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## Preface

Electrochemistry has certainly got rid of its classical image and has taken new directions of growth and continuous change. Gone are the days when electrochemistry was considered a nineteenth century solution chemistry useful for calculating the activity coefficient and transport number. The electrode kinetics, of course, occupies the centre stage for the past three or four decades, but many new pathways and emerging frontiers are branching out from time to time around this centre stage. Advances in model-building and instrumental facilities for evaluating these models now enable us to understand quite comprehensively almost all the events that take place at the electrode-electrolyte interface at least at the molecular level, if not at the quantum mechanical level.

Quite comprehensive information is now available on the thermodynamics and kinetics of interfacial electron transfer reactions. The reactivity of the electrochemically generated radical species that leads to a variety of chemical reactions such as dimerization, disproportionation, protonation and deprotonation are now amenable to quantitative kinetic evaluation even if the chemical reactions have half-life periods in the range of milliseconds. The mass transport associated with these processes have received very accurate descriptions. In addition to these classical fields, several new and exciting developments are taking place in electrochemistry. We can now form a thin layer on an electrode surface, so thin that the thickness amounts to just one atomic layer. We can prepare many other types of thin or thick films, oxide or metal films, homogeneous or heterogeneous films and redox or conducting polymer films. We can evaluate the catalytic behaviour of metals, oxides, carbon or any other type of surface-modified electrodes. We can use photons or light energy for analysing the electrode-electrolyte interface or for tapping the solar energy and converting it into electrochemical energy. In spite of such fast emergence of new

frontiers in electrochemistry, most, if not all, of the textbooks available in this field treat the subject only at the classical level. There is certainly a need for sketching electrochemistry in a new perspective with classical aspects as well as new developments in surface studies, electrocatalysis and photoelectrocatalysis.

The enormous growth in electrochemical activity in recent times was actually made possible by the parallel developments in electro-analytical methods. A variety of analytical techniques from classical polarography through ultra high vacuum techniques to *in situ* spectro-electrochemical methods are being employed with quite sophisticated instrumentation for investigating interfacial electrochemical processes. We may also associate each technique with a specific application, say polarography for analysis, rotating disc electrode for mass transfer effects, ring-disc electrode for intermediate identification and impedance spectroscopy for surface processes. But if one is to identify the most common and simple electrochemical technique that can be employed for qualitative as well as quantitative analysis of almost all types of interfacial processes involving electron transfer, he would certainly point out cyclic voltammetry as the candidate. Cyclic voltammetric investigation today is the first choice of any electrochemical research that may look for further information from other techniques subsequently. In spite of such pivotal position occupied by cyclic voltammetry in electrochemical research, not a single monograph has appeared so far which comprehensively deals with all the theoretical and applied aspects of this field. This is even more surprising if we notice that a large number of monographs on other techniques such as polarography and rotating disc electrode voltammetry and even on optical methods in electrochemistry are available.

Hence we set out two parallel objectives when we initiated this work. The first objective was to introduce interfacial electrochemistry in all its splendid colours in a systematic and unified fashion. The second is to introduce the methodology as well as application of cyclic voltammetry and related techniques in the study of all these interfacial processes. When such a broad objective is chosen, the monograph should also orient towards a very broad audience. In addition to physical chemistry students who would like to specialize in electrochemistry, we also notice many new entrants in this field. The electrochemists who are engaged in industrial

research and development in different areas of electrochemistry, now intend to know more about the basic processes involved in the technologies of interest to them. In addition, applied physicists developing electron transfer theories, biochemists studying bioredox processes, synthetic organic chemists seeking new organic synthetic routes, analytical chemists seeking improved and faster analytical techniques, polymer chemists interested in conducting and insulating polymer films, surface physicists and chemists looking for the structure, catalytic and inhibitive properties of materials and photophysicists and photochemists engaged in semiconductor-electrode-electrolyte interfaces are also entering the electrochemical field with keen interest. We felt that it would be desirable to develop a monograph in electrochemistry that would cater to the needs of people with such divergent interests and backgrounds. The book should start from the elementary level which can be followed by anybody with a little physical chemistry background. At the same time, it should also reach a sufficiently advanced stage in every specialization, so that the reader can comprehend any other current literature in his own field of interest with the help of this book. We have tried our level best to arrange and present the material to achieve these ambitious targets.

The book essentially contains seventeen chapters in six major parts. The first part is of introductory nature. The next four parts deal with the solution phase processes, surface processes, electrocatalysis and photoelectrochemical processes in a systematic fashion. The fourteen chapters in these sections have been arranged uniformly in five major sections. The first section is an introductory one. The models involved in dealing with the process of interest and the voltammetric methodology are treated in the next two sections. Selected examples of voltammetric investigations are treated in the fourth section. The analytical applications and future scope are then treated. We have certainly adopted an unconventional approach in the selection and classification of material to be presented and the method of presentation. But we hope that we have developed a framework which is comprehensive and easy to grasp at the same time. The last part of the book is a sort of epilogue containing one chapter which tries to sketch some recent developments and future trends. Selected literature that have been published quite recently are also included in this last chapter.

