the growing field of chemical sensors (including modern biosensors, gas sensors, solid-state devices, and sensor arrays). I have tried to provide numerous references to review literature at the end of each chapter. By discussing the very latest advances, it is hoped to bridge the common gap between recent research literature and standard textbooks.

This second edition of *Analytical Electrochemistry* is extensively revised and updated, and reflects the rapid growth of electroanalytical chemistry during the 1990s. It contains a number of new topics, including self-assembled monolayers, DNA biosensors, sol-gel surface modification, detection for capillary electrophoresis, single molecule detection, and micromachined analyzers ("Lab-on-a-Chip"). Other topics such as the fundamentals of faradaic processes, principles of potentiometric measurements, spectroelectrochemistry, modified and microelectrodes, scanning electron microscopy, electrical communication between redox enzymes and electrodes, and enzyme and immunoelectrodes, have been greatly expanded. The entire text has been updated to cover the very latest (as of 1999) developments in electroanalytical chemistry. Numerous new worked examples and end-of-chapter questions have been added to this edition. The organization of the book has been changed somewhat, by moving the study of electrode reactions forward to Chapter 2. In the five years since the first edition I received numerous suggestions, many of which have been incorporated in the second edition.

Finally, I wish to thank my wife, Ruth, and my daughter, Sharon, for their love and patience; the editorial and production staff of Wiley Inc. for their help and support; and the numerous electrochemists across the globe who led to the advances reported in this textbook. Thank you all!

Joseph Wang
Las Cruces, New Mexico, U.S.A.

ABBREVIATIONS AND SYMBOLS

<i>a</i>	Activity
<i>A</i>	Absorbance
<i>A</i>	Area of electrode
<i>Ab</i>	Antibody
<i>AdSV</i>	Adsorptive stripping voltammetry
<i>AES</i>	Auger electron spectroscopy
<i>AFM</i>	Atomic force microscopy
<i>Ag</i>	Antigen
<i>ASV</i>	Anodic stripping voltammetry

B Adsorption coefficient

<i>C</i>	Concentration
<i>C_{dl}</i>	Differential capacitance
<i>C_{Hg}</i>	Concentration in amalgam
<i>CSV</i>	Cathodic stripping voltammetry
<i>CWE</i>	Coated-wire electrode
<i>CME</i>	Chemically modified electrode
<i>CV</i>	Cyclic voltammetry
<i>CZE</i>	Capillary zone electrophoresis

<i>D</i>	Diffusion coefficient
<i>DC</i>	Direct current
<i>DNA</i>	Deoxyribonucleic acid

DME	Dropping mercury electrode
DPV	Differential pulse voltammetry
E	Potential (V)
ΔE	Pulse amplitude; step height
E_B	Binding energy (in XPS)
E_{eq}	Equilibrium potential
E°	Standard electrode potential
$E_{1/2}$	Half wave potential
E_p	Peak potential
E_{pzc}	Potential of zero charge
EC	Electrode process involving an electrochemical reaction followed by a chemical step
ECL	Electrochemiluminescence
EQCM	Electrochemical quartz crystal microbalance
ESCA	Electron spectroscopy for chemical analysis
EXAFS	X-ray adsorption fine structure
F	Faraday constant
FET	Field-effect transistor
FIA	Flow injection analysis
f	Activity coefficient; frequency
Δf	Frequency change (in EQCM)
ΔG	Free energy
ΔG^\ddagger	Free energy of activation
HMDE	Hanging mercury drop electrode
i	Electric current
i_c	Charging current
i_l	Limiting current
i_t	Tunneling current
Δi	Current difference
IHP	Inner Helmholtz plane
IRS	Internal reflectance spectroscopy
ISE	Ion-selective electrode
ISFET	Ion-selective field-effect transistor
J	Flux
k_{ij}^{pot}	Potentiometric selectivity coefficient
k^c	Standard rate constant
K_m	Michaelis–Menten constant; mass transport coefficient

