ELECTROCHEMICAL METHODS

Fundamentals and Applications

THIRD EDITION

ALLEN J. BARD

LARRY R. FAULKNER

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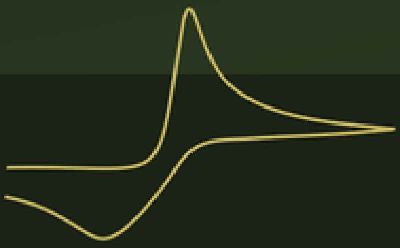

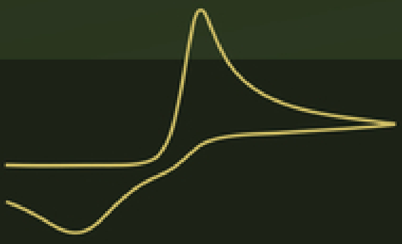

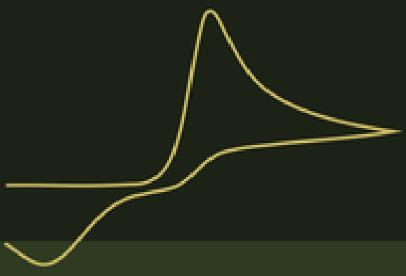

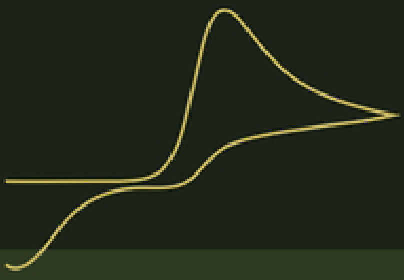

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Electrochemical Methods

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Fundamentals and Applications

Third Edition

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Preface

Since the appearance of our 1980 and 2001 editions, electrochemistry has developed remarkably. Phenomena are better understood; experimental tools have become more sophisticated; and new methods have emerged. With this new edition, we have striven to accommodate an evolved, enlarged field, while extending this book's value as a general introduction.

Our overall goal is to provide an authoritative resource for students and new practitioners, covering the core of what they now must know to be successful in research. Accordingly, the emphasis has shifted in this edition to methods that are extensively practiced and to phenomenological questions of current concern. The reconception has led to changes in scope and organization as outlined below.

Moreover, we now address a much broader audience. Electrochemistry's clear relevance to energy and environment has attracted scientists and engineers with educational backgrounds outside of chemistry and chemical engineering. The prior editions were written principally for graduate students in chemistry and for practicing researchers in electrochemistry, for whom a formal preparation through physical chemistry could be assumed. In this edition, we teach, instead, from a foundation of basic university courses in general chemistry, physics, and mathematics. We have sought to make the book self-contained by developing almost all key ideas from fundamental principles of chemistry and physics.

This volume includes numerous problems and chemical examples; illustrations are used to clarify presentations; and the style is pedagogical throughout. The book can be used in formal courses at the senior undergraduate and graduate levels, but we have also tried to write in a way that enables self-study by interested individuals in mid-career. Because we stress foundations and limits of application, the book continues to present the mathematical theory underlying methodology; however, the key ideas are consistently discussed apart from the mathematical basis. The end-of-chapter problems have been devised as teaching tools, often extending concepts introduced in the text or showing how experimental data are reduced to fundamental results. The cited literature is extensive, but mainly includes only seminal papers and reviews.

Major changes are found throughout:

- An entirely new Chapter 5 ("Steady-State Voltammetry at Ultramicroelectrodes") has been created in support of the authors' view that steady-state voltammetry is now the best starting point for the methodological sequence. Potential step methods—formerly providing the starting point—are now treated in a redesigned Chapter 6 ("Transient Methods Based on Potential Steps").
- Also completely new is Chapter 15 ("Inner-Sphere Electrode Reactions and Electrocatalysis"), giving a substantial introduction to the electrode kinetics of important complex reactions.

