

UNDERSTANDING VOLTAMMETRY:

Problems and Solutions

伏安法教程题解

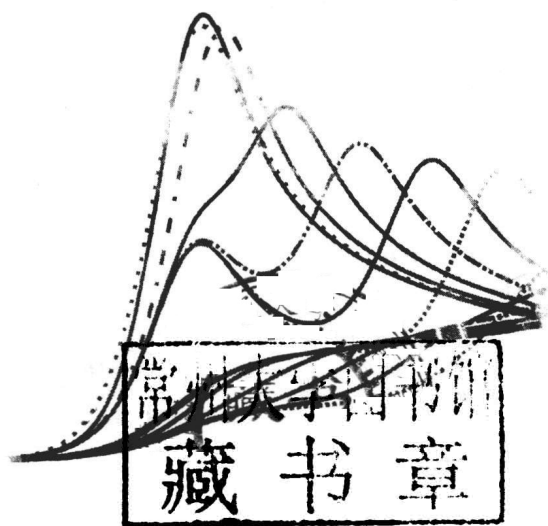
RICHARD G COMPTON
CHRISTOPHER BATCHELOR-MCAULEY
EDMUND J F DICKINSON

World Scientific

世界图书出版公司
www.wpcbj.com.cn

UNDERSTANDING VOLTAMMETRY:

Problems and Solutions



RICHARD G COMPTON
CHRISTOPHER BATCHELOR-MCAULEY
EDMUND J F DICKINSON

University of Oxford, UK

Published by

Imperial College Press
57 Shelton Street
Covent Garden
London WC2H 9HE

Distributed by

World Scientific Publishing Co. Pte. Ltd.
5 Toh Tuck Link, Singapore 596224
USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601
UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

UNDERSTANDING VOLTAMMETRY

Problems and Solutions

Copyright © 2012 by Imperial College Press

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN-13 978-1-84816-730-8

ISBN-10 1-84816-730-X

ISBN-13 978-1-84816-731-5 (pbk)

ISBN-10 1-84816-731-8 (pbk)

Reprint arranged with World Scientific Co. Pte. Ltd., Singapore.

本书由新加坡 World Scientific Publishing Co. (世界科技出版公司) 授权重印出版, 限于中国大陆地区发行。

UNDERSTANDING
VOLTAMMETRY:
Problems and Solutions

Publisher's Foreword

Understanding Voltammetry: Problems and Solutions is a companion volume to the textbook *Understanding Voltammetry 2nd Edition*, by Richard G. Compton and Craig E. Banks, published in 2011. The structure of this volume follows that of the textbook.

Understanding Voltammetry considers how to go about designing, explaining and interpreting experiments centred around various forms of voltammetry, including cyclic, microelectrode and hydrodynamic, amongst others.

The book gives clear introductions to the theories of electron transfer and of diffusion in its early chapters. These are developed to interpret voltammetric experiments at macroelectrodes before considering microelectrode behaviour. A subsequent chapter introduces convection and describes hydrodynamic electrodes. Later chapters describe the voltammetric measurement of homogeneous kinetics, the study of adsorption on electrodes and the use of voltammetry for electroanalysis.

Glossary of Symbols and Abbreviations

Roman symbols

A	area	m^2
A	Debye-Hückel constant = $0.509 \text{ mol}^{-\frac{1}{2}} \text{ kg}^{\frac{1}{2}}$	
a_i	activity of species i	
c_i	concentration of species i	mol dm^{-3}
$c_{i,0}$	surface concentration of species i	mol dm^{-3}
c^*	bulk concentration	mol dm^{-3}
D	diffusion coefficient	$(\text{cm}^2 \text{ s}^{-1})$
E	cell potential	V
$E^\ominus$	reduction potential under standard conditions	V
$E_f^\ominus$	formal reduction potential	V
F	the Faraday constant = $96485.3 \text{ C mol}^{-1}$	
G	Gibbs energy	J
$\Delta G^\ominus$	change in Gibbs energy under standard conditions	J mol^{-1}
$\Delta G^\ddagger$	activation energy	J mol^{-1}
$\Delta H^\ominus$	change in enthalpy under standard conditions	J mol^{-1}
h	height or half-height of a cell	m
I	current passed	A
I_{pf}	forward peak current	A
I	ionic strength	mol kg^{-1}
J	flux	$\text{mol m}^{-2} \text{ s}^{-1}$
K	equilibrium coefficient	

