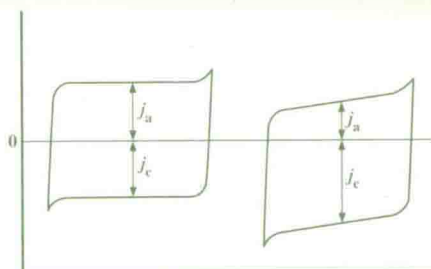
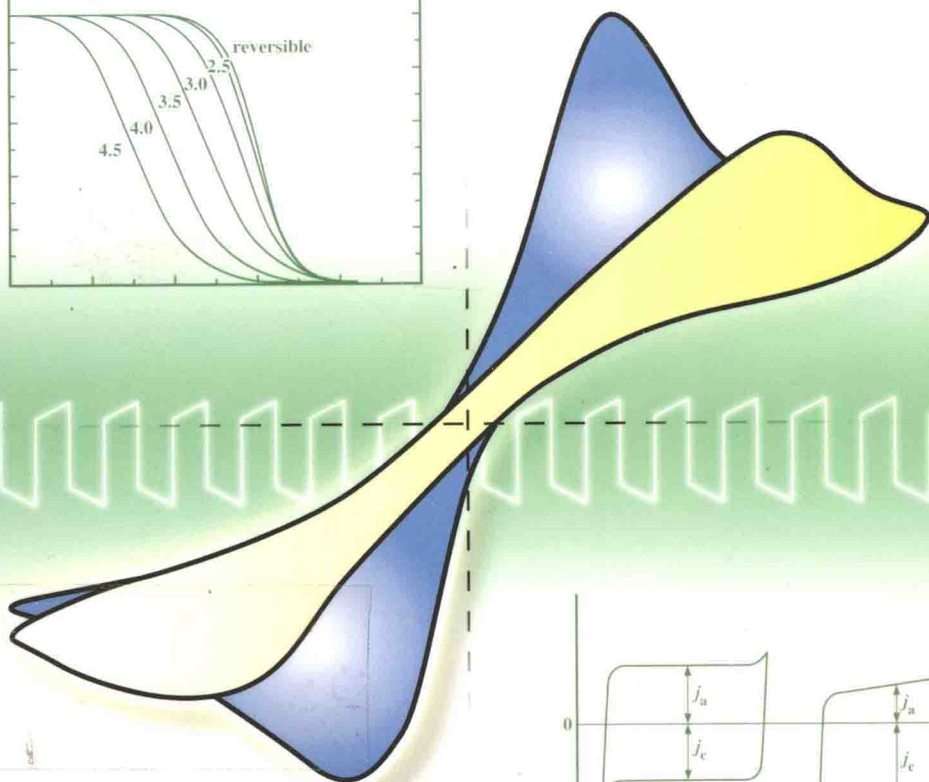
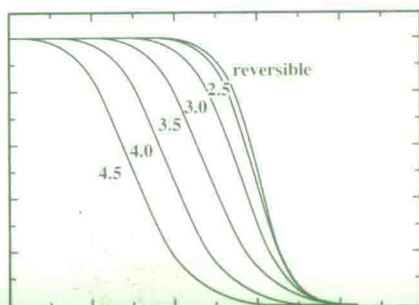


Eliezer Gileadi

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Fundamentals, Techniques and Applications



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Fundamentals, Techniques and Applications



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Preface

Interfacial electrochemistry is a multi-disciplinary subject. Its core is the study of the mechanism of electron transfer and the theory of the double layer capacitance at the metal/solution interface, but it is related to many aspects of fundamental chemistry, biology and engineering, as well as to applied science. There are many applications of electrochemistry in industry, such as metal winning of Al and Mg, the production of chlorine, electroforming, electromachining and electropolishing, electro-organic synthesis, biosensors, corrosion protection, electroplating, batteries and fuel cells.

In spite of its importance, interfacial electrochemistry is rarely, if ever, included in the undergraduate curriculum of chemistry or chemical engineering in universities around the world. There are several texts that can be used for a graduate course in the field, but none that could be classified as a textbook, upon which such a course could be based.

The purpose of the present book is to satisfy this need. The book starts by covering the basic subjects of interfacial electrochemistry. This is followed by a description of some of the most important techniques (such as cyclic voltammetry, the rotating disc electrode, electrochemical impedance spectroscopy, and the electrochemical quartz-crystal microbalance). Finally, there is a rather detailed discussion of electroplating (including alloy deposition), corrosion, and electrochemical energy conversion devices (batteries, fuel cells and super-capacitors).

Admittedly, the book contains more than could be taught in one semester. This is deliberate, in order to allow some choice for the teacher to concentrate on aspects of the field that fit best the needs of the particular class. However, even covering one half or two thirds of the material in this book should provide students with some understanding of interfacial electrochemistry, the techniques applied, and at least one of the technologies of particular interest for them, and facilitate the learning and understanding of some specific subject which may be needed later in his or her professional life.

This book is also recommended as a text suitable for self-learning, which could be used to introduce scientists and engineers, who have not had an opportunity to participate in a formal course on interfacial electrochemistry, to aspects of this field needed for their research and development.

