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Comprehensive Treatise of Electrochemistry

***Volume 4: Electrochemical
Materials Science***

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Comprehensive Treatise of Electrochemistry

*Volume 4: Electrochemical
Materials Science*

COMPREHENSIVE TREATISE OF ELECTROCHEMISTRY

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Edited by J. O'M. Bockris, Brian E. Conway, and Ernest Yeager
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Ralph E. White
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Preface to Comprehensive Treatise of Electrochemistry

Electrochemistry is one of the oldest defined areas in physical science, and there was a time, less than 50 years ago, when one saw "Institute of Electrochemistry and Physical Chemistry" in the chemistry buildings of European universities. But, after early brilliant developments in electrode processes at the beginning of the twentieth century and in solution chemistry during the 1930s, electrochemistry fell into a period of decline which lasted for several decades. Electrochemical systems were too complex for the theoretical concepts of the quantum theory. They were too little understood at a phenomenological level to allow their ubiquity in application in so many fields to be comprehended.

However, a new growth began faintly in the late 1940s, and clearly in the 1950s. This growth was exemplified by the formation in 1949 of what is now called The International Society for Electrochemistry. The usefulness of electrochemistry as a basis for understanding conservation was the focal point in the founding of this Society. Another very important event was the choice by NASA in 1958 of fuel cells to provide the auxiliary power for space vehicles.

With the new era of diminishing usefulness of the fossil fuels upon us, the role of electrochemical technology is widened (energy storage, conversion, enhanced attention to conservation, direct use of electricity from nuclear-solar plants, finding materials which interface well with hydrogen). This strong new interest is not only in the technological applications of electrochemistry. Quantum chemists have taken great interest in redox processes. Organic chemists are interested in situations where the energy of electrons is as easily controlled as it is at electrodes. Some biological processes are now seen in electrodic terms, with electron transfer to and from materials which would earlier have been considered to be insulators.

It is now time for a comprehensive treatise to look at the whole field of electrochemistry.

The present treatise was conceived in 1974, and the earliest invitations to authors for contributions were made in 1975. The completion of the early volumes has been delayed by various factors.

There has been no attempt to make each article emphasize the most recent situation at the expense of an overall statement of the modern view. This treatise is not a collection of articles from *Recent Advances in Electrochemistry* or *Modern Aspects of Electrochemistry*. It is an attempt at making a mature statement about the present position in the vast area of what is best looked at as a new interdisciplinary field.

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Preface to Volume 4

The science of degradation of materials involves a vast area of science and technology, the economic importance of which rivals that of any other clearly defined area affecting the standard of life. The basis of the corrosion process is the electrochemical charge-transfer reaction, and the center of the subject of the degradation of materials is electrochemical material science.

It is obviously correct to begin this volume with a chapter on the treatment of the thermodynamics of corrosion. Next we include a chapter on corrosion kinetics. Chapter 3, on electrochemical passivation, comes from a very noted school that was ahead of its time regarding present theories of passivation. The next chapter covers the electrochemical passivation of metals.

The kinetics of the growth of oxides (Chapter 5) is a vital area, less discussed than the more commonly referred to "inhibition" problem (Chapter 6).

One of the more puzzling aspects of corrosion—not clearly integrated into the discipline of electrochemistry until the mid-1900s—was that of stress corrosion cracking (Chapter 7); the most important corrosion occurs beneath the surface. The subject of corrosion is also associated with the latent effects of hydrogen, the catalyst of cracking (Chapter 8).

In the last two chapters we discuss topics that are somewhat different in character than those treated in earlier chapters. We felt it necessary to have a chapter on friction, because it is a vital and much neglected subject, describing how electrochemical forces can affect the contacts of two solids through the medium of an ionic liquid (Chapter 9). Chapter 10, on nonmetallic electrode materials, stresses the fact that electrochemistry no longer deals with metals only—in many instances it need not deal with metals at all—and will soon involve not only the treatment of the semiconductor–solution interface but also

that of the insulator-solution interface, which is now a part of the electrodic treatment of bioelectrochemical problems.

