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R. Holze

Surface and Interface Analysis

An Electrochemists Toolbox

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Rudolf Holze

Surface and Interface Analysis

An Electrochemists Toolbox

With 207 Figures

Springer

Professor Dr. Rudolf Holze
Technische Universität Chemnitz
Institut für Chemie
09107 Chemnitz, Germany
E-Mail: rudolf.holze@chemie.tu-chemnitz.de

Series Editors:
Professor A.W. Castleman, Jr.
Department of Chemistry, The Pennsylvania State University
152 Davey Laboratory, University Park, PA 16802, USA

Professor J.P. Toennies
Max-Planck-Institut für Strömungsforschung
Bunsenstrasse 10, 37073 Göttingen, Germany

Professor K. Yamanouchi
University of Tokyo, Department of Chemistry
Hongo 7-3-1, 113-0033 Tokyo, Japan

Professor W. Zinth
Universität München, Institut für Medizinische Optik
Öttingerstr. 67, 80538 München, Germany

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Preface

As undertaken by electrochemists, spectroscopic, topographical and numerous other non-electrochemical methods extensively covered in this book have driven the investigation of structure and dynamics at phase boundaries between condensed matter influenced by the presence and action of both an electric field and charged particles (like ions in solution or electrons in a metal) towards significant advances in recent years. They are based in particular upon an intense use of spectroscopic and surface sensitive methods adapted to the particular needs of *in situ* investigations of these electrochemical interfaces. Consequently the area is called (not completely exactly) spectroelectrochemistry. More recently, scanning probes capable of mapping the interface and providing a more or less topographic image have become available.

Numerous reviews covering single methods or families of related methods have appeared in journals, monographs and volumes of series. In addition, books containing collected review papers have been published. The articles were written by specialists and experts in the respective methods and describe fundamental and applied aspects, including examples of successful applications. Unfortunately this approach cannot provide the full picture because coherence is lacking between methods and different but related properties and other aspects of a given system investigated with various methods. In addition, the papers are generally of a somewhat different level; sometimes they are filled with a flood of details or extensive repetitions of fundamental information already provided in standard textbooks. The present book attempts to close this gap by providing the generalist's view. It offers a broad collection of spectroscopic and surface sensitive techniques currently employed in investigations of electrochemical systems. Relationships between different methods pertaining both to the principles of the methods and the properties of the investigated systems are highlighted. In many cases examples illustrating the power and the potential of a combined use of several spectroelectrochemical techniques are discussed in detail.

As presumably nobody can be an expert in all discussed methods and techniques, this book will not cover all methods with the same intensity and expertise. Nevertheless, all reported methods are described in sufficient detail, enabling the reader to access the current literature, to evaluate the methods and to choose methods of potential use for his given problem. This is the main purpose of the book: to serve as a guide to the successful application of spectroelectrochemistry and surface analytical methods in electrochemistry—just like a toolbox.

This book is based on numerous original papers and reviews. Because of the immense number of original papers and reviews, I have only provided references to those that I have assumed to be of particular importance as an introduction or that offer essential details not covered in this text. I wish to express my sincere apologies to all authors who have published important results and are not quoted explicitly within this book. Their contributions are nevertheless highly esteemed. Personal communications and experience with several methods in the laboratory of our research group and numerous contributions from coworkers and colleagues added to the base of this book. Some of them provided papers and preprints, examined experimental details, supplied original data or checked parts of the manuscript. Help and contributions from V. Brandl, M. Bron, C.H. Hamann, J. Lippe, A. Malinauskas, M. Probst, S. Schomaker, B. Speiser and B. Westerhoff are gratefully acknowledged. W. Vielstich introduced me to electrochemistry, E.B. Yeager provided inspiring access to new areas of research and to new methods during my postdoctoral stay at his laboratory, G. Comsa initiated a continuing interest in surface science and C.H. Hamann was an inspiring discussion partner. Without their stimulating support this book would have remained unwritten. Close cooperation and helpful assistance in planning and preparing this book by the staff of Springer-Verlag (Heidelberg), in particular by Claus Ascheron, Angela Lahee and Adelheid Duhm, are gratefully appreciated. My wife's tolerance for many hours spent in front of computer terminals and scientific papers was the essential prerequisite. The book would have been impossible without this.