K	dimensionless rate constant	
K_a	acid dissociation constant	
K_{eq}	equilibrium coefficient (in follow-up kinetics)	
K_{sp}	solubility product	
k^0	heterogeneous rate constant	(c)m s ⁻¹
k	rate constant	
m_i	molality of species i	mol kg ⁻¹
n	number of electrons transferred	
p	pressure as a multiple of standard pressure	bar
pK_a	$\equiv -\log_{10} K_a$	
Q	reaction quotient	
Q	charge transferred	C
q_{rev}	reversible heat transferred	J mol ⁻¹
q	charge	C
R	the gas constant = 8.31447 J K ⁻¹ mol ⁻¹	
Re	the Reynolds number	
r	radius or radial coordinate	m
r_e	electrode radius	m
$\Delta S^\ominus$	change in entropy under standard conditions	J K ⁻¹ mol ⁻¹
T	temperature	K
t	time	s
t_i	transport number of species i	
V_f	volume flow rate	m ³ s ⁻¹
ν	voltammetric scan rate	V s ⁻¹
W	rotation speed	s ⁻¹
w	electrode width	m
x	linear space coordinate	m
z_i	charge number of species i	

Greek symbols

α	Butler–Volmer transfer coefficient for reduction	
β	Butler–Volmer transfer coefficient for oxidation	
Γ	surface coverage	mol (c)m ⁻²
γ_i	activity coefficient of species i	m ³ mol ⁻¹
δ	Nernst diffusion layer thickness	m
ϵ_0	the permittivity of free space = 8.854 × 10 ⁻¹² F m ⁻¹	
ϵ_s	relative permittivity or dielectric constant of a solvent	
Λ	the Matsuda–Ayabe parameter	
λ	Marcus reorganisation energy	J

μ_i	chemical potential of species i	J mol^{-1}
ν_i	stoichiometric coefficient of species i	
ν	kinematic viscosity	$\text{m}^2 \text{s}^{-1}$
ρ	density	kg m^{-3}
τ	Shoup–Szabo time coordinate $\equiv (4Dt/r_e^2)$	
ϕ	potential	V
ϕ_M	potential of a (metal) electrode	V
ϕ_s	potential of the solution phase	V
$\Delta\phi_{\text{OD}}$	ohmic drop	V
Θ	fractional surface coverage	
$\ominus$	dimensionless potential $\equiv \phi \times (F/RT)$	
θ	dimensionless overpotential $\equiv (F/RT) \times (E - E_f^\ominus)$	

Abbreviations

BDD	boron-doped diamond
BPPG	basal-plane pyrolytic graphite
EMF	electromotive force
EPPG	edge-plane pyrolytic graphite
$\text{erf}(x)$	the error function
$\text{erfc}(x)$	the complementary error function, $\equiv 1 - \text{erf}(x)$
HOPG	highly ordered pyrolytic graphite
TBAP	tetra- <i>n</i> -butylammonium perchlorate
$[i]$	concentration of species i
$[i]_0$	surface concentration of species i
$\ominus$	standard state

Contents

Publisher's Foreword	v
----------------------	---

Glossary of Symbols and Abbreviations	xiii
---------------------------------------	------

1	Equilibrium Electrochemistry and the Nernst Equation	1
1.1	Cell Thermodynamics	1
1.2	The Nernst Equation	2
1.3	The Nernst Equation	3
1.4	The Nernst Equation	5
1.5	Theory of the Nernst Equation	5
1.6	The Debye–Hückel Limiting Law	7
1.7	Cell Reaction and Equilibrium Constant	10
1.8	Cell Reaction and Equilibrium Constant	11
1.9	Cell Reaction and Solubility Product	12
1.10	Cell Reaction and pK_a	13
1.11	Cell Thermodynamics and Temperature	14
1.12	Cell Thermodynamics and Temperature	15
1.13	Cell Energetics	16
1.14	Cell EMF and pH	17
1.15	Cell Reaction and Equilibria	18
1.16	Cell Reaction and K_w	19
1.17	Cell Reaction and Disproportionation	20
1.18	Fuel Cell Energetics	21
1.19	Fuel Cell Energetics	22