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Notation

a_{\pm}	mean activity; a_i , a_j activities of species i , j	E_{CB}	energy of conduction band
c	concentration (molar); velocity of light (cm s^{-1})	E_F	Fermi level
C_1 , C_2 , etc.	differential capacities of regions 1, 2, etc.	E_H	measured potential on the hydrogen scale in the <i>same</i> solution
cn	coordination number	E_{NHE}	measured potential on the scale of the normal hydrogen electrode
d	thickness, e.g., of a film, or of a dielectric	E_{SS}	energy of surface states
D	diffusion coefficient	E_{VB}	energy of valence band
$D_{x_{\psi}}$	dissociation energy for molecule x_{ψ}	\mathcal{E}	electrostatic field
D	dielectric displacement	f_{\pm}	rational activity coefficient (mean)
e	electron charge	F	Faraday constant
E	potential (cf. electrode, on metal-solution potential difference, in kinetics)	g	interaction parameter, in non-Langmuir isotherms
E_{cal}	measured potential on the scale of the normal calomel electrode	$g_{ij}(r_{ij})$	radial distribution function (of distance r_{ij}); pair correlation function

G, H, S	free energy enthalpy, and entropy (per mole)	n_p^0	concentration of holes in bulk
h	Planck's constant	N_A	concentration of charge acceptors
i	current density	N_D	concentration of charge donors
I_0	intensity of light	N_{ss}	concentration of surface states
I	current moment of inertia	P	pressure (Pa), e.g., P_{O_2} , presence of a gas, O_2 ;
J	flux; quantum number for rotation		momentum
k	with subscript, rate constants	$P(E)$	probability (for state of energy E)
k_s	salting out (Setschenow) coefficient	q, Q	partition function
k^*	Boltzmann constant	Q_i	charge for some species, i , e.g., on a surface
K	thermodynamic equilibrium constant	r_i	radius of an ion
K_1, K_2 , etc.	integral capacities of regions 1, 2, etc.	r_{ij}	distance between particles i, j
m	concentration (molal); mass of particle	R	molar gas constant; resistance
M	molarity; N no longer used; number of particles	t	time
n	solvation number; quantum number for vibration	T	absolute temperature (K); with subscript, nmr relaxation times (T_1, T_2)
n_{CB}	density of electronic states in the conduction band	U	internal energy
n_e	concentration of electrons	v	velocity (usually of a reaction); mobility of ion under 1 V cm^{-1} charge
n_e^s	concentration of electrons at the surface	V	volume; partial molar volume
n_e^0	concentration of electrons in bulk	x, y, z	coordinate system; distances
n_p	concentration of holes	y_{\pm}	stoichiometric activity coefficient (mean, molar)
n_e^s	concentration of holes at the surface	\neq	activated state (used as superscript)

Greek Symbols

α	light absorption coefficient; transfer coefficient; specific expansibility	κ	conductivity; Debye-Hückel parameter
β	charge-transfer symmetry factor; specific compressibility	$\Lambda_{\pm,c}$	molar ionic conductivity at concentration c
γ	surface tension	Λ_c	molar conductivity at concentration c
γ_{\pm}	stoichiometric activity coefficient (mean) molal	Λ_{∞}	molar conductivity at infinite dilution
δ	diffusion-layer thickness; barrier thickness	$\Lambda_{\pm,\infty}$	molar ionic conductivity at infinite dilution
$\Delta_i^{i,b}\varphi$	potential inside a metal ($i = m$), semiconductor ($i = sc$), or insulator ($i = ins$)	μ	electric dipole moment; or chemical potential
$\Delta_1^i\varphi$	potential drop at the inner Helmholtz plane φ ($i = M, sc, ins, etc.$)	μ_e	mobility of electrons
$\Delta_b^2\varphi$	potential in the diffuse (Gouy) double layer	μ_p	mobility of holes
$\Delta_2^i\varphi$	potential in the Helmholtz layer ($i = M, sc, or ins$)	μ^0	standard chemical potential
Γ_i	surface excess of species i	$\tilde{\mu}$	electrochemical potential
ϵ	permittivity; quantum efficiency	ν	stoichiometric number; frequency of vibration (s^{-1})
ζ	zeta potential	$\tilde{\nu}$	wave number (cm^{-1})
η	overpotential; viscosity	ρ	density of space charge; resistivity
θ	fractional surface coverage; relative permittivity; dielectric constant	$\rho(E)$	volume charge density
		$\rho_i(E)$	density of states ($i = M, sc, or ins$)
		σ	surface charge density in distribution; charge in double-layer region (subscripted) divided by area
		σ_e	capture cross section of electrons
		σ_m	charge on metal surface, divided by area

σ_p capture cross section
of holes
 τ relaxation time
 ϕ double-layer
potential
(subscripted for
indication of region)
 ϕ_x apparent molar
function of x ; with
subscript \bar{x} , partial

molar function
of x
 φ inner potential
 $\Delta\varphi$ Galvani potential
 χ surface potential
 $\Delta\chi$ surface potential
difference
 ψ outer potential
 $\Delta\psi$ Volta potential
 ω angular frequency

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