There are different criteria by which the quality of a textbook could be judged. From my own point of view, the success or failure of this book will be judged by its ability to enhance and spread the teaching of interfacial electrochemistry, and establish it as the basis for graduate courses offered widely in universities around the world.

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Dedication

Dedicated to my wife Dalia, for her love, continued support, encouragement and patience. Without her, my scientific career would not be what it is and this book would not have been written.

Abbreviations

AC	alternating current
ASV	anodic stripping voltammetry
CE	counter electrode
CV	cyclic voltammetry
CVD	chemical vapour deposition
DC	direct current
DME	dropping mercury electrode
DMFC	direct methanol fuel cell
DP	differential pulse (polarography)
EC	ethylene carbonate
EDS	electron dispersive spectroscopy
EIS	electrochemical impedance spectroscopy
EQCM	electrochemical quartz-crystal microbalance
ETE	electric-to-electric
FE	Faradaic efficiency
HER	hydrogen-evolution reaction
HTSO	high-temperature solid-oxide (fuel cell)
ICE	internal combustion engine
IHP	inner Helmholtz plane
LPSV	linear potential sweep voltammetry
LSV	linear sweep voltammetry
MEMS	micro-electrical mechanical systems
mpy	thousandth of an inch per year (corrosion rate)
NP	normal pulse (polarography)
OHP	outer Helmholtz plane
PAFC	phosphoric acid fuel cell
PC	propylene carbonate
PEM	polymer electrolyte membrane
PVD	physical vapour deposition
PZC	potential of zero charge (E_2)
RConeE	rotating cone electrode
RCylE	rotating cylinder electrode

RDE	rotating disc electrode
rds	rate-determining step
RE	reference electrode
RHE	reversible hydrogen electrode
RRDE	rotating ring–disc electrode
RT	room temperature
SASV	subtractive anodic stripping voltammetry
SDME	static dropping mercury electrode
SEI	solid electrolyte interface
SHE	standard hydrogen electrode
SW	square-wave polarography
TP	throwing power
UPD	underpotential deposition
WE	working electrode
XPS	X-ray photoelectron spectroscopy

Symbols

a	activity	mol.cm^{-3}
A	affinity	J mol^{-1}
A	surface area	cm^2
b	Tafel slope	V decad^{-1}
c_b	bulk concentration	mol cm^{-3}
c_s	concentration at the surface ($x=0$)	mol cm^{-3}
C_{dl}	double-layer capacitance	$\mu\text{F cm}^{-2}$
C_ϕ	adsorption pseudo-capacitance	$\mu\text{F cm}^{-2}$
C_L	adsorption pseudo-capacitance (based on the Langmuir isotherm)	$\mu\text{F cm}^{-2}$
C_F	adsorption pseudo-capacitance (based on the Frumkin isotherm)	$\mu\text{F cm}^{-2}$
C_H (C_{M-S})	Helmholtz double-layer capacitance	$\mu\text{F cm}^{-2}$
$C_{G,C}$ (C_{2-S})	diffuse double-layer capacitance	$\mu\text{F cm}^{-2}$
d	Distance between the tip of the Luggin capillary and the working electrode	cm
D	diffusion coefficient	$\text{cm}^2 \text{s}^{-1}$
E	potential	Volt
\bar{E}	rational potential ($E-E_z$)	Volt
$E_{1/2}$	half-wave potential (in polarography)	Volt
E_b	breakdown potential (of passivity)	Volt
E_{pp}	primary passivation potential	Volt
E_{rev}	reversible potential	Volt
E_{rp}	re-passivation potential	Volt
E_z	potential of zero charge	Volt
E_-/E_+	potential with respect to a reference electrode that is reversible with respect to the anion/cation in solution	Volt
ΔE_{UPD}	difference between the reversible and the peak potentials during UPD formation	Volt
$\Delta E_{1/2}$	the width of the peak at half height (UPD)	Volt

