ELECTROCHEMISTRY

Principles, Methods, and Applications

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PREFACE

Electrochemistry has undergone significant transformations in the last few decades. It is not now the province of academics interested only in measuring thermodynamic properties of solutions or of industrialists using electrolysis or manufacturing batteries, with a huge gulf between them. It has become clear that these two, apparently distinct subjects, and others, have a common ground and they have grown towards each other, particularly as a result of research into the rates of electrochemical processes. Such an evolution is due to a number of factors, but principally the possibility of carrying out reproducible, dynamic experiments under an ever-increasing variety of conditions with reliable and sensitive instrumentation. This has enabled many studies of a fundamental and applied nature to be carried out.

The reasons for this book are twofold. First to show the all-pervasive and interdisciplinary nature of electrochemistry, and particularly of electrode reactions, through a description of modern electrochemistry. Secondly to show to the student and the non-specialist that this subject is not separated from the rest of chemistry, and how he or she can use it. Unfortunately, these necessities are, in our view, despite efforts over recent years, still very real.

The book has been organized into three parts, after Chapter 1 as general introduction. We have begun at a non-specialized, undergraduate level and progressed through to a relatively specialized level in each topic. Our objective is to transmit the essence of electrochemistry and research therein. It is intended that the chapters should be as independent of one another as possible. The sections are: Chapters 2–6 on the thermodynamics and kinetics of electrode reactions, Chapters 7–12 on experimental strategy and methods, and Chapters 13–17 on applications. Also included are several appendices to explain the mathematical basis in more detail. It is no accident that at least 80 per cent of the book deals with current–voltage relations, and not with equilibrium. The essence of any chemical process is change, and reality reflects this.

We have not filled the text with lots of details which can be found in the references given, and, where appropriate, we make ample reference to recent research literature. This is designed to kindle the enthusiasm and interest of the reader in recent, often exciting, advances in the topics described.

A major preoccupation was with notation, given the traditionally different type of language that electrochemists have used in relation to other branches of chemistry, such as exchange current which measures rate constants, and given differences in usage of symbols between different branches of electrochemistry. Differences in sign conventions are another way of confusing the unwary beginner. We have decided broadly to follow IUPAC recommendations.

Finally some words of thanks to those who have helped and influenced us throughout our life as electrochemists. First to Professor W. J. Albery FRS, who introduced us to the wonders of electrochemistry and to each other. Secondly to our many colleagues and students who, over the years, with their comments and questions, have aided us in deepening our understanding of electrochemistry and seeing it with different eyes. Thirdly to anonymous referees, who made useful comments based on a detailed outline for the book. And last, but not least, to Oxford University Press for its interest in our project and enabling us to bring it to fruition.

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Notation and Units

As far as possible without straying too far from common usage, the guidelines of IUPAC have been followed, described in *Quantities, units and symbols in physical chemistry* (Blackwell, Oxford, 1988). Other, more detailed information has been taken from the following sources in the IUPAC journal, *Pure and Applied Chemistry:*

> 'Electrode reaction orders, transfer coefficients and rate constants. Amplification of definitions and recommendations for publication of parameters', 1979, **52,** 233.
>
> 'Interphases in systems of conducting phases', 1986, **58,** 454.
>
> 'Electrochemical corrosion nomenclature', 1989, **61,** 19.
>
> 'Terminology in semiconductor electrochemistry and photoelectrochemical energy conversion', 1991, **63,** 569.
>
> 'Nomenclature, symbols, definitions and measurements for electrified interfaces in aqueous dispersions of solids', 1991, **63,** 896.

The units quoted are those recommended. In practice, in electrochemistry, much use is made of sub-multiples: for example, cm instead of m and μA or mA instead of A, for obvious reasons. The text tends to use the commonly employed units.

In the list of symbols, those used at only one specific point in the text are mostly omitted, in order to try and reduce the length of the list, since explanation of their meaning can be found next to the relevant equation. We have also provided a list of frequently used subscripts, a list of abbreviations, and values of important constants and relations derived from these.