- A third new unit is Chapter 19 ("Single-Particle Electrochemistry"), which explores a frontier where individual elementary events come into focus.
- Chapter 1 ("Overview of Electrode Processes") has been reorganized and revised to improve its effectiveness for new readers coming into electrochemistry from diverse backgrounds.
- Chapter 3 ("Basic Kinetics of Electrode Reactions") now includes an extensive treatment of Marcus kinetics as applied to electrode reactions.
- Chapter 4 ("Mass Transfer by Migration and Diffusion") includes a fuller introduction to migration, which is now regularly encountered in the chapters on methodology.
- Chapter 11 ("Electrochemical Impedance Spectroscopy and ac Voltammetry") has a stronger focus on EIS with an expanded presentation.
- Chapter 13 ("Electrode Reactions with Coupled Homogeneous Chemical Reactions") has been streamlined using cyclic voltammetry as a consistent methodological context and including more experimental examples.
- Chapter 18 ("Scanning Electrochemical Microscopy") is now wholly dedicated to SECM and SECCM. This domain has greatly expanded since the second edition appeared in 2001.
- Chapter 21 ("*In situ* Characterization of Electrochemical Systems") has been reconceived to emphasize methods with *in situ* or *operando* capabilities.
- All other chapters have been edited toward clear, efficient presentation of current knowledge and practice.
- Finally, we have added Lab Notes to many chapters to help newcomers with the transition from concept to actual practice in the laboratory.

A goal has been to keep this book as close in size as possible to the 2001 edition. Naturally, we have deleted or abbreviated topics to make room for more current matters. In such cases, references have been provided to the corresponding passages in earlier editions, so that interested readers can still find coverage of a deleted or attenuated topic. In general, we have excluded or reduced the coverage of techniques that, while functional, are not widely practiced. Apart from what we include in the Lab Notes, laboratory procedures remain outside our intended scope.

Just after this Preface, the reader will find a convenient unit, "Major Symbols and Abbreviations," offering definitions, units, and section references. Indeed, Tables 1–5 contained in that unit comprise a functional alternative index. Table 5 identifies abbreviated chemical substances by names recognized by CAS and with references to chemical structures, most displayed in Figure 1, following Table 5. Our uses of symbols usually adhere to the recommendations of the IUPAC Commission on Electrochemistry [R. Parsons et al., *Pure Appl. Chem.*, **37**, 503 (1974)]. Exceptions have been made where customary usage or clarity of notation seemed compelling.

As with both prior editions, we owe thanks to others. Commissioning Editor Sarah Higginbotham and Managing Editor Stefanie Volk of John Wiley & Sons provided calm support and excellent judgment from start to finish. Sundaramoorthy Balasubramani was invaluable to us during the process of production. Once again, Cynthia Zoski and Johna Leddy generously agreed to prepare the "Instructor's Solutions Manual" and have often commented helpfully as we developed the book manuscript. Valuable comments or answers to queries were also provided by C. Amatore, A. Bond, F. Dalton, B. Dunn, B. Feldman, W. Geiger, P. He, W. Heineman, A. Heller, P. Kissinger, S. Lin, S. Minteer, M. Mirkin, B. Mullins, M. Neurock, D. Pletcher, H. Ren, M. Robert, L. Sombers, P. Unwin, J. Wadhawan, and F. Zamborini. The late Jean-Michel Savéant, an invaluable colleague for decades, was a helpful commentator on all three editions. He remains in our memories as a beacon of science, representing the finest of insight and quality. We thank all we have named and our many other colleagues throughout

the electrochemical community, who have taught us patiently over the years. Once more, we thank our families for affording us the time and freedom required for this large project.

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Major Symbols and Abbreviations

In five tables below are symbols and abbreviations used in several chapters or in large portions of a chapter. Similar symbols may have different local meanings. Usage normally follows the recommendations of the IUPAC Commission on Electrochemistry [R. Parsons et al., *Pure Appl. Chem.*, **37**, 503 (1974).]; however, there are exceptions.

A bar over a concentration or a current [e.g., $\overline{C}_O(x, s)$] indicates the Laplace transform of the variable. The exception is when $\bar{i}$ indicates an average current in dc polarography.

Table 1 Standard Subscripts and Superscripts.

0	standard (superscript)	dl	double layer	O	for species O in $O + e \rightleftarrows R$
a	anodic	eq	equilibrium	p	(a) peak
ads	adsorbed	f	(a) forward		(b) *p*-type carrier
c	(a) cathodic		(b) faradaic	R	(a) for species R in $O + e \rightleftarrows R$
	(b) charging	l	limiting		(b) ring
D	disk	M	metal (superscript)	r	reverse
d	diffusion	n	*n*-type carrier	S	solution (superscript)

Table 2 Roman Symbols.

