Ellis Horwood Series in Physical Chemistry

INSTRUMENTAL METHODS IN ELECTROCHEMISTRY

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D. PLETCHER
J. ROBINSON*
Department of Chemistry, University of Southampton
* now Department of Physics, University of Warwick

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Preface

The idea for this book arose from a one-week residential postgraduate course entitled 'Advanced Instrumental Methods in Electrode Kinetics' which has been organised almost yearly since 1969 by the Electrochemistry Group at Southampton University. Our experience with this course persuaded us of the need for a book which treats not only the fundamental concepts of electrode reactions, but also covers the methodology and practical application of the many versatile electrochemical techniques now available. The book is pitched at the senior undergraduate and postgraduate level, and it should also benefit physical chemists and engineers in industry or research who wish to have an up-to-date survey of the wider uses of electrochemical techniques. The organisation of the book reflects the structure of the course in which successive lectures cover alternately fundamentals and techniques, but all the chapters have been completely rewritten so as to bring them up to date and to extend them to include many advanced topics and illustrative examples. Thus, the book goes well beyond the original content of the course lectures. Much of the additional material was chosen as the result of discussions with course participants over the years, either in the laboratory or in the more convivial atmosphere of the bar. Each chapter is essentially self-contained for those who wish to select a specialised topic of particular interest, but cross-references between chapters and many literature references are included.

The writing of a book of this kind must always cause the authors to take stock and reflect on progress in their field. In the present case, that progress has been systematically documented and emphasised by the successive revisions and updating of the lecture notes and experiments. While the basic principles have remained largely unchanged, modern instrumentation and data-handling techniques have simplified the experiments and their analysis. Improvements in the way experiments are carried out and the emergence of a range of *in situ* spectroscopic techniques have greatly increased our ability to unravel complex reaction mechanisms. Overall, electrochemical techniques have become so powerful that their field of applications now spreads throughout chemistry and related sciences. The last fifteen years represent an exciting and critical period in the development of electrochemistry. The authors hope that this is reflected in their book.

The present authors would like to thank those many current and former colleagues who have contributed to earlier versions of the lecture notes and thereby influenced the content of this book; it is proper to mention here the names of such valued colleagues as Martin Fleischmann, Graham Hills, Alan Bewick, Gamini Gunawardena, Bob Jansson, and David Schiffrin. Because, however, we decided to rewrite completely and extend substantially the lecture notes to form this book, responsibility for the content and presentation, as well as for errors, must lie entirely with us. Without the expert manuscript preparation of Kate Welfare, this book would never have reached the printers, and to her we are especially grateful. The preparation of the illustrations was carried out with great patience and skill by Laurie Dykes. Finally, we express our thanks for the forbearance of our families who have encouraged us and tolerated the many hours that we have spent with pen in hand.

List of symbols

Regrettably, the symbols used in the electrochemical literature remain far from uniform. Hence the symbols used in this book are listed below as an aid to the reader. In general, when selecting symbols we have tried to conform to the IUPAC convention (see ref. 1 in Chapter 1); in a few instances there is an obvious clash between the convention and present practice, and in some of these cases, after a struggle with our consciences, we have come down on the side of current practice.

It will be seen that the list is long; even so, symbols used *only in one place* in the book, and there clearly defined, have been omitted. It will also be found that symbols appear in some places in the text with an additional subscript or superscript in order to emphasise a point. Again this is clearly explained in the text, and we hope the reader is aided and not confused! Finally, it will be seen below that some symbols have several different meanings. This is unfortunate but unavoidable, and in all cases the different usages are well separated in the text and conform to common usage. The units in brackets indicate those used throughout the book except where specifically stated.

a	radius of ion (cm)
a_i	activity of the species i (mol cm^{-3})
A	geometric area of electrode (cm^{2})
	or rate constant for nucleation (s^{-1})
	or gain of amplifier
$A(\lambda)$	absorbance at the wavelength λ (dimensionless)
c_i	concentration of species i (mol cm^{-3})