Following recommended usage, $\log_e$ is written as ln and $\log_{10}$ is written as lg.

Notation: main symbols

		Units
a	activity	—
a	nozzle diameter of impinging jet	m
a	radius of colloidal particle	m
A	area	m^2
A	'constant'	varies
b	Tafel slope	V^{-1}
c	concentration	$mol\ m^{-3}$
c_0	concentration at electrode surface	
c_∞	bulk concentration	
C	capacity	F
C_d	differential capacity of double layer	
C_i	integral capacity of double layer	
C_s	capacity in RC series combination	
C_{sc}	capacity of semiconductor space–charge layer	
D	diffusion coefficient	$m^2\ s^{-1}$
e	electron charge	C
$\mathbf{E}$	electric field strength	$V\ m^{-1}$
E	electrode potential	V
$E^\ominus$	standard electrode potential	
$E^{\ominus\prime}$	formal potential	
E_{cell}	cell potential (electromotive force)	
E_{cor}	corrosion potential	
$E_{1/2}$	half-wave potential	
E_j	liquid junction potential	
E_m	membrane potential	
E_p	peak potential	
E_z	potential of zero charge	
E_λ	inversion potential in cyclic voltammetry	
E_c	lowest energy of semiconductor conduction band	eV
E_g	bandgap energy in semiconductor	eV
E_v	highest energy of semiconductor valence band	eV
E_F	Fermi energy	eV
E_{redox}	energy of redox couple	eV
f	frequency	Hz
f	$F(E - E^\ominus)/RT$	—

f_{DL}	Frumkin double layer correction	—
F	force	N
g	acceleration due to gravity	$\mathrm{m\,s^{-2}}$
g	constant in Temkin and Frumkin isotherms	—
G	Gibbs free energy	$\mathrm{J\,mol^{-1}}$
h	height	m
H	enthalpy at constant pressure	$\mathrm{J\,mol^{-1}}$
I	electric current	A
I_{c}	capacitative current	
I_{f}	faradaic current	
I_{l}	diffusion limited current	
I_{p}	peak current	
I	ionic strength	$\mathrm{mol\,m^{-3}}$
j	electric current density	$\mathrm{A\,m^{-2}}$
J	volume flux	$\mathrm{m^3\,s^{-1}}$
k	rate constant: homogeneous first order	$\mathrm{s^{-1}}$
	rate constant: heterogeneous	$\mathrm{m\,s^{-1}}$
k_{a}	rate constant for oxidation at electrode	
k_{c}	rate constant for reduction at electrode	
k_{d}	mass transfer coefficient	
$k_{i,j}^{\mathrm{pot}}$	potentiometric selectivity coefficient	—
K	equilibrium constant	—
l	length of electrode	m
m	mass	kg
m_{l}	mass flux of liquid	$\mathrm{kg\,s^{-1}}$
m	molality	$\mathrm{kg\,m^{-3}}$
n	number of electrons transferred	—
n'	number of electrons transferred in rate determining step	—
n_i	number density of species i	$\mathrm{m^{-3}}$
p	$(D_{\mathrm{O}}/D_{\mathrm{R}})^s$ where $s = 1/2$ (stationary electrodes and DMEs), $s = 2/3$ (hydrodynamic electrodes), $s = 1$ (microelectrodes)	—
p_i	partial pressure of i	Pa
P	pressure (total)	Pa
Pe	Peclet number ($Pe = vl/D$)	—
Q	electric charge	C
r	radial variable	m
r_0	radius of (hemi-)spherical electrode	
r_1	radius of disc electrode	
r_2	inner radius of ring electrode	
r_3	outer radius of ring electrode	
r_{c}	capillary radius	