Symbol	Meaning	Usual Units	Section
A	(a) area	cm^2	1.1.5
	(b) cross-sectional area of a porous electrode	cm^2	12.5.1
	(c) frequency factor in a rate constant	depends on nature and order	3.1.2
	(d) open-loop gain of an amplifier	none	16.1.1
A_{dc}	dc open-loop gain of an amplifier	none	16.1.2(*a*)
A_g	geometric area of an electrode	cm^2	6.1.5
A_m	microscopic area of an electrode	cm^2	6.1.5

(Continued)

Table 2 (Continued)

Symbol	Meaning	Usual Units	Section
a	(a) activity	none	2.1.5
	(b) internal area of a porous electrode	cm^2	12.5.1
	(c) radius of a disk-shaped tip in SECM	μm, nm	18.2
a_j	(a) activity of substance j	none	2.1.5
	(b) interaction parameter among adsorbates	none	17.2.2
a_j^α	activity of substance j in a phase α	none	2.1.5
a_p	in flow electrolysis, total open area on the face of a porous electrode	cm^2	12.5.1
b	$\alpha Fv/RT = \alpha fv$	s^{-1}	7.4.1(*a*)
b_j	for adsorption of species j, $\beta_j\Gamma_{j,\mathrm{s}}$	mol/cm^2	14.5.4
C	capacitance	F	1.6.2, 11.2
c	speed of light *in vacuo*	m/s	
C_B	series equivalent capacitance of a cell	F	11.1, 11.3
C_D	predicted differential capacitance of a diffuse layer	F, F/cm^2	14.3.2(*c*), 14.3.3
C_d	differential capacitance of the double layer	F, F/cm^2	1.6.2, 14.2.2
C_GCS	in the Gouy–Chapman–Stern model, predicted differential capacitance of the double layer	F, F/cm^2	14.3.3
C_H	predicted differential capacitance of a Helmholtz layer	F, F/cm^2	14.3.1, 14.3.3
C_i	integral capacitance of the double layer	F, F/cm^2	14.2.2
C_j	(a) concentration of species j	M, mol/cm^3	
	(b) capacitance of an electrical element j	F, F/cm^2	
C_j^*	bulk concentration of species j	M, mol/cm^3	1.3.2, 4.5.1
C_j^0	standard-state concentration of species j	M	2.1.5
$C_j(0, t)$	concentration of species j at the electrode surface at time t (linear system)	M, mol/cm^3	4.5.1(*c*)
$C_j(0, t)_\mathrm{m}$	in impedance theory, mean concentration of species j at the electrode surface at time t (linear system where $t \gg 1/\omega$)	M, mol/cm^3	11.4.1
$C_j(r)$	concentration of species j at radius r (radial system)	M, mol/cm^3	5.1.1
$C_j(r = r_0)$	concentration of species j at the electrode surface (radial system)	M, mol/cm^3	5.1.1
$C_j(r, t)$	concentration of species j at radius r at time t (radial system)	M, mol/cm^3	4.4.2
$C_j(r_0, t)$	concentration of species j at the electrode surface at time t (radial system)	M, mol/cm^3	6.1.2

Table 2 (Continued)

Symbol	Meaning	Usual Units	Section
C_j(surface)	concentration of species *j* at the electrode surface (a general symbol encompassing multiple geometries and methods)	M, mol/cm^3	5.2.5
$C_j(x)$	concentration of species *j* at distance *x* (linear system)	M, mol/cm^3	1.3.1, 4.1
$C_j(x = 0)$	concentration of species *j* at the electrode surface (linear system)	M, mol/cm^3	1.3.2
$C_j(x, t)$	concentration of species *j* at distance *x* at time *t* (linear system)	M, mol/cm^3	4.4.2
$C_j(y)$	concentration of species *j* at distance *y* away from a rotating electrode	M, mol/cm^3	10.2.2
$C_j(y = 0)$	surface concentration of species *j* at a rotating electrode	M, mol/cm^3	10.2.4
$C_j(z = 0)$	surface concentration of species *j* at a disk UME	M, mol/cm^3	5.2.2
C_s	series capacitive component of Z_f	F	11.3.1, 11.3.2(*c*)
C_g^S	in CNT, supersaturation concentration of a species in solution required to nucleate a gas bubble	M, mol/cm^3	15.6.4
C_SC	space charge capacitance	F/cm^2	20.2.1(*d*)
D, D_j	diffusion coefficient (of species *j*)	cm^2/s	1.3.1, 4.4
D_E	diffusion coefficient for electrons in a modifying layer on an electrode	cm^2/s	17.5.2(*c*)
D_e	effective diffusion coefficient for a redox couple engaged in redox cycling	cm^2/s	19.6
$D_j(\lambda, \mathbf{E})$	concentration density of states for species *j*	cm^{-3} eV^{-1}	3.5.5(*a*)
$\mathbf{D}_\mathrm{M}$	in simulation, model diffusion coefficient	none	B.1.3, B.1.8
D_S	in a modifying layer on an electrode, diffusion coefficient for the primary reactant (substrate)	cm^2/s	17.5.2(*b*)
d	(a) in AFM, SECM, or STM, distance of the tip from the substrate	µm, nm	18.1, 21.1.1
	(b) in a nanoscale redox-cycling cell, electrode separation	cm, µm, nm	19.6
d_j	density of phase *j*	kg/L, g/cm^3	
E	(a) potential of an electrode *vs.* a reference	V	1.1.2, 2.1.4
	(b) emf of a reaction	V	2.1.3
	(c) amplitude of an ac voltage	V	11.2
ΔE	(a) in DPV, pulse height	mV	8.4.2
	(b) in ac voltammetry, amplitude of ac excitation (1/2 peak-to-peak)	mV	11.5.1