l	Film thickness
LCEC	Liquid chromatography/electrochemistry
LEED	Low-energy electron diffraction
m	Mercury flow rate (in polarography); electron mass (in STM)
Δm	Mass change (in EQCM)
M	Mediator
MFE	Mercury film electrode
N	Collection efficiency
NADH	Dihyronicotinamide adenine dinucleotide
n	Number of electrons transferred
NP	Normal pulse
O	The oxidized species
OHP	Outer Helmholtz plane
OTE	Optically transparent electrode
PAD	Pulsed amperometric detection
PSA	Potentiometric stripping analysis
q	Charge
QCM	Quartz crystal microbalance
r	distance; radius
R	Resistance; gas constant
RDE	Rotating disk electrode
Re	Reynolds number
RRDE	Rotating ring disk electrode
RVC	Reticulated vitreous carbon
S	Barrier width (in STM)
SAM	Self-assembled monolayers
Sc	Schmidt number
SECM	Scanning electrochemical microscopy
SERS	Surface enhanced Raman scattering
STM	Scanning tunneling microscopy
SWV	Square-wave voltammetry
T	Temperature
t	Time
t_d	Deposition time
t_m	Transition time (in PSA)
U	Flow rate, stirring rate

v	Potential scan rate
V_{Hg}	Volume of mercury electrode
V_{max}	Maximum rate
$W_{1/2}$	Peak width (at half height)
WE	Working electrode
WJD	Wall jet detector
XPS	X-ray photoelectron spectroscopy
α	Transfer coefficient
Γ	Surface coverage
ϵ	Dielectric constant; molar absorptivity
γ	Surface tension
δ	Thickness of the diffusion layer
δ_H	Thickness of the hydrodynamic boundary layer
η	Overvoltage
μ	Ionic strength
ν	Kinematic viscosity
ω	Angular velocity

**ANALYTICAL
ELECTROCHEMISTRY
SECOND EDITION**

CONTENTS

PREFACE	xi
ABBREVIATIONS AND SYMBOLS	xiii
1 FUNDAMENTAL CONCEPTS	1
1-1 Why Electroanalysis? / 1	
1-2 Faradaic Processes / 3	
1-2.1 Mass Transport-Controlled Reactions / 4	
1-2.1.1 Potential Step Experiment / 7	
1-2.1.2 Potential-Sweep Experiments / 8	
1-2.2 Reactions Controlled by the Rate of Electron Transfer / 11	
1-2.2.1 Activated Complex Theory / 16	
1-3 The Electrical Double Layer / 18	
1-4 Electrocapillary Effect / 22	
Supplementary Reading / 25	
References / 26	
Questions / 26	
2 STUDY OF ELECTRODE REACTIONS	28
2-1 Cyclic Voltammetry / 28	
2-1.1 Data Interpretation / 30	

2-1.1.1	Reversible Systems /	31
2-1.1.2	Irreversible and Quasi-Reversible Systems /	32
2-1.2	Study of Reaction Mechanisms /	33
2-1.3	Study of Adsorption Processes /	36
2-1.4	Quantitative Applications /	39
2-2	Spectroelectrochemistry /	40
2-2.1	Experimental Arrangement /	40
2-2.2	Principles and Applications /	41
2-2.3	Other Spectroelectrochemical and Spectroscopic Techniques /	44
2-3	Scanning Probe Microscopy /	46
2-3.1	Scanning Tunneling Microscopy /	46
2-3.2	Atomic Force Microscopy /	47
2-3.3	Scanning Electrochemical Microscopy /	49
2-4	Electrochemical Quartz Crystal Microbalance /	52
	References /	54
	Examples /	56
	Questions /	59