Defining such an ambitious goal for writing a monograph was comparatively an easy job. The difficulties involved came to surface only during the period of execution. Threading the different lines of developments in the recent past turned out to be a tough task. Selection of material again was quite difficult. We could still have left out some important contributions in spite of the fact that we have covered almost 2000 references. We found that certain areas have grown faster than the others. In some areas the model development is far behind compared with experimental investigation. We could do nothing better than pointing out the lapses and advances as they are available today and hence point out the scope for further work.

We have worked consistently for almost three long years to accomplish this task. We hope that this work would further the cause of electrochemistry, especially in bringing new entrants into the field and help them to pick up and develop their own field of specialization. There are bound to be a few lapses in the work of this magnitude. We would be happy to receive any constructive criticism and suggestions for improvement.

M. NOEL  
K.I. VASU

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## List of Common Roman Symbols

Symbol	Meaning	First appears in Section
$A$	Surface area of electrode	1.4.2
$a_j$	Activity of species $j$	1.4.2
$C_{dl}$	Differential capacity of double layer	1.4.1
$C_j$	Concentration of species $j$	1.4.1
$C_j(x, t)$	Concentration of species $j$ at time $t$ at a distance $x$ from the electrode surface	1.4.11
$D_e$	Electron diffusion coefficient	10.2.4
$D_{exp}$	Experimental diffusion coefficient	10.2.4
$D_j$	Diffusion coefficient of species $j$	1.4.11
$E$	Electrode potential	1.3
$E_a$	Applied potential	2.7.1
$E_{cell}$	e m f of cell	3.2.1
$E_{eq}$	Equilibrium electrode potential	1.4.2
$E_t$	Initial potential	1.5.3
$E_m$	Measured potential	2.7.1
$E_m$	Mixed potential	12.2
$E_p$	Peak potential	3.3.1
$E_{pzc}$	Potential of zero charge	1.3.1
$E^\circ$	Standard electrode potential	1.4.2
$E^\circ_a$	Standard electrode potential of adsorption	1.4.3
$E^\circ_{cell}$	Standard emf of cell	3.2.1
$E^\circ_s$	Standard electrode potential surface reaction	9.2.1
$E^f$	Formal electrode potential	3.2.1
$\Delta E_{1/2}$	Half peak width	7.3.1
$e$	Electron	1.4.2
exp	Exponential	1.4.1

Symbol	Meaning	First appears in Section
$F$	Faraday constant	1.4.2
$f$	$F/RT$	1.4.3
$\Delta G$	Free energy change	1.4.1
$\Delta G^\circ$	Molar free energy change	3.2.1
$\Delta G^\ddagger$	Change of free energy of activation	1.4.1
$g$	Lateral interaction constant	1.4.3
$\Delta H$	Enthalpy change	3.2.2
$h$	Hole	1.4.10
	Plank's constant	16.2.2
$I$	Semi integral of current	3.3.1
$i$	Current	1.4.2
$i_o$	Exchange current density	4.2.1
$i_a$	Adsorption current	1.4.3
$i_l$	Limiting current	8.3.6
$i_m$	Mixed current	12.2
$i_{nf}$	Non-faradaic current	3.3.1
$i_p$	Peak current	3.3.1
$J$	Flux of molecules	1.4.11
$K$	Equilibrium constant	3.2.1
	Equilibrium constant for adsorption	1.4.3
	Conductivity	8.3.5
$K_{f/s}$	Partition coefficient	10.2.6
$K_c$	Chemical equilibrium constant	1.4.1
$K_T$	Transition probability	1.4.9
$k_a^\circ$	Standard adsorption rate constant	1.4.3
$k_c$	Chemical reaction rate constant	1.4.1
$k_{ex, l}$	Place exchange rate constant for a film of thickness $l$	1.4.8
$k_{fg}^\circ$	Standard rate constant for film growth	1.4.7
$k_g^\circ$	Standard rate constant for phase growth	1.4.5
$k_h^\circ$	Standard heterogeneous rate constant	1.4.2
$k_{h, a}^\circ$	Apparent standard heterogeneous rate constant	11.2.1
$k_{j, f}$	Rate constant $k_j$ for forward reaction	1.4.1
$k_{j, b}$	Rate constant $k_j$ for backward reaction	1.4.1
$k_{n, i}^\circ$	Potential independent nucleation rate constant of dimension $i$ (2 or 3)	1.4.4