c_i^∞	concentration of species i in the bulk solution (mol cm^{-3})
c_i^σ	concentration of species i at the electrode surface, i.e. $x = 0$ (mol cm^{-3})
C	capacitance (F cm^{-2})
C_{dl}	double layer capacitance (F cm^{-2})
C^d	capacitance of diffuse layer (F cm^{-2})
C^i	capacitance of inner layer (F cm^{-2})
C_s	pseudo-capacitance (F cm^{-2})
d	diameter of the tip of the Luggin capillary (cm)
D	diffusion coefficient (cm^2 s^{-1})
e	charge on the electron (C)
E	potential vs a reference electrode (V)
E_e	equilibrium (or reversible potential) (V). Sometimes superscripted ^{A} or ^{C} to denote anode or cathode respectively
$E_e^\ominus$	standard potential (V)
E_{CELL}	difference between cathode and anode potentials (V)
E_1	initial potential e.g. for a sweep experiment (V)
E_p	peak potential, sometimes superscripted A or C to denote anodic or cathodic process respectively (V)
$E_{p/2}$	half peak potential. Superscripts ^{A} and ^{C} as above (V)
$E_{1/2}$	half wave potential (V)
E_{FB}	flat band potential (V)
$\mathbf{E}$	phasor potential (V)
ΔE	amplitude of a modulated potential e.g. in an ac experiment (V)
E_i	energy of a species i (J mol^{-1})
E_F	Fermi energy (eV)
f	frequency, either revolutions per s of a rotating disc electrode *or* cycles per s of an ac modulation (s^{-1})
f'	frequency of a rotating disc in r.p.m.
F	the Faraday (C mol^{-1})
$F(t)$	convoluted current (A $s^{1/2}$)
F_L	limiting value of convoluted current (A $s^{1/2}$)
g	coefficient in Frumkin isotherm (dimensionless)
ΔG_i	free energy change (J mol^{-1} of species i)
ΔG_{ADS}	free energy of adsorption (J mol^{-1})
$\Delta G^\ddagger$	free energy of activation (J mol^{-1})
$\Delta\overrightarrow{G}^\ddagger$	free energy of activation for the forward electron transfer process (J mol^{-1})
$\Delta\overleftarrow{G}^\ddagger$	free energy of activation for the back electron transfer process (J mol^{-1})
$^\ominus\Delta G^\ddagger$	standard free energy of activation for the electron transfer reaction (at the equilibrium potential) (J mol^{-1})
ΔG_c	critical free energy for phase growth (J mol^{-1})
h	thickness of a monolayer deposit (cm) *or* Planck constant (J s)
ΔH	enthalpy of reaction (J mol^{-1})

i	current (A)
i_0	exchange current (A)
i_D	current at rotating disc electrode (A)
i_R	current at ring electrode (A)
$(i_R)_{SH}$	current at ring electrode when shielded by the disc (A)
i_p	peak current (A). Superscripts ^{A} and ^{C} indicate anodic and cathodic processes respectively
I	current density (A cm^{-2})
I_0	exchange current density (A cm^{-2})
$\vec{I}$	partial cathodic current density (A cm^{-2})
$\overleftarrow{I}$	partial anodic current density (A cm^{-2})
I_p	peak current density (A cm^{-2}). Superscripts ^{A} and ^{C} denote anodic and cathodic processes respectively
I_L	limiting (plateau) current density (A cm^{-2})
I_D	diffusion limited current density (A cm^{-2})
$I_{t=0}$	current density obtained by extrapolation to $t = 0$ (A cm^{-2})
I_{dl}	current density due to double layer charging (A cm^{-2})
I_m	current at maximum in an $I - t$ transient (A cm^{-2})
$\mathbf{I}$	vector current density (A cm^{-2})
J_i	flux of species i (mol cm^{-2} s^{-1})
k	rate constant for a chemical reaction (generally s^{-1}) Various subscripts depending on type mechanism
k_B	Boltzmann constant (J K^{-1})
$k^{\ominus}$	standard rate constant for an electron transfer couple (cm s^{-1})
$\vec{k}$	rate constant for cathodic process (cm s^{-1})
$\overleftarrow{k}$	rate constant for anodic process (cm s^{-1})
$\vec{k}_0$	rate constant for cathodic process at 0V vs reference electrode (cm s^{-1})
$\overleftarrow{k}_0$	rate constant for anodic process at 0V vs reference electrode (cm s^{-1})
K	equilibrium constant
L	length of a plate or electrode (cm)
l	thickness of thin layer cell (cm)
m	mols of electroactive species in electrolysis cell (mol)
M	molecular wt (g mol^{-1}) *or* integration constant *or* flow rate of mercury (g s^{-1})
n	number of electrons involved in overall electrode reaction (dimensionless)
n_α	number of electrons involved before and including the rate determining step (dimensionless)
n_i	number concentration of species i (cm^{-3}) *or* refractive index of phase i (dimensionless)
n_o	bulk electron density (cm^{-3})
n_s	surface electron density (cm^{-3})
N	collection efficiency of RRDE (dimensionless)