3 CONTROLLED-POTENTIAL TECHNIQUES

60

3-1	Chronoamperometry /	60
3-2	Polarography /	62
3-3	Pulse Voltammetry /	67
3-3.1	Normal-Pulse Voltammetry /	67
3-3.2	Differential-Pulse Voltammetry /	68
3-3.3	Square-Wave Voltammetry /	72
3-3.4	Staircase Voltammetry /	74
3-4	AC Voltammetry /	74
3-5	Stripping Analysis /	75
3-5.1	Anodic Stripping Voltammetry /	76
3-5.2	Potentiometric Stripping Analysis /	79
3-5.3	Adsorptive Stripping Voltammetry and Potentiometry /	80
3-5.4	Cathodic Stripping Voltammetry /	82
3-5.5	Applications /	84
3-6	Flow Analysis /	84
3-6.1	Principles /	87
3-6.2	Cell Design /	88
3-6.3	Mass Transport and Current Response /	90
3-6.4	Detection Modes /	92

References / 94

Examples / 96

Questions / 98

4 PRACTICAL CONSIDERATIONS

100

4-1 Electrochemical Cells / 100

4-2 Solvents and Supporting Electrolytes / 102

4-3 Oxygen Removal / 103

4-4 Instrumentation / 104

4-5 Working Electrodes / 107

4-5.1 Mercury Electrodes / 108

4-5.2 Solid Electrodes / 110

4-5.2.1 Rotating Disk and Ring-Disk Electrodes / 111

4-5.2.2 Carbon Electrodes / 113

4-5.2.2.1 Glassy-Carbon Electrodes / 114

4-5.2.2.2 Carbon-Paste Electrodes / 115

4-5.2.2.3 Carbon-Fiber Electrodes / 115

4-5.2.3 Metal Electrodes / 117

4-5.3 Chemically Modified Electrodes / 118

4-5.3.1 Self-Assembled Monolayers / 118

4-5.3.2 Sol-Gel Encapsulation of Reactive Species / 120

4-5.3.3 Electrocatalytic Modified Electrodes / 121

4-5.3.4 Preconcentrating Electrodes / 121

4-5.3.5 Permselective Coatings / 123

4-5.3.6 Conducting Polymers / 124

4-5.4 Microelectrodes / 128

4-5.4.1 Diffusion at Microelectrodes / 129

4-5.4.2 Configurations of Microelectrodes / 130

4-5.4.3 Composite Electrodes / 131

References / 135

Examples / 138

Questions / 138

5 POTENTIOMETRY

140

5-1 Principles of Potentiometric Measurements / 140

5-2 Ion-Selective Electrodes / 147

5-2.1 Glass Electrodes / 147

5-2.1.1 pH Electrodes / 147

5-2.1.2	Glass Electrodes for Other Cations /	151
5-2.2	Liquid-Membrane Electrodes /	152
5-2.2.1	Ion-Exchanger Electrodes /	152
5-2.2.2	Neutral Carrier Electrodes /	154
5-2.3	Solid-State Electrodes /	156
5-2.4	Coated-Wire Electrodes /	160
5-3	On-Line and In-Vivo Potentiometric Measurements /	161
	References /	165
	Examples /	167
	Questions /	169

6 ELECTROCHEMICAL SENSORS

171

6-1	Electrochemical Biosensors /	171
6-1.1	Enzyme-Based Electrodes /	172
6-1.1.1	Impractical and Theoretical Considerations /	172
6-1.1.2	Enzyme Electrodes of Analytical Significance /	176
6-1.1.2.1	Glucose Sensors /	176
6-1.1.2.2	Ethanol Electrodes /	178
6-1.1.2.3	Urea Electrodes /	181
6-1.1.2.4	Toxin (Enzyme Inhibition) Biosensors /	181
6-1.1.3	Tissue and Bacteria Electrodes /	182
6-1.2	Affinity Biosensors /	183
6-1.2.1	Immunosensors /	183
6-1.2.2	DNA Hybridization Biosensors /	185
6-1.2.3	Receptor-Based Sensors /	186
6-2	Gas Sensors /	188
6-2.1	Carbon Dioxide Sensors /	189
6-2.2	Oxygen Electrodes /	190
6-3	Solid-State Devices /	191
6-3.1	Microfabrication of Solid-State Sensor Assemblies /	193
6-3.2	Microfabrication Techniques /	193
6-4	Sensor Arrays /	197
	References /	198
	Examples /	201
	Questions /	202

FUNDAMENTAL CONCEPTS

1-1 WHY ELECTROANALYSIS?