Chemnitz, September 2008 R. Holze

The best books are those which make the reader supplement them.
(Voltaire, Philosophical Dictionary, Foreword)

It is vain to do with more what can be done with less (Entia non sunt multiplicanda praeter necessitatem).
(William of Occam)

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List of Acronyms

Commonly used acronyms in surface analysis, surface spectroscopy and spectroelectrochemistry

aSNOM	Apertureless scanning near field optical microscopy
AAS	Atomic absorption spectroscopy
AC-SECM	Alternating current scanning electrochemical microscopy
ADXD	Angular dispersive X-ray diffraction
AEAPS	Auger electron appearance potential spectroscopy
AES	Auger electron spectroscopy
AES-SAM	Auger electron spectroscopy scanning Auger microscopy
AFM	Atomic force microscopy
AGFM	Alternating gradient field magnetometry
AIRS	Absorption infrared spectroscopy, also: abnormal infrared effect
AIS	Atom inelastic scattering
ALE	Atomic layer epitaxy
APD	Azimuthal photoelectron diffraction
APS	Appearance potential spectroscopy
ARAES	Angle-resolved Auger electron spectroscopy
ARPEFS	Angle-resolved photoemission extended fine structure
ARUPS	Angle-resolved ultraviolet photoelectron spectroscopy
ATR	Attenuated total reflection (spectroscopy), see also: FTIR
AXAFS	Atomic X-ray absorption fine structure spectroscopy
BAW	Bulk acoustic wave
BB-SFG	Broad band sum frequency generation
CD	Circular dichroism
CDAD	Circular dichroism photoelectron angular distribution
CDP	Current density probe
CELS	Characteristic energy loss spectroscopy
CER	Contact electric resistance
CFM	Chemical force microscopy
CL	Cathodoluminescence, Chemiluminescence
CLSM	Confocal laser scanning microscopy
CTR	Crystal truncation rod
CV	Cyclic voltammetry
DAPS	Disappearance potential spectroscopy

DCTS	Differential conductance tunneling spectroscopy
DEMS	Differential electrochemical mass spectroscopy
DESERS	Deenhanced surface enhanced Raman spectroscopy
DFT	Density functional theory
DPDS	Differential photothermal deflection spectroscopy
DRIFT	Diffuse reflection infrared Fourier transform spectroscopy
DRIFTS	same as DRIFT
DS	Desorption spectroscopy
DXAFS	Dispersive X-ray absorption fine structure (spectroscopy, measurement)
DTS	Distance tunneling spectroscopy
EBMA	Electron beam micro analysis, see EMMA
EBSD	Electron backscatter diffraction
ECESR	Electrochemical ESR spectroscopy
ECL	Electrochemiluminescence
ECTDMS	Electrochemical thermal desorption mass spectrometry
EC-STM	Electrochemical scanning tunneling microscopy
EDX	Energy dispersive X-ray (analysis)
EDXD	Energy dispersive X-ray diffraction
EELS	Electron energy loss spectroscopy
EER	Electrolyte electroreflectance
EFM	Electric force microscopy
EFTEM	Energy filtered transmission electron microscopy
EIS	Electron impact spectroscopy (also: electrochemical impedance spectroscopy)[1]
ECALE	Electrochemical atomic layer epitaxy
ELEED	Elastic low energy electron diffraction
ELL	Ellipsometry
ELS	Energy loss spectroscopy
EMIRS	Electrode potential modulated infrared spectroscopy
EMLC	Electrochemically modulated liquid chromatography
EM(MA)	Electron microprobe (mass analysis)
EMP	Electron micro probe, see EMMA
EMSI	Ellipsomicroscopy
EQCB	Electrochemical quartz crystal balance
EQCM	Electrochemical quartz crystal microbalance
EQMB	Electrochemical quartz (crystal) microbalance
ERS	Electroreflectance spectroscopy
ESCA	Electron spectroscopy for chemical analysis
ESD	Electron stimulated desorption
ESDIAD	Electron stimulated desorption ion angular distribution
ESI	Electrospray ionization

---

[1] The use of spectroscopy in connection with impedance measurements is not reasonable, thus it is frequently discouraged.

