

Ellis Horwood Series in Physical Chemistry

# INSTRUMENTAL METHODS IN ELECTROCHEMISTRY

SOUTHAMPTON ELECTROCHEMISTRY GROUP

R. GREEF  
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**R. GREEF**

**R. PEAT**

**L. M. PETER**

**D. PLETCHER**

**J. ROBINSON\***

**Department of Chemistry, University of Southampton**

**\* now Department of Physics, University of Warwick**



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# **INSTRUMENTAL METHODS IN ELECTROCHEMISTRY**



## ELLIS HORWOOD SERIES IN PHYSICAL CHEMISTRY

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# Contents

<b>Preface</b>	7
<b>List of symbols</b>	9
<b>1 Introduction to the fundamental concepts of electrochemistry</b>	15
<b>2 Steady state and potential step techniques</b>	42
<b>3 Electron transfer</b>	76
<b>4 Convective diffusion systems – the rotating disc and ring-disc electrodes</b>	113
<b>5 The electrical double layer</b>	149
<b>6 Potential sweep techniques and cyclic voltammetry</b>	178
<b>7 Electrocatalysis</b>	229
<b>8 A.C. techniques</b>	251
<b>9 Electrocrystallisation</b>	283
<b>10 Spectroelectrochemistry</b>	317
<b>11 The design of electrochemical experiments</b>	356
<b>APPENDIX</b>	
<b>Mathematical methods for the development of a theory for electrochemical experiments</b>	388
<b>Index</b>	439



# 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 tech-



## 8 Preface

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

## 10 List of symbols

$c_i^{\infty}$	concentration of species $i$ in the bulk solution ( $\text{mol cm}^{-3}$ )
$c_i^0$	concentration of species $i$ at the electrode surface, i.e. $x = 0$ ( $\text{mol cm}^{-3}$ )
$C$	capacitance ( $\text{F cm}^{-2}$ )
$C_{dl}$	double layer capacitance ( $\text{F cm}^{-2}$ )
$C^d$	capacitance of diffuse layer ( $\text{F cm}^{-2}$ )
$C^i$	capacitance of inner layer ( $\text{F cm}^{-2}$ )
$C_s$	pseudo-capacitance ( $\text{F cm}^{-2}$ )
$d$	diameter of the tip of the Luggin capillary (cm)
$D$	diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )
$e$	charge on the electron (C)
$E$	potential vs a reference electrode (V)
$E_0$	equilibrium (or reversible potential) (V). Sometimes superscripted <sup>A</sup> or <sup>C</sup> to denote anode or cathode respectively
$E_0^{\ominus}$	standard potential (V)
$E_{\text{CELL}}$	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 <sup>A</sup> and <sup>C</sup> as above (V)
$E_{1/2}$	half wave potential (V)
$E_{\text{FB}}$	flat band potential (V)
$E$	phasor potential (V)
$\Delta E$	amplitude of a modulated potential e.g. in an ac experiment (V)
$E_i$	energy of a species $i$ ( $\text{J mol}^{-1}$ )
$E_{\text{F}}$	Fermi energy (eV)
$f$	frequency, either revolutions per s of a rotating disc electrode or cycles per s of an ac modulation ( $\text{s}^{-1}$ )
$f'$	frequency of a rotating disc in r.p.m.
$F$	the Faraday ( $\text{C mol}^{-1}$ )
$F(t)$	convoluted current ( $\text{A s}^{1/2}$ )
$F_L$	limiting value of convoluted current ( $\text{A s}^{1/2}$ )
$g$	coefficient in Frumkin isotherm (dimensionless)
$\Delta G_i$	free energy change ( $\text{J mol}^{-1}$ of species $i$ )
$\Delta G_{\text{ADS}}$	free energy of adsorption ( $\text{J mol}^{-1}$ )
$\Delta G^{\ddagger}$	free energy of activation ( $\text{J mol}^{-1}$ )
$\Delta \vec{G}^{\ddagger}$	free energy of activation for the forward electron transfer process ( $\text{J mol}^{-1}$ )
$\Delta \overleftarrow{G}^{\ddagger}$	free energy of activation for the back electron transfer process ( $\text{J mol}^{-1}$ )
$\ominus \Delta G^{\ddagger}$	standard free energy of activation for the electron transfer reaction (at the equilibrium potential) ( $\text{J mol}^{-1}$ )
$\Delta G_c$	critical free energy for phase growth ( $\text{J mol}^{-1}$ )
$h$	thickness of a monolayer deposit (cm) or Planck constant (J s)
$\Delta H$	enthalpy of reaction ( $\text{J mol}^{-1}$ )