Electroanalytical techniques are concerned with the interplay between electricity and chemistry, namely the measurements of electrical quantities, such as current, potential, or charge, and their relationship to chemical parameters. Such use of electrical measurements for analytical purposes has found a vast range of applications, including environmental monitoring, industrial quality control, and biomedical analysis. Advances in the 1980s and 1990s—including the development of ultramicroelectrodes, the design of tailored interfaces and molecular monolayers, the coupling of biological components and electrochemical transducers, the synthesis of ionophores and receptors containing cavities of molecular size, the development of ultratrace voltammetric techniques or of high-resolution scanning probe microscopies, and the microfabrication of molecular devices or efficient flow detectors—have led to a substantial increase in the popularity of electroanalysis, and to its expansion into new phases and environments. Indeed, electrochemical probes are receiving a major share of the attention in the development of chemical sensors.

In contrast to many chemical measurements that involve homogeneous bulk solutions, electrochemical processes take place at the electrode–solution interface. The distinction between various electroanalytical techniques reflects the type of electrical signal used for the quantitation. The two principal types of electroanalytical measurements are potentiometric and potentiostatic. Both types require at least two electrodes (conductors) and a contacting sample (electrolyte) solution, which constitute the electrochemical cell. The electrode surface is thus a junction between an ionic conductor and an electronic conductor. One of the two electrodes responds

to the target analyte(s) and is thus termed the indicator (or working) electrode. The second one, termed the reference electrode, is of constant potential (that is, independent of the properties of the solution). Electrochemical cells can be classified as electrolytic (when they consume electricity from an external source) or galvanic (if they are used to produce electrical energy).

Potentiometry (discussed in Chapter 5), which is of great practical importance, is a static (zero current) technique in which the information about the sample composition is obtained from measurement of the potential established across a membrane. Different types of membrane materials, possessing different ion-recognition processes, have been developed to impart high selectivity. The resulting potentiometric probes have thus been widely used for several decades for direct monitoring of ionic species such as protons or calcium, fluoride, and potassium ions in complex samples.

Controlled-potential (potentiostatic) techniques deal with the study of charge-transfer processes at the electrode–solution interface, and are based on dynamic (no zero current) situations. Here, the electrode potential is being used to derive an electron-transfer reaction and the resultant current is measured. The role of the potential is analogous to that of the wavelength in optical measurements. Such a controllable parameter can be viewed as “electron pressure,” which forces the chemical species to gain or lose an electron (reduction or oxidation, respectively).

TABLE 1-1 Properties of Controlled-Potential Techniques

Technique ^a	Working Electrode ^b	Detection Limit (M)	Speed (time per cycle) (min)	Response Shape
DC polarography	DME	10^{-5}	3	Wave
NP polarography	DME	5×10^{-7}	3	Wave
DP polarography	DME	10^{-8}	3	Peak
DP voltammetry	Solid	5×10^{-7}	3	Peak
SW polarography	DME	10^{-8}	0.1	Peak
AC polarography	DME	5×10^{-7}	1	Peak
Chronoamperometry	Stationary	10^{-5}	0.1	Transient
Cyclic voltammetry	Stationary	10^{-5}	0.1–2	Peak
Stripping voltammetry	HMDE, MFE	10^{-10}	3–6	Peak
Adsorptive stripping voltammetry	HMDE	10^{-10}	2–5	Peak
Adsorptive stripping voltammetry	Solid	10^{-9}	4–5	Peak
Adsorptive-catalytic stripping voltammetry	HMDE	10^{-12}	2–5	Peak

^aDC = direct current; NP = normal pulse; DP = differential pulse; SW = square wave; AC = alternating current.

^bDME = dropping mercury electrode; HMDE = hanging mercury drop electrode; MFE = mercury film electrode.