R	resistance	Ω
	R_{ct} charge transfer resistance	
	R_s resistance in RC series combination	
	R_{Ω} cell solution resistance	
R	radius of tube	m
Re	Reynolds number ($Re = vl/\nu$)	—
S	entropy	$\mathrm{J\ mol^{-1}\ K^{-1}}$
Sc	Schmidt number ($Sc = \nu/D$)	—
Sh	Sherwood number ($Sh = k_d l/D$)	—
t	time	s
t_i	transport number of species i	—
T	temperature	K
u_i	mobility of species i	$\mathrm{m^2\ V^{-1}\ s^{-1}}$
	u_e electrophoretic mobility	
U	potential (same meaning as E, used in photo- and semiconductor electrochemistry)	V
	U_{fb} flat-band potential	
v	velocity	$\mathrm{m\ s^{-1}}$
v	potential scan rate	$\mathrm{V\ s^{-1}}$
V	voltage (in operational amplifiers, etc.)	V
V	volume	$\mathrm{m^3}$
V_f	volume flow rate	$\mathrm{m^3\ s^{-1}}$
W	rotation speed	Hz
x	distance	m
X	reactance	Ω
Y	admittance	S
z	ion charge	—
Z	impedance	Ω
	Z_s impedance of RC series combination	
	Z' real part of impedance	
	Z'' imaginary part of impedance	
	Z_f Faradaic impedance	
	Z_w Warburg impedance	

α	electrochemical charge transfer coefficient	—
	α_a anodic	
	α_c cathodic	
α	electrode roughness parameter	—
α	double hydrodynamic electrode geometric constant	—
β	double hydrodynamic electrode geometric constant	—
β	Esin–Markov coefficient	—
β	energetic proportionality coefficient	—

γ	activity coefficient	—
γ	surface tension	$\mathrm{N\,m^{-1}}$
γ	dimensionless concentration variable	—
Γ	surface excess concentration	$\mathrm{mol\,m^{-2}}$
δ	diffusion layer thickness	m
δ_H	hydrodynamic boundary layer thickness	m
ϵ	molar absorption coefficient	$\mathrm{m^2\,mol^{-1}}$
ϵ	permittivity	$\mathrm{F\,m^{-1}}$
ϵ_0	permittivity of vacuum	$\mathrm{F\,m^{-1}}$
ϵ_r	relative permittivity	—
ϵ	porosity of material	—
ζ	zeta (electrokinetic) potential	V
ζ	$(nF/RT)(E - E_{1/2})$	—
η	overpotential	V
η	viscosity	Pa s
θ	contact angle	
θ	fractional surface coverage	—
θ	$\exp[(nF/RT)(E - E^{\ominus})]$	—
κ	conductivity	$\mathrm{S\,m^{-1}}$
λ	value of t where sweep is inverted in cyclic voltammetry	s
Λ	molar conductivity	$\mathrm{S\,m^2\,mol^{-1}}$
μ	chemical potential	$\mathrm{J\,mol^{-1}}$
$\bar{\mu}$	electrochemical potential	$\mathrm{J\,mol^{-1}}$
ν	frequency of electromagnetic radiation	$\mathrm{s^{-1}}$
ν	stoichiometric number	—
ν	kinematic viscosity	$\mathrm{m^2\,s^{-1}}$
ρ	resistivity	Ω m
ρ	density	$\mathrm{kg\,m^{-3}}$
σ	surface charge density	$\mathrm{C\,m^{-2}}$
σ	$v(nF/RT)$	$\mathrm{s^{-1}}$
σ	mass-transport dependent expression (Table 8.2)	
τ	characteristic time in experiment	s
ϕ	electrostatic potential	V
ϕ	inner electric potential	V
ϕ	phase angle	
χ	surface electric potential	V
ψ	outer electric potential	V
ω	angular velocity, rotation speed	$\mathrm{rad\,s^{-1}}$
ω	circular frequency	$\mathrm{rad\,s^{-1}}$

Subscripts

a	anodic
c	cathodic
C	capacitive
det	detector electrode
D	disc electrode
f	faradaic
f	final value
gen	generator electrode
i	species *i*
i	initial value
L	diffusion-limited value
max	maximum value
min	minimum value
O	oxidized species
p	peak value
R	reduced species
R	ring electrode
0	at zero distance (electrode surface)
∞	at infinite distance (bulk solution)
*	at OHP