$i$	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 <sup>A</sup> and <sup>C</sup> indicate anodic and cathodic processes respectively
$I$	current density ( $A\text{ cm}^{-2}$ )
$I_0$	exchange current density ( $A\text{ cm}^{-2}$ )
$\vec{i}$	partial cathodic current density ( $A\text{ cm}^{-2}$ )
$\overleftarrow{i}$	partial anodic current density ( $A\text{ cm}^{-2}$ )
$I_p$	peak current density ( $A\text{ cm}^{-2}$ ). Superscripts <sup>A</sup> and <sup>C</sup> denote anodic and cathodic processes respectively
$I_L$	limiting (plateau) current density ( $A\text{ cm}^{-2}$ )
$I_D$	diffusion limited current density ( $A\text{ cm}^{-2}$ )
$I_{t=0}$	current density obtained by extrapolation to $t = 0$ ( $A\text{ cm}^{-2}$ )
$I_{dl}$	current density due to double layer charging ( $A\text{ cm}^{-2}$ )
$I_m$	current at maximum in an $I-t$ transient ( $A\text{ cm}^{-2}$ )
$\mathbf{I}$	vector current density ( $A\text{ cm}^{-2}$ )
$J_i$	flux of species $i$ ( $\text{mol cm}^{-2}\text{ s}^{-1}$ )
$k$	rate constant for a chemical reaction (generally $\text{s}^{-1}$ ) Various subscripts depending on type mechanism
$k_B$	Boltzmann constant ( $\text{J K}^{-1}$ )
$k^\ominus$	standard rate constant for an electron transfer couple ( $\text{cm s}^{-1}$ )
$\vec{k}$	rate constant for cathodic process ( $\text{cm s}^{-1}$ )
$\overleftarrow{k}$	rate constant for anodic process ( $\text{cm s}^{-1}$ )
$\vec{k}_0$	rate constant for cathodic process at 0V vs reference electrode ( $\text{cm s}^{-1}$ )
$\overleftarrow{k}_0$	rate constant for anodic process at 0V vs reference electrode ( $\text{cm s}^{-1}$ )
$K$	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 ( $\text{g mol}^{-1}$ ) or integration constant or flow rate of mercury ( $\text{g s}^{-1}$ )
$n$	number of electrons involved in overall electrode reaction (dimensionless)
$n_\alpha$	number of electrons involved before and including the rate determining step (dimensionless)
$n_i$	number concentration of species $i$ ( $\text{cm}^{-3}$ ) or refractive index of phase $i$ (dimensionless)
$n_o$	bulk electron density ( $\text{cm}^{-3}$ )
$n_s$	surface electron density ( $\text{cm}^{-3}$ )
$N$	collection efficiency of RRDE (dimensionless)