E^0	standard potential	Volt
E_0^0	the standard potential for UPD formation	Volt
F	Faradays constant (96,485)	Coulomb
\vec{F}	electrostatic field	V m^{-1}
f	the Frumkin lateral interaction parameter	dimensionless
f_0	resonance frequency of a quartz-crystal microbalance	Hertz
Δf	change of the resonance frequency of a quartz-crystal microbalance	sec^{-1}
G	Gibbs energy	J mol^{-1}
ΔG	change of the Gibbs energy (in a reaction)	J mol^{-1}
$\Delta \bar{G}$	change of the electrochemical Gibbs energy	J mol^{-1}
ΔG_{ads}	Gibbs energy of adsorption	J mol^{-1}
$\Delta G^{0\#}$	standard Gibbs energy of activation	J mol^{-1}
$\Delta \bar{G}^{0\#}$	standard electrochemical Gibbs energy of activation	J mol^{-1}
ΔG_{hydr}	Gibbs energy of hydration (of an ion)	J mol^{-1}
$\Delta \bar{H}^{0\#}$	standard electrochemical enthalpy of activation	J mol^{-1}
h	Plank constant 6.6261×10^{-34}	J s
h	roughness parameter	μm
I	current	Amper
$\text{Im}Z/\text{Re}Z$	imaginary/real part of the double layer impedance	Ohm
j	current density	A cm^{-2}
j_{ac}	activation-controlled current density	A cm^{-2}
j_0	exchange current density	A cm^{-2}
j_{L}	limiting current density	A cm^{-2}
k	rate constant	$\text{mol cm}^3 \text{s}^{-1}$
$k_{\text{s,h}}$	standard heterogeneous rate constant	cm s^{-1}
k_{B}	Boltzmann constant 1.38065×10^{-23}	J degree^{-1}
$k_{\text{f}}/k_{\text{b}}$	forward/backward rate constant (heterogeneous)	cm s^{-1}
K	equilibrium constant	dimensionless
M	molecular weight	gram mol^{-1}
N	rotation rate	rpm
N_{A}	Avogadro number 6.022×10^{23}	mol^{-1}
n	number of electrons transferred per molecule	dimensionless
nF	charge transferred per mol	Coulomb mol^{-1}
P	pressure	Atm., Pascal
Q	charge	Coulomb
q_{F}	Faradaic charge	Coulomb
q_1	surface charge density for $\theta = 1$	Coulomb cm^{-2}
q_{M}	excess surface charge density	Coulomb cm^{-2}
R_{ct}	charge-transfer resistance	Ohm cm^2
$\text{Re}Z/\text{Im}Z$	real/imaginary part of the double layer impedance	Ohm cm^2

R_F	Faradaic resistance	Ohm cm^2
R_p	polarization resistance (in corrosion)	Ohm cm^2
R_s	uncompensated solution resistance	Ohm cm^2
Re	Reynolds number	dimensionless
r	rate of change of the Gibbs energy of adsorption with coverage	J mol^{-1}
TP	throwing power	dimensionless
t	time	sec.
U_{hydr}	hydration energy of ions	J mol^{-1}
v	velocity	m s^{-1}
v	heterogeneous reaction rate	$\text{mol s}^{-1} \text{cm}^{-2}$
v	rate of potential sweep	V s^{-1}
v_{equi}	exchange rate (at equilibrium)	$\text{mol s}^{-1} \text{cm}^{-2}$
W	Warburg impedance (diffusion)	Ohm cm^2
W_a	Wagner number (in electroplating)	dimensionless
z	charge number, valency	dimensionless
Z	impedance	Ohm
$\alpha_{\text{an}}/\alpha_{\text{c}}$	anodic/cathodic transfer coefficient	dimensionless
β	symmetry factor	dimensionless
Γ	surface excess, surface concentration	mol cm^{-2}
Γ	imaginary part of the response of the EQCM	Hertz (s^{-1})
Γ'	relative surface excess	mol cm^{-2}
Γ_{max}	maximum surface excess, (full coverage)	mol cm^{-2}
γ	activity coefficient	dimensionless
γ	surface tension/excess surface Gibbs energy	$\text{N m}^{-1}/\text{J m}^{-2}$
δ	Nernst diffusion-layer thickness	μm
δ	thickness of the Helmholtz double layer	nm
ϵ_0	permittivity of free space 8.8542×10^{-12}	$\text{Coul}^2 \text{N}^{-1} \text{m}^{-2}$
ϵ	dielectric constant	dimensionless
η	viscosity	cP
η	overpotential	Volt
$\eta_{\text{ac}}/\eta_{\text{conc}}/\eta_{\text{R}}$	activation/concentration/resistance overpotential	Volt
θ	fractional surface coverage ($\Gamma/\Gamma_{\text{max}}$)	dimensionless
Θ	ratio of surface concentrations $[c_{\text{Ox}}(0; t)/c_{\text{Red}}(0; t)]$	dimensionless
κ	specific conductivity	S cm^{-1}
λ	solvent reorganization energy	J mol^{-1}
λ	dimensionless rate constant ($\lambda \equiv k_h \sqrt{t/D}$)	dimensionless
μ	chemical potential	J mol^{-1}
$\bar{\mu}$	electrochemical potential	J mol^{-1}
$\vec{\mu}$	dipole moment	Debye
μ_q	shear modulus (of a quartz crystal)	G Pascal
σ	lateral interaction parameter (c.f. electrosorption)	dimensionless

τ_c	time constant for the parallel combination of a capacitor and a resistor ($C_d \times R_F$)	sec
τ_d	time constant for a diffusion controlled process	sec
ν	kinematic viscosity (η/ρ)	$\text{cm}^2 \text{s}^{-1}$
Π	two-dimensional surface pressure	N m^{-1}
ρ_1/ρ_2	reaction order at constant potential/constant overpotential	dimensionless
ρ	density	g cm^{-3}
ρ	specific resistivity of electrolyte	Ohm cm
ϕ	inner potential of a phase	Volt
${}^M\Delta^S\phi$	metal-solution potential difference	Volt
χ	dimensionless distance ($\chi = x/\sqrt{4Dt}$)	dimensionless
κ	reciprocal Debye length	cm^{-1}
ω	angular velocity ($\omega = 2\pi f$)	sec^{-1}
∇^2	the Laplace operator (del-square)	dimensionless

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