1.20	The Influence of Temperature on the Self-Ionisation of Water . .	23
1.21	Cell Reaction and Complexation	24
1.22	Reference Electrodes	26
1.23	Formal Potentials	27
1.24	Formal Potentials	28
1.25	Standard Potentials and pH	29
1.26	Standard Potentials and pH	30
1.27	Standard Potentials and pH	31
2	Electrode Kinetics	35
2.1	Faraday's Laws of Electrolysis	35
2.2	Electrodeposition	36
2.3	Tafel Analysis: One-Electron Processes	39
2.4	Tafel Analysis: Electrochemically Reversible Processes	39
2.5	Tafel Analysis: Mass Transport Correction	41
2.6	Tafel Analysis: Two-Electron Processes	42
2.7	The Butler–Volmer Equation and the Nernst Equation	45
2.8	The Hydrogen Evolution Reaction	46
2.9	Requirement for Supporting Electrolyte	47
2.10	Frumkin Corrections	49
2.11	Marcus Theory and Standard Electrochemical Rate Constants . .	51
2.12	Marcus Theory and Butler–Volmer Kinetics	52
2.13	Marcus Theory and the Role of Solvent	54
2.14	Marcus Theory and the Inverted Region	55
3	Diffusion	57
3.1	Fick's Laws of Diffusion	57
3.2	Fick's Laws of Diffusion	58
3.3	Diffusion Distances	59
3.4	The Cottrell Equation	60
3.5	Derivation of the Cottrell Equation	62
3.6	Diffusion and Root-Mean-Square Displacement	66
4	Cyclic Voltammetry at Macroelectrodes	67
4.1	Cyclic Voltammetry: Electrochemically Reversible Voltammetry	67
4.2	Cyclic Voltammetry: Electrochemically Irreversible Voltammetry	69
4.3	Reversible vs Irreversible Voltammetry	71
4.4	Voltammetric Diagnostics	72
4.5	Voltammetry and Scan Rate Effects	73

4.6	Ferrocene Voltammetry	75
4.7	Ferrocene Voltammetry	75
4.8	Features of Cyclic Voltammograms	76
4.9	Derivation of the Randles–Ševčík Equation	77
4.10	Reversible Two-Electron Transfer	81
4.11	The Influence of pH on Cyclic Voltammetry	82
4.12	The Scheme of Squares	84
4.13	The EE-Comproportionation Mechanism	86
5	Voltammetry at Microelectrodes	91
5.1	Steady-State Concentration Profile in Spherical Space	91
5.2	Current Transients at a Spherical Electrode	93
5.3	Linear vs Convergent Diffusion	94
5.4	Dissolution of Microparticles	95
5.5	Steady-State Limiting Current at a Microdisc	97
5.6	Microdisc vs Planar Electrode	98
5.7	The Shoup–Szabo Equation	98
5.8	Steady-State Electrolysis	100
5.9	Effect of Unequal Diffusion Coefficients	101
5.10	Temperature Effects on Steady-State Currents	101
5.11	ECE Mechanism at a Microdisc Electrode	103
5.12	EC' Mechanism at a Microdisc Electrode	105
5.13	Size Effects on Half-Wave Potentials	106
5.14	Extracting Parameters from Microdisc Chronoamperometry	107
5.15	Extracting Parameters from Microdisc Chronoamperometry	109
6	Voltammetry at Heterogeneous Surfaces	111
6.1	Graphitic Electrodes	111
6.2	Carbon Nanotubes and Their Reactivity	113
6.3	Highly Ordered Pyrolytic Graphite and the Influence of Defects	114
6.4	Advantages of Arrays	115
6.5	Diffusional 'Cases'	116
6.6	Geometry of a Regular Array	117
6.7	Analysis of Diffusion to Electrode Arrays	119
6.8	Partially Blocked Electrodes	121
7	Cyclic Voltammetry: Coupled Homogeneous Kinetics and Adsorption	123
7.1	EE Mechanism and Comproportionation	123
7.2	EE mechanism: The Reduction of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}][\text{BF}_4]_2$	124