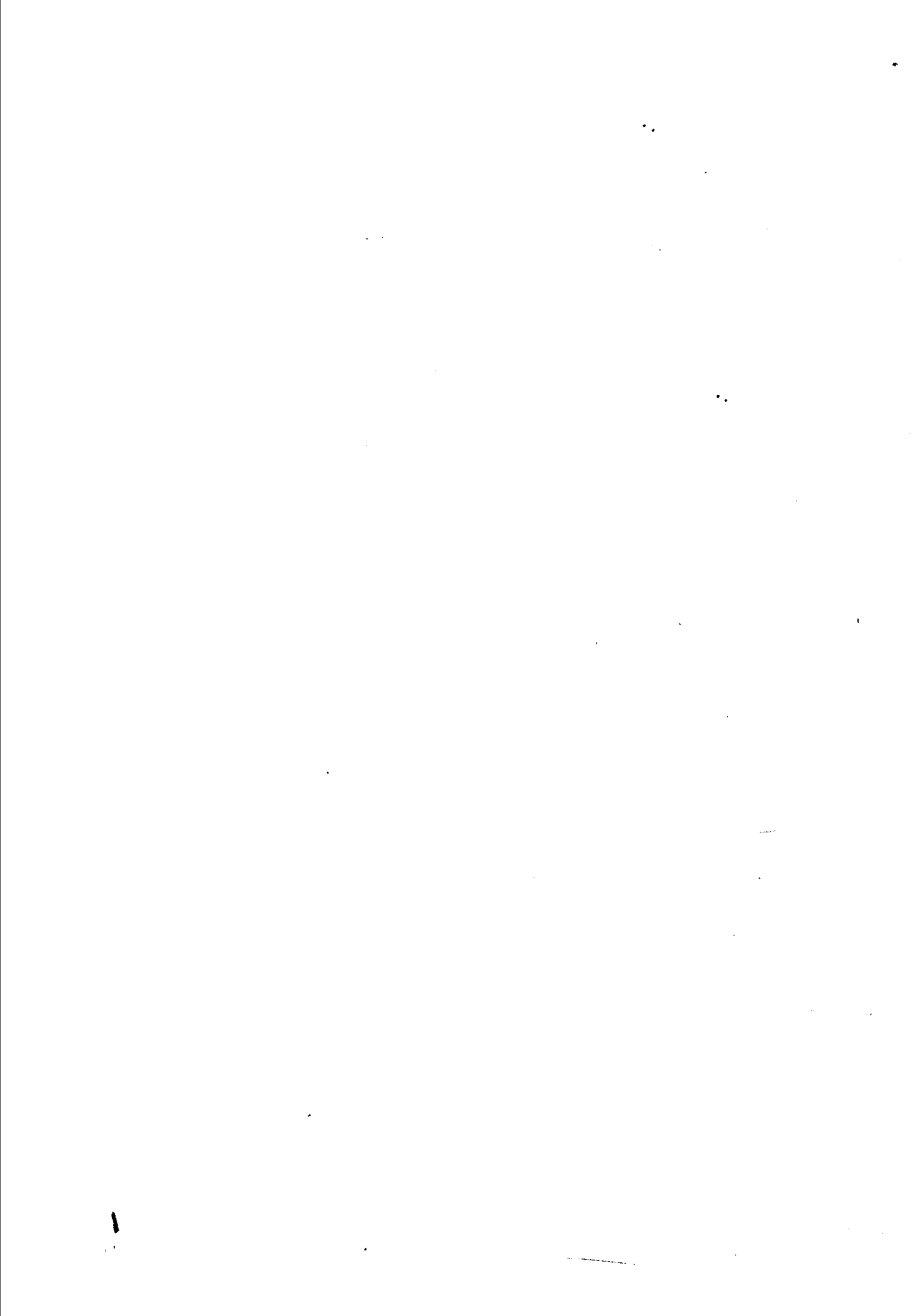
12 List of symbols

$N_0$	number of sites where nucleation can occur ( $\text{cm}^{-2}$ )
$N(t)$	number of nuclei at time $t$ ( $\text{cm}^{-2}$ )
$p$	partial pressure ( $\text{N m}^{-2}$ )
$P$	pressure ( $\text{N m}^{-2}$ )
$q$	charge (C)
$Q$	charge density ( $\text{C cm}^{-2}$ )
$r$	coordinate in spherical or cylindrical coordinates (cm)
$r_0$	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 ( $\text{J K}^{-1} \text{mol}^{-1}$ ) or resistance ( $\Omega$ ) or reflectivity (dimensionless)
$\Delta R$	change in reflectivity due to a modulation (dimensionless)
$R_u$	uncompensated resistance between reference electrode probe and working electrode ( $\Omega$ )
$R_{ct}$	charge transfer resistance ( $\Omega \text{cm}^2$ )
$Re$	Reynolds number (dimensionless)
$s$	variable of Laplace transform ( $\text{s}^{-1}$ )
$S$	entropy ( $\text{J mol}^{-1} \text{K}^{-1}$ ) or surface area of growing nucleus ( $\text{cm}^2$ )
$Sc$	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 $r, \theta, z$ etc. to indicate direction of flow ( $\text{cm s}^{-1}$ ) or solution volume ( $\text{cm}^3$ )
$\bar{V}$	molar volume ( $\text{cm}^3 \text{mol}^{-1}$ )
$V_{IR}$	voltage drop due to uncompensated resistance (V)
$x$	distance perpendicular to the electrode surface (cm)
$x_0$	half space between steps on growing surface (cm)
$X$	capacitive reactance ( $\Omega$ )
$Y$	admittance ( $\Omega^{-1}$ )
$z$	distance perpendicular to the surface of a rotating disc (cm)
$z_i$	charge number on ion $i$
$Z$	impedance ( $\Omega$ ) or pre-exponential factor (as corresponding rate constant)
$Z_W$	Warburg impedance ( $\Omega$ )
$Z'$	real component of impedance ( $\Omega$ )
$Z''$	imaginary component of impedance ( $\Omega$ )
$\alpha$	transfer coefficient. Subscripts $A$ and $C$ indicate anodic and cathodic processes respectively (dimensionless)