ESI-FTMS	Electrospray ionization Fourier transform mass spectrometry
ESID	Electron stimulated ion desorption
ESI-MS	Electrospray ionization mass spectroscopy
ESR	Electron spin resonance (spectroscopy)
EXAFS	Extended X-ray absorption fine structure (analysis), see also: NEXAFS, SEXAFS
EXELFS	Extended electron loss fine structure spectroscopy
FAB	Fast atom bombardment
FAB-MS	Fast atom bombardment mass spectrometry
FCS	Fluorescence correlation spectroscopy
FD	Flash desorption
FDS	Flash desorption spectroscopy
FES	Field emission spectroscopy
FFC	Filiform corrosion
FIM	Field ion microscopy
FIS	Field ion spectroscopy
FMIR	Frustrated multiple internal reflectance (spectroscopy)
FSCV	Fast scan cyclic voltammetry
FSCV–SECM	Fast scan cyclic voltammetry scanning electrochemical microscope
FT-EMIRS	Fourier transform electrode potential modulated infrared spectroscopy
FTIR[2]	Fourier transform infrared (spectroscopy), see also: FTIRRAS, MIRFTIRS, PMFTIRRAS, SNIFTIRS, SPAIRS
FTIR	Frustrated total internal reflection[3]
FT-IR	Fourier transform infrared (spectroscopy)
FTIR-DRS	Fourier transform infrared diffuse reflection spectroscopy
FTIRRAS	Fourier transform infrared reflection absorption spectroscopy
FT-SERS	Fourier transform surface enhanced Raman spectroscopy
GAIRS	Grazing angle absorption infrared spectroscopy
GC	Glassy carbon
GISAXS	Grazing incidence small angle X-ray scattering
μGISAXS	Microbeam grazing incidence small angle X-ray scattering
GIXAFS	Grazing incidence X-ray absorption fine structure spectroscopy
GI-XAS	Grazing incidence X-ray absorption spectroscopy
GIX(R)D	Grazing incidence X-ray diffraction
HAADF	High angle angular dark field (imaging in TEM)
HEED	High energy electron diffraction
HEIS	High energy ion scattering
HIID	Heavy ion induced desorption
HIKE	High kinetic energy photoemission spectroscopy
HIXE	Proton induced X-ray emission spectroscopy

---

[2] Sometimes also written FT-IR, see there.

[3] This term is hardly used anymore, see instead ATR.

HOPG	Highly ordered pyrolytic graphite
HOPG	Highly oriented pyrolytic graphite
HPXPS	High pressure X-ray photoelectron spectroscopy
HREELS	High resolution electron energy loss spectroscopy
HRSKP	Height-regulated scanning Kelvin probe (also: HR-SKP)
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-AESE	Inductively coupled plasma atomic emission spectroelectrochemistry
ICP-MS	Inductively coupled plasma mass spectrometry
IES	Inelastic electron tunneling spectroscopy
IETS	same as IES
ILEED	Inelastic low energy electron diffraction
ILIT	Indirect laser-induced temperature jump (technique)
IMMA	Ion microprobe mass analysis
IMXA	Ion microprobe X-ray analysis
IMPS	Intensity modulated photocurrent spectroscopy
IMVS	Intensity modulated photovoltage spectroscopy
INS	Ion neutralisation spectroscopy
INSEX	*In situ* X-ray reflection/transmission diffraction
IPS	Inverse photoelectron spectroscopy
IR	Infrared spectroscopy, see also: EMIRS, IRRAS, LPSIRS
IRD	Information rich detection
IRE	Infrared emission spectroscopy, internal reflection element
IRPDS	Infrared photothermal deflection spectroscopy
IRRAS	Infrared reflection absorption spectroscopy, see also: PMFTIRRAS
IRS	Internal reflectance spectroscopy
IS	Ionisation spectroscopy
ISS	Ion surface scattering (spectroscopy)
IES	Inelastic tunneling spectroscopy
ITIES	Interface between two immiscible electrolyte solutions
ITO	Indium (doped) tin oxide
KFM	Kelvin force microscopy
LAMMA	Laser microprobe mass analysis
LD	Laser desorption, see also: linear dichroism
LEED	Low energy electron diffraction
LEEM	Low energy electron microscopy
LEIS	Low energy ion scattering
LEIS	Localized (scanning) electrochemical impedance spectroscopy
LFM	Lateral force microscopy
LIBS	Laser induced breakdown spectroscopy
LID	Laser induced fluorescence
LIMS	Laser ionisation mass spectroscopy
LIPS	Laser induced plasma spectroscopy