Abbreviations

AES	Auger electron spectroscopy
AFM	atomic force microscopy
ASV	anodic stripping voltammetry
AdSV	adsorptive stripping voltammetry
BLM	bilayer lipid membrane
CDE	channel double electrode
CE	electrode process involving chemical followed by electrochemical step
C'E	catalytic electrode process involving chemical followed by electrochemical step
CV	cyclic voltammetry
DDPV	differential double pulse voltammetry
DISP	electrode process involving electrochemical followed by chemical, followed by disproportionation step to regenerate reagent
DME	dropping mercury electrode
DNPV	differential normal pulse voltammetry
DPV	differential pulse voltammetry
DSA	dimensionally stable anode
EC	electrode process involving electrochemical followed by chemical step
ECE	electrode process involving electrochemical followed by chemical, followed by electrochemical step
ECL	electrochemiluminescence
ECMS	electrochemical mass spectroscopy
EELS	electron energy loss spectroscopy
EMIRS	electrochemically modulated infrared spectroscopy
EQCM	electrochemical quartz crystal microbalance
ESR	electron spin resonance
EXAFS	extended X-ray absorption fine structure
FFT	fast Fourier transform
GC	glassy carbon
HMDE	hanging mercury drop electrode
HOPG	highly oriented pyrolytic graphite
HPLC	high-performance liquid chromatography
IHP	inner Helmholtz plane

IRRAS	infrared reflection absorption spectroscopy
ISE	ion-selective electrode
ISFET	ion-selective field effect transistor
ISM	ion-selective membrane
LEED	low-energy electron diffraction
LSV	linear sweep voltammetry
MCFC	molten carbonate fuel cell
MS	mass spectrometry
NHE	normal hydrogen electrode
NPV	normal pulse voltammetry
OA	operational amplifier
OHP	outer Helmholtz plane
OTE	optically transparent electrode
OTTLE	optically transparent thin-layer electrode
PAFC	phosphoric acid fuel cell
PAS	photoacoustic spectroscopy
PSA	potentiometric stripping analysis
QCM	quartz crystal microbalance
RDE	rotating disc electrode
RHEED	reflection high-energy electron diffraction
RRDE	rotating ring-disc electrode
SCC	stress corrosion cracking
SCE	saturated calomel electrode
SCM	surface compartment model
SECM	scanning electrochemical microscopy
SEM	scanning electron microscopy
SHG	second harmonic generation
SICM	scanning ion conductance microscopy
SIMS	secondary ion mass spectroscopy
SMDE	static mercury drop electrode
SNIFTRS	subtractively normalized interfacial Fourier transform infrared spectroscopy
SOFC	solid oxide fuel cell
STM	scanning tunnelling microscopy
SWV	square wave voltammetry
TDE	tube double electrode
TEM	transmission electron microscopy
WJRDE	wall-jet ring-disc electrode
XANES	X-ray absorption near edge structure
XPS	X-ray photoelectron spectroscopy

Fundamental physical constants

c	speed of light in vacuum	2.99792458×10^{8} m s^{-1}
e	unit of electron charge	1.602177×10^{-19} C
F	Faraday constant	9.6485×10^{4} C mol^{-1}
k_B	Boltzmann constant	1.38066×10^{-23} J K^{-1}
R	gas constant	8.31451 J K^{-1} mol^{-1}
h	Planck constant	6.62608×10^{-34} Js
N_A	Avogadro constant	6.02214×10^{23} mol^{-1}
ϵ_0	permittivity of vacuum	8.85419×10^{-12} J^{-1} C^{2} m^{-1}
g	acceleration due to gravity	9.80665 m s^{-2}

Mathematical constants

π	3.14159265359
e	2.71828182846
ln 10	2.302585

Useful relations at 25°C (298.15 K) involving fundamental constants

RT/F	25.693 mV
(RT/F) ln 10	59.160 mV
$k_B T$	25.7 meV (4.12×10^{-21} J)

CONTENTS

PART I Principles