$\gamma$	surface tension ( $\text{J cm}^{-2}$ ) <i>or</i> ratio $c_A^\infty/c_P^\infty$ in redox catalysis (dimensionless)
$\Gamma_i$	surface excess of species $i$ ( $\text{mol cm}^{-2}$ )
$\delta$	diffusion layer thickness (cm) <i>or</i> reaction length (cm)
$\epsilon_i$	relative permittivity of phase $i$
$\hat{\epsilon}$	complex optical constant for phase $i$
$\epsilon_0$	permittivity of free space ( $\text{F cm}^{-1}$ )
$\epsilon(\lambda)$	molar absorbance at wavelength $\lambda$ ( $\text{mol}^{-1} \text{cm}^2$ )
$\eta$	overpotential, $E-E_e$ (V). Subscripts $A$ and $C$ indicate anode and cathode respectively
$\theta$	angular coordinate of rotating disc <i>or</i> fractional surface coverage <i>or</i> angle of incidence
$\lambda$	wavelength of light (nm) <i>or</i> reorganisation energy ( $\text{J mol}^{-1}$ or eV)
$\mu$	viscosity (centipoise)
$\mu_i$	chemical potential of species $i$ ( $\text{J mol}^{-1}$ )
$\bar{\mu}_i$	electrochemical potential of species $i$ ( $\text{J mol}^{-1}$ ). Superscript indicates phase
$\mu_i^\ominus$	standard chemical potential of species $i$ ( $\text{J mol}^{-1}$ )
$\nu$	potential scan rate ( $\text{V s}^{-1}$ ) <i>or</i> kinematic viscosity ( $\text{cm}^2 \text{s}^{-1}$ )
$\pi$	surface pressure ( $\text{N m}^{-2}$ )
$\rho$	density ( $\text{g cm}^{-3}$ ) <i>or</i> charge density ( $\text{C cm}^{-2}$ )
$\sigma$	surface excess charge density ( $\text{C cm}^{-2}$ ). Superscript indicates phase <i>or</i> Warburg coefficient ( $\Omega \text{s}^{-1/2}$ )
$\tau$	transition time (s)
$\phi$	electrical (Galvani) potential of phase (V). Superscript indicates phase <i>or</i> phase shift in ac experiment (dimensionless)
$\Delta\phi_{\text{SC}}$	potential drop in semiconductor (V)
$\omega$	angular rotation rate of disc ( $\text{s}^{-1}$ ) <i>or</i> angular frequency of ac excitation ( $\text{s}^{-1}$ )
$\Delta\omega$	amplitude in modulation of $\omega$ ( $\text{s}^{-1}$ )

### 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 extremely 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

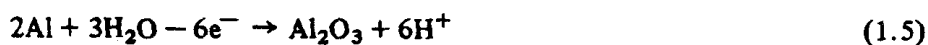


it is, at least, essential to be certain that the conditions for the experiment are appropriate to the results taken from the literature. Furthermore, the reliable employment of electrochemical techniques requires an appreciation of the way in which the electrode and cell should be designed, the way in which the equipment operates, and the ways in which the procedure for carrying out the experiment can determine the quality of the data.

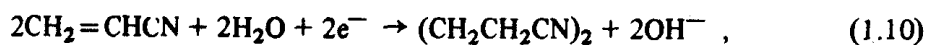
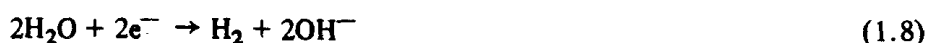
Hence the structure of this book quite deliberately follows that of the course. The theoretical background to electrochemistry and the discussion of electrochemical techniques are developed as parallel themes. The general principles of instrumentation and experiment design are introduced in later chapters, 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.



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.



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