LPSIRS	Linear potential scan infrared spectroscopy
LRS	Laser Raman spectroscopy
LSM	Layered synthetic microstrucutures
LSPR	Localized surface plasmon resonance
MBRS	Molecular beam relaxation spectroscopy
MBS	Mössbauer spectroscopy
MBSS	Molecular beam surface scattering
MCD	Magnetic circular dichroism
MCT	Mercury cadmium telluride (detector)
MEF	Metal enhanced fluorescence
MEIS	Medium energy ion scattering
MER(S)	Multiple external reflectance (spectroscopy)
MFM	Magnetic force microscopy
MFON	Metal film over nanospheres
MFTIRS	Microscope Fourier transform infrared spectroscopy
MIR(S)	Multiple internal reflectance (spectroscopy)
MIRFTIRS	Multiple internal reflection Fourier transform infrared spectroscopy
MMC	Metal matrix composite
MOKE	Magneto-optical Kerr effect
MORE	Micro-optical ring electrode
MR	Micro Raman (spectroscopy)
MSHG	Magnetization induced second harmonic generation
MSS	Molecule-surface scattering
NEXAFS	Near edge X-ray absorption fine structure spectroscopy
NIR	Near infrared (spectroscopy)
NIR-SERS	Near infrared surface enhanced Raman spectroscopy
NIS	Neutron inelastic scattering
NR(S)	Normal Raman (spectroscopy)
NPD	Neutron powder diffraction
NSOM	Near field scanning optical microscope
OLEMS	Online electrochemical mass spectrometry
ORC	Oxidation-reduction electrode potential cycling
OPG	Ordinary pyrolytic graphite
OSEE	Optically stimulated exoelectron spectroscopy
OTE	Optically transparent electrode
PAM	Photoacoustic method
PAS	Photoacoustic spectroscopy
PASCA	Positron annihilation spectroscopy for chemical analysis
PAX	Photoelectron spectroscopy with adsorbed xenon
PBD	Probe beam deflection
PCS	Photocurrent spectroscopy
PD	Photodesorption
PDATRFTIRS	Potential dependent attenuated total reflectance Fourier transform infrared spectroscopy

PDBS	Photothermal beam deflection spectroscopy
PDFTIRRAS	Potential difference Fourier transform infrared reflection absorption spectroscopy
PDFTIRES	Potential difference Fourier transform infrared emission spectroscopy
PDIRS	Potential difference infrared spectroscopy
PDMS	Plasma desorption mass spectrometry
PDS	Photothermal deflection spectroscopy
PECM	Photoelectrochemical microscope
PEEM	Photoelectron emission microscopy
PEIS	Photoelectrochemical impedance spectroscopy[4]
PEM	Photoelastic modulator
PEM	Photoelectrochemical measurement
PES	Photoelectron spectroscopy, see also: ESCA, UPS, XPS
PFM-AFM	Pulsed-force mode atomic force microscopy
PG	Pyrolytic graphite
PhD	Photoelectron diffraction
PHEEM	Photoemission electron microscopy
PI	Penning ionization
PIG	Paraffin-impregnated graphite
PIGME	Particle induced gamma ion emission
PIXE	Particle induced X-ray emission spectroscopy
PMFTIRRAS	Polarisation modulated Fourier transform infrared reflection absorption spectroscopy
PMFS	Potential modulated fluorescence spectroscopy
PMR	Potential modulated reflectance
PMRS	Potential modulated reflectance spectroscopy
PPES	Photopyroelectric (photothermal) spectroscopy
PSD	Photon-stimulated desorption
PSI	Phase-shift interferometry
PSP	Plasmon surface polaritons
PSTM	Photon scanning-tunneling microscope
PTS	Photothermal spectroscopy
PVS	Photovoltage spectroscopy
QEXAFS	Quick-scanning extended X-ray absorption fine structure (analysis)
RAIRS	Reflection absorption infrared spectroscopy
RAS	Raman spectroscopy [also NR(S)], see also: DESERS,SERRS, SERS, SRS, SRRS, SUERS
RAS	Reflection anisotropy spectroscopy, see also: RDS
RBS	Rutherford backscattering
RDE-EIS	Rotating disc electrode electrochemical impedance spectroscopy

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[4] See footnote on p. xii.