N_o	number of sites where nucleation can occur (cm^{-2})
$N(t)$	number of nuclei at time t (cm^{-2})
p	partial pressure (N m^{-2})
P	pressure (N m^{-2})
q	charge (C)
Q	charge density (C cm^{-2})
r	coordinate in spherical or cylindrical coordinates (cm)
r_o	radius of a disc or sphere (cm)
r_1, r_2, r_3	dimensions of rotating ring disc electrode (cm)
r_c	critical radius for spontaneous growth of a nucleus (cm)
R	gas constant (J K^{-1} mol^{-1})
	or resistance (Ω)
	or reflectivity (dimensionless)
ΔR	change in reflectivity due to a modulation (dimensionless)
R_u	uncompensated resistance between reference electrode probe and working electrode (Ω)
R_{ct}	charge transfer resistance (Ω cm^2)
Re	Reynolds number (dimensionless)
s	variable of Laplace transform (s^{-1})
S	entropy (J mol^{-1} K^{-1})
	or surface area of growing nucleus (cm^2)
Sc	Schmidt number (dimensionless)
Sh	Sherwood number (dimensionless)
t	time from commencement of experiment (s)
t_L	constant in equation for chronocoulometry (s)
t_m	time to maximum in I-t transient (s)
T	temperature (K)
V	cell voltage or applied voltage (V)
	or solution flow rate subscripted zero in situations where it varies to indicate initial flow rate or x, y, z, or r, θ, z etc. to indicate direction of flow (cm s^{-1})
	or solution volume (cm^3)
$\bar{V}$	molar volume (cm^3 mol^{-1})
V_{IR}	voltage drop due to uncompensated resistance (V)
x	distance perpendicular to the electrode surface (cm)
x_o	half space between steps on growing surface (cm)
X	capacitive reactance (Ω)
Y	admittance (Ω^{-1})
z	distance perpendicular to the surface of a rotating disc (cm)
z_i	charge number on ion i
Z	impedance (Ω)
	or pre-exponential factor (as corresponding rate constant)
Z_W	Warburg impedance (Ω)
Z'	real component of impedance (Ω)
Z''	imaginary component of impedance (Ω)
α	transfer coefficient. Subscripts $_A$ and $_C$ indicate anodic and cathodic processes respectively (dimensionless)

γ	surface tension (J cm^{-2})
	or ratio c_A^∞/c_P^∞ in redox catalysis (dimensionless)
Γ_i	surface excess of species i (mol cm^{-2})
δ	diffusion layer thickness (cm)
	or reaction length (cm)
ϵ_i	relative permittivity of phase i
$\hat{\epsilon}$	complex optical constant for phase i
ϵ_0	permittivity of free space (F cm^{-1})
$\epsilon(\lambda)$	molar absorbance at wavelength λ (mol^{-1} cm^2)
η	overpotential, E-E_e (V). Subscripts $_A$ and $_C$ indicate anode and cathode respectively
θ	angular coordinate of rotating disc
	or fractional surface coverage
	or angle of incidence
λ	wavelength of light (nm)
	or reorganisation energy (J mol^{-1} or eV)
μ	viscosity (centipoise)
μ_i	chemical potential of species i (J mol^{-1})
$\bar{\mu}_i$	electrochemical potential of species i (J mol^{-1}). Superscript indicates phase
$\mu_i^\ominus$	standard chemical potential of species i (J mol^{-1})
ν	potential scan rate (V s^{-1})
	or kinematic viscosity (cm^2 s^{-1})
π	surface pressure (N m^{-2})
ρ	density (g cm^{-3})
	or charge density (C cm^{-2})
σ	surface excess charge density (C cm^{-2}). Superscript indicates phase
	or Warburg coefficient (Ω s$^{-1/2}$)
τ	transition time (s)
ϕ	electrical (Galvani) potential of phase (V). Superscript indicates phase
	or phase shift in ac experiment (dimensionless)
$\Delta\phi_{SC}$	potential drop in semiconductor (V)
ω	angular rotation rate of disc (s^{-1})
	or angular frequency of ac excitation (s^{-1})
$\Delta\omega$	amplitude in modulation of ω (s^{-1})

Sign convention

The IUPAC convention is followed. Thus anodic currents are positive and cathodic currents are negative, while moving to more positive potentials corresponds to increasing the driving force for an oxidation, or moving to more negative potentials corresponds to increasing the driving force for reduction.