(Continued)

Table 2 (Continued)

Symbol	Meaning	Usual Units	Section
$\mathbf{E}$	(a) energy	J, eV	
	(b) electron energy	eV	2.2.5, 3.5.5(*a*)
$\mathcal{E}$	electric field strength	V/cm	2.2.1
$\boldsymbol{\mathcal{E}}$	electric field strength vector	V/cm	2.2.1
$\dot{E}$	voltage or potential phasor	V	11.2
$E^0, E^0_{\mathrm{O/R}}$ $E^0(\mathrm{O/R})$	(a) standard potential of an electrode or a couple (with subscript or parentheses, of the O/R couple)	V	2.1.4
	(b) standard emf of a half-reaction (with subscript, of the O/R half-reaction)	V	2.1.4
ΔE^0	difference in standard potentials for two couples, $E^0_2 - E^0_1$	V	13.3.6(*a*)
$E^{0'}, E^{0'}_{\mathrm{O/R}}$ $E^{0'}(\mathrm{O/R})$	formal potential of an electrode or a couple (with subscript or parentheses, of the O/R couple)	V	2.1.7
$\Delta E^{0'}$	difference in formal potentials for two couples, $E^{0'}_2 - E^{0'}_1$	V	7.5.2, 13.3.6
$\mathbf{E}^{0'}$	electron energy corresponding to the formal potential of a couple	eV	3.5.5(*a*)
$E^{0\mathrm{a}}, E^{0\mathrm{a}}_{\mathrm{O/R}}$	standard potential of an electrode or a couple on the absolute scale (with subscript, of the O/R couple)	V	2.2.5(*a*)
$E_{1/2}$	(a) in voltammetry, measured or expected half-wave potential	V	1.3.2, 5.3–5.4, 6.2–6.3
	(b) in derivations for diffusing systems, the “reversible” half-wave potential, $E^{0'} + (RT/nF)\ln(D_{\mathrm{R}}^{1/2}/D_{\mathrm{O}}^{1/2})$	V	6.2.2
$E_{1/4}$	potential where $i = i_{\mathrm{d,c}}/4$ (or $i_l/4$)	V	5.3.1(*a*)
$E_{3/4}$	potential where $i = 3i_{\mathrm{d,c}}/4$ (or $3i_l/4$)	V	5.3.1(*a*)
E_{A}	activation energy of a reaction	kJ/mol	3.1.2
$\mathbf{E}_{\mathrm{A}}$	in a doped semiconductor, acceptor level	eV	20.1.3
E_{ac}	ac component of potential	mV	11, 11.4.1
E_{appl}	voltage applied at the working electrode *vs.* the reference electrode	V	1.2.2, 1.5.1, 1.6.4(*d*)
E_{b}	base potential in NPV and RPV	V	8.2.1, 8.3
$\mathbf{E}_{\mathrm{C}}$	in a solid, electron energy at the bottom of the CB (CB edge)	eV	20.2.1(*a*)
E_{D}	potential of a rotating disk electrode	V	10.3.2
$\mathbf{E}_{\mathrm{D}}$	in a doped semiconductor, donor level	eV	20.1.3