RDS	Reflectance difference spectroscopy, see also: RAS
RC-SECM	Redox competition mode scanning electrochemical microscopy
ReflEXAFS	EXAFS at a grazing angle below the critical angle of total reflection
REMPI	Resonance enhanced multiphoton ionization
RHEED	Reflected high energy electron diffraction
RIBS	Rutherford ion backscattering spectroscopy
RRS	Resonance Raman spectroscopy
RTIL	Room temperature ionic liquid
SAES	Scanning Auger electron spectroscopy
SAM	Scanning Auger microprobe
SAM	Self-assembled monolayer
SANS	Small angle neutron scattering
SAPG	Stress-annealed pyrolytic graphite
SAXS	Small angle X-ray scattering
SC	Surface conductivity (measurement)
SDD	Surface differential X-ray diffraction
SDEMS	Scanning differential electrochemical mass spectroscopy
SECM	Scanning electrochemical microscope
SEF	Surface enhanced fluorescence
SEI	Solid electrolyte interface
SEIDAS	Surface enhanced infrared difference absorption spectroscopy
SEIRAS	Surface enhanced infrared absorption spectroscopy
SEIRRAS	Surface enhanced infrared reflection absorption spectroscopy
SEM	Scanning electron microscope
SERS	Surface enhanced Raman spectroscopy
SEHRS	Surface enhanced hyper-Raman spectroscopy scattering
SERHRS	Surface enhanced resonance hyper-Raman spectroscopy
SERRS	Surface enhanced resonance Raman spectroscopy
SES	Surface enhanced spectroscopy
SESHG	Surface enhanced second harmonic generation
SEVS	Surface enhanced vibrational spectroscopy
SEXAFS	Surface extended X-ray absorption fine structure (analysis) spectroscopy
SFG	Sum frequency generation
SFIRS	Synchrotron far infrared spectroscopy
SFM	Scanning force microscopy, see also: AFM
SG/TC	Substrate generation/tip collection (mode)
SHEED	Surface high energy electron diffraction
SHG	Second harmonic generation
SI	Surface ionisation
SICM	Scanning ion conductance microscopy
SIET	Scanning ion-sensitive electrode technique
SIMS	Secondary ion mass spectroscopy

SKP	Scanning Kelvin probe
SKPFM	Scanning Kelvin probe force microscopy
SMD	Single molecule detection
SMOKE	Surface magneto-optical Kerr effect
SMS	Single molecule spectroscopy
sm-SERS	Single molecule surface enhanced Raman spectroscopy
SMS-SERS	Single molecule surface enhanced Raman spectroscopy
SNMS	Secondary (sputtered) neutral (ion) mass spectroscopy
SNIFTIRS	Subtractively normalized interfacial Fourier transform infrared spectroscopy
SNIM	Scanning near field infrared microscopy
SNOM	Scanning near field optical microscopy
SORS	Spatially offset Raman spectroscopy
SP	Surface plasmon
SPAIR(S)	Single potential alteration infrared (spectroscopy)
SPFELS	Surface plasmon field enhanced light scattering
SPLS	Surface plasmon enhanced light scattering (see also SPFELS)
SPM	Scanning probe microscopy, see also: STM, EFM, MFM, AFM, SEM
SPPL	Surface plasmon enhanced photoluminescence
SPR	Surface plasmon resonance
SPS	Surface photovoltage spectroscopy
SQUID	Superconducting quantum interference device
SRET	Scanning reference electrode technique
SR-GIX(R)D	Synchrotron radiation grazing incidence X-ray diffraction
SRRS	Surface resonance Raman spectroscopy
SRS	Surface Raman spectroscopy
SRS	Specular reflectance spectroscopy
STEM	Scanning transmission electron microscopy
STM	Scanning tunneling microscopy
STS	Scanning tunneling spectroscopy
SUERS	Surface unenhanced Raman spectroscopy
SVET	Scanning vibrating electrode technique
SW-FTIRS	Square wave Fourier transform infrared reflection spectroscopy
SWNT	Single-wall carbon nanotube
SXAPS	Soft X-ray appearance potential spectroscopy
SXES	Soft X-ray emission spectroscopy
SXS	Surface X-ray scattering
TDMS	Thermodesorption mass spectroscopy
TDS	same as TDMS
TEAS	Thermal energy atom scattering
TEF	Tip enhanced fluorescence
TERS	Tip enhanced Raman scattering
THG	Third harmonic generation