Symbol	Meaning	First appears in Section
$L$	Diffusion length	1.4.11
	Thickness of a phase	1.4.7
$l$	Half barrier width	1.4.7
$M$	Metal atom on a lattice	1.4.2
$M$	Molecular weight	8.3.5
$N$	Numbers of nuclei at time $t$	1.9.4
$N_o$	Number of active sites	1.4.4
$N_A$	Avagadro number	7.2.4
$N_c$	Critical nuclear size	7.2.3
$N_T$	Total number of sites per unit area	7.2.4
$n$	Number of electrons	1.4.2
$n_s$	Surface concentration of electrons	16.2.3
$O_x$	Oxidized species of electrochemical reaction	1.4.2
$p$	Dimensionless parameter for non-linear diffusion effects	3.3.2
	Number of ligands involved in complex formation	3.2.2
$p'$	Dimensionless parameter for film thickness and diffusion	6.3.9
$p_s$	Surface concentration of holes	16.2.3
$q$	Charge	1.3
$q_{mon}$	Charge corresponding to one monolayer	1.4.3
$R$	Gas constant	1.4.1
$R$	Radius of growth centre	1.4.5
$R$	Reduced species of an electrochemical reaction	1.4.2
$R_o$	Resistance of medium	8.3.5
$R_{c,t}$	Charge transfer resistance	12.3.3
$R_u$	Uncompensated resistance	2.2.2
$r$	Reaction order	4.2.2
	Partial charge transfer factor	7.2.2
$r_o$	Radius of the spherical electrode	3.3.2
$S$	Surface area of growing phase	1.4.6
$S_{ex}$	Extended surface area	1.4.6
$\Delta_S$	Entropy change	3.2.2
$T$	Absolute temperature	1.4.1
$t$	Time	1.4.3
$V$	Volume of growing phase	1.4.5



xx *List of Common Roman Symbols*

Symbol	Meaning	First appears in Section
$v$	Potential sweep rate	1.5.3
	Stoichiometric numbers	4.2.2
	Velocity of flowing liquid	1.4.12
	Velocity of chemical reaction	1.4.1
$\nu_0$	Frequency	16.2.2
$\nu_k$	Frequency factor	1.4.1
$\Delta W_{1/2}$	Potential at half peak width	6.3.4
$w$	Width of single surface layer	8.2.7
$X$	Electronegative species	1.4.2
	Fraction of the surface covered by an adsorbed species	1.4.3
$x$	Distance	1.4.10
	Number of layers	8.2.7
$Z$	Electroinactive species	3.2.2
	Frequency factor	4.4.1

## List of Common Greek Symbols

Symbol	Meaning	First appears in Section
$\alpha$	Transfer coefficient	4.2.2
$\beta$	Symmetry factor	1.4.2
$\mu$	Surface concentration	7.2.2
$\tau$	Activity coefficient	3.2.1
	Ratio of diffusion coefficient	4.3.2
$\delta$	Electron exchange distance	10.2.4
	Film thickness	8.3.5
$\delta(t)$	Chronicker delta function	1.4.4
$\eta$	Overpotential	4.2.1
$\theta$	Fractional surface coverage	7.2.1
$k$	Transition probability	4.4.1
$\Lambda$	Dimensionless parameter for charge transfer and diffusion	4.3.2
$\lambda$	Dimensionless parameter for chemical reaction and diffusion	5.2.3
	Time taken for a linear sweep	3.3.1
$\mu$	Surface concentration	7.2.1
$\rho$	Density	8.3.5
$\rho_m$	Molar density of growing phase	1.4.5
$\sigma$	Surface free energy	7.2.3
$\tau$	Surface concentration	9.2.1
$\Delta\phi$	Potential difference at the interface	10.2.2
$\chi$	Dimensionless current function	3.3.1
$\psi$	Dimensionless current function	4.3.2

# List of Common Abbreviations

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Abbreviation	Meaning
AES	Auger electron spectroscopy
ASV	Anodic stripping voltammetry
C	Chemical step in a reaction sequence
CSV	Cathodic stripping voltammetry
CSV	Convolution stripping voltammetry
CV	Cyclic voltammetry
Disp	Disproportionation
DME	Dropping mercury electrode
DMF	Dimethyl formamide
DPASV	Differential pulse anodic stripping voltammetry
E	Electrochemical step in a reaction sequence
ESR	Electron spin resonance
HMDE	Hanging mercury drop electrode
IHP	Inner Helmholtz plane
LCP	Linear current potential analysis
LSV	Linear sweep voltammetry
MSV	Multisweep cyclic voltammetry
NGCM	Nucleation-growth-collision model
NGO	Nucleation-growth-overlap
NHE	Normal hydrogen electrode
NPSV	Normalized potential sweep voltammetry
OHP	Outer Helmholtz Plane
PSV	Potential step voltammetry
PZC	Potential of zero charge
RAM	Random adsorption model
RDE	Rotating disc electrode

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Abbreviation	aMenngi
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RRDE	Rotating ring disc electrode
SA	Semi-integral analysis
SACV	Small amplitude cyclic voltammetry
SCE	Saturated calomel electrode
SERS	Surface enhanced Raman spectroscopy
SHE	Standard hydrogen electrode
SMDE	Static mercury drop electrode
TAA	Tetra alkyl ammonium
TBA	Tetra butyl ammonium
TEA	Tetra ethyl ammonium
TLV	Thin layer voltammetry
UPD	Under potential deposition
XPS	X-ray photoelectron spectroscopy

Part A

**INTRODUCTION**