7.3	EC ₂ Mechanism: The Reduction of the 2,6-Diphenyl Pyrylium Cation	126
7.4	Analysis of an Unknown Reaction Mechanism	128
7.5	EC Mechanism: Diethyl Maleate	130
7.6	ECE Mechanism: <i>p</i> -chlorobenzonitrile	133
7.7	ECE vs DISP 1: Voltammetry of Fluorescein	135
7.8	Reduction of Anthracene in DMF	137
7.9	CE Mechanism	140
7.10	EC' Mechanism	142
7.11	EC' Mechanism: Cysteine and Ferrocyanide	143
7.12	EC' Mechanism: Oxygen and Anthraquinone	145
7.13	Chronoamperometry of Adsorbed Species	146
7.14	Voltammetry of an Ideal Adsorbed Species	147
7.15	Non-Ideal Adsorbed Species	150
7.16	Irreversible Electron Transfer and Adsorbed Redox Species	153
7.17	Voltammetry of Ferrocyanide/Ferricyanide	157
8	Hydrodynamic Electrodes	159
8.1	Channel Electrodes and Limiting Currents	159
8.2	Channel Electrodes and Reynolds Number	160
8.3	Flow to Rotating Discs and in Channels	161
8.4	Channel Electrodes and ECE Processes	162
8.5	Channel Electrodes and ECE Processes	164
8.6	Channel Electrodes and Entry Length	167
8.7	Channel Electrodes and Diffusion Coefficients	167
8.8	Channel Electrodes and Current Distribution	169
8.9	Wall-Jet Electrodes and Current Distribution	170
8.10	Wall-Jet Electrodes and Diffusion Coefficients	170
8.11	Wall-Jet Electrode and a DISP 1 Process	172
8.12	Wall-Jet Electrode and EC Processes	173
8.13	Sono-Voltammetry	177
8.14	Rotating Disc Electrodes and Reynolds Number	178
8.15	Wall-Jet and Rotating Disc Electrodes	178
8.16	Rotating Disc Electrodes and ECE Processes	180
9	Voltammetry for Electroanalysis	183
9.1	Electrochemical Sizing of Gold Surfaces	183
9.2	Differential Pulse Voltammetry	185
9.3	Square-Wave Voltammetry	186
9.4	Square-Wave Voltammetry and Dissolved Oxygen	187
9.5	Stripping Voltammetry	188

9.6	Analysis of DNA	189
9.7	The Clark Cell	191
9.8	Calibration and Limits of Detection	193
9.9	Enzyme Electrodes	195
9.10	Glucose Biosensors	196
9.11	Detection of Vitamin B ₁₂	198
9.12	The Anodic Stripping Voltammetry of Industrial Effluent	200
9.13	Adsorptive Stripping Voltammetry at Carbon Nanotube Modified Electrodes	202
9.14	Surface Modified Electrodes	205
9.15	Electron Transfer Rates at Carbon Electrodes	208
10	Voltammetry in Weakly Supported Media: Migration and Other Effects	211
10.1	Coulomb's Law	211
10.2	The Nernst–Planck Equation	212
10.3	Migration and the Electric Field	215
10.4	Transport Numbers and Liquid Junction Potentials	217
10.5	Transport Numbers and the Hittorf Method	220
10.6	The Gouy–Chapman Equation	221
10.7	Ohmic Drop	225
10.8	The Zero-Field Approximation	227
10.9	Self-Supported Reduction of the Cobaltocenium Cation	228
11	Voltammetry at the Nanoscale	233
11.1	Debye Length vs Diffusion Layer Thickness	233
11.2	Altered Electrode Kinetics and Reactivity at the Nanoscale	235
11.3	Nanoparticles: Case 4 Behaviour	236
11.4	'Coulomb Staircase' Effects	238
11.5	Ultrafast 'Single Molecule' Voltammetry	239
11.6	Thin-Layer Effects in Nanoscale Voltammetry	242
11.7	Voltammetry in a Nanochannel	244
	Index	249