1

Introduction to the fundamental concepts of electrochemistry

This book was initially prepared as lecture notes for an electrochemistry course which has been presented regularly in Southampton and elsewhere during the past fifteen years. The course seeks to develop an understanding of electrochemical experiments and to illustrate the applications of electrochemical methods to, for example, the study of redox couples, homogeneous chemical reactions, and surface science. In many studies, several of the techniques will be equally applicable, but there are situations where one technique has a unique advantage and hence the course also seeks to discuss the selection of method and the design of experiments to aid the solution of both chemical and technological problems.

It will be shown that the methods are, in general, based on very similar principles. Commonly the need is to carry out an experiment so as to separate the effects on the measurements of the kinetics of electron transfer or a coupled chemical reaction from those which arise from mass transport of species to and from the electrode surface. Thus it is important to understand how the measurement of current as a function of time in potential step methods, of potential scan rate in cyclic voltammetry, of frequency in ac methods, or of rotation rate in experiments with a rotating disc electrode, can be used to isolate pure kinetic information. A grasp of the fundamentals of electrochemistry and an understanding of the theoretical background to the methods is extremly helpful to the experimental electrochemist for another reason – although often disguised by our use of the literature, e.g. of equations or dimensionless plots, the conclusions from electrochemical experiments always come from a comparison of the experimental data with a theoretical response, derived from a mathematical description of the experiment and the solution of the resulting equations. Hence it is, at least, essential to be certain that the conditions for the experiment are appropriate to the results taken from the literature. Furthermore, the reliable employment of electrochemical techniques requires an appreciation of the way in which the electrode and cell should be designed, the way in which the equipment operates, and the ways in which the procedure for carrying out the experiment can determine the quality of the data.

Hence the structure of this book quite deliberately follows that of the course. The theoretical background to electrochemistry and the discussion of electrochemical techniques are developed as parallel themes. The general principles of instrumentation and experiment design are introduced in later chapters, while those readers interested in the mathematical and computational techniques used in electrochemistry are directed to the appendix. The purpose of this first chapter is to give an overview of electrochemistry and to summarise those important equations and ideas which will be used repeatedly throughout the book and which will also be more fully justified in later chapters.

1.1 ELECTRODE REACTIONS AND CELL CHEMISTRY

An electrode reaction is a heterogeneous chemical process involving the transfer of electrons to or from a surface, generally a metal or a semiconductor. The electrode reaction may be an anodic process whereby a species is oxidised by the loss of electrons to the electrode, e.g.

$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \tag{1.1}$$

$$Ce^{3+} - e^- \rightarrow Ce^{4+} \tag{1.2}$$

$$2Cl^- - 2e^- \rightarrow Cl_2 \tag{1.3}$$

$$Pb + SO_4^{--} - 2e^- \rightarrow PbSO_4 \tag{1.4}$$

$$2Al + 3H_2O - 6e^- \rightarrow Al_2O_3 + 6H^+ \tag{1.5}$$

By convention [1], the current density, I, for an anodic process is a positive quantity. Conversely, the charge transfer may be a cathodic reaction in which a species is reduced by the gain of electrons from the electrode, e.g.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{1.6}$$

$$Cu^{2+} + 2e^- \rightarrow Cu \tag{1.7}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1.8}$$

$$PbO_2 + 4H^+ + SO_4^{--} + 2e^- \rightarrow PbSO_4 + 2H_2O \tag{1.9}$$

$$2CH_2{=}CHCN + 2H_2O + 2e^- \rightarrow (CH_2CH_2CN)_2 + 2OH^- \ , \tag{1.10}$$

and the current density for a cathodic process is a negative quantity. The diversity of electrode reactions can already be seen from Equations (1.1)-(1.10): the electroactive species may be organic or inorganic, neutral or charged, a species