TLC	Thin layer cell
TPD	Temperature-programmed desorption
TPRS	Temperature-programmed reaction spectroscopy
TR-SFG	Time-resolved sum frequency generation
TRBD	Total reflection Bragg diffraction
UME	Ultramicroelectrode
UPS	Ultraviolet photoelectron spectroscopy
UV-Vis	Spectroscopy with UV and visible light
VASE	Variable angle spectroscopic ellipsometry
VSF	Visible sum frequency
VSFG	Vibrational sum frequency generation
VTS	Voltage tunneling spectroscopy
WAXS	Wide-angle X-ray scattering
WDX	Wavelength dispersive X-ray (analysis)
XANES	X-ray absorption near edge structure
XES	X-ray emission spectroscopy
XPD	X-ray photoelectron diffraction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRR	X-ray reflection
XSW	X-ray standing wave

α	Accommodation coefficient measurement
σ	Adsorption isotherm measurement
θ	Degree of coverage
$\varnothing$	Work function
$\varnothing_{\mathrm{PE}}$	Work function determination by photoemission measurement
$\varnothing_{\mathrm{TE}}$	Work function determination by thermoemission measurement
$\varnothing_{\mathrm{FE}}$	Work function determination by field emission measurement
$\varnothing_{\mathrm{FERP}}$	Work function determination by field emission retarding potential measurement
$\varnothing_{\mathrm{DTERP}}$	Work function determination by diode thermoemission retarding potential measurement
$\varnothing_{\mathrm{K}}$	Work function determination by Kelvin method

List of Symbols

Common symbols and abbreviations used in electrochemistry[1]

A	Area, constant, optical absorption
a	Activity, absorption coefficient
a_i	Debye length
CV	Cyclic voltammogram
C	Capacitance / µF
C_D	Double layer capacity / µF
C_diff	Differential double layer capacity
C_int	Integral double layer capacity
c	Concentration / **M**
c_s	Surface concentration
c_0	Bulk concentration / **M**
D	Diffusion coefficient / $\mathrm{cm}^2\ \mathrm{s}^{-1}$
d	Distance
E	Electrode potential / V
$\boldsymbol{E}$	Electrical field strength
E_A	Activation energy / $\mathrm{kJ\ mol}^{-1}$
E_F	Fermi energy
E_H	Electrode potential vs. standard hydrogen electrode, see also: E_NHE
$E_{\mathrm{Hg_2SO_4}}$	$= E_\mathrm{MSE}$
E_MSE	electrode potential vs. mercurous sulfate electrode, $c_\mathrm{sulfate} = 0.1\ \mathbf{M}$
E_m	Electrode potential of measurement, also: E_meas
E_NCE	Electrode potential vs. normal calomel electrode
E_NHE	Electrode potential vs. normal (i.e. standard) hydrogen electrode[2]
E_pzc	Electrode potential of zero charge
E_ref	Reference electrode potential, electrode potential of reference measurement, see also: E_r
E_r	Reference electrode potential, electrode potential of reference measurement, also: E_ref

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[1] For further details of electrochemical symbols, see R. Parsons, *Pure Appl. Chem.* **37** (1974) 499.

[2] The term "normal electrode" should be avoided because normal may be misunderstood as a designation of a certain concentration.

E_{SCE}	Electrode potential vs. saturated calomel electrode
E_{SHE}	Electrode potential vs. standard hydrogen electrode
E_0	Electrode potential at rest (i.e. $I = 0\ \mathrm{mA\,cm^{-2}}$)
E_{00}	Standard electrode potential
ΔE	Difference of electrode potentials, e.g. peak potentials
e_0	Elementary charge
F	Faraday constant
I	Ionic strength
I	Current / A
I_{ct}	Charge transfer current / A
j_{ct}	Charge transfer current density / A cm^{-2}
k	Extinction coefficient
M	Molarity / $\mathrm{mol{\cdot}l^{-1}}$
M	Molar mass
m	Molality
N_{L}	Loschmidt number
n	Number of mols, electrode reaction valency, refractive index
R	Resistance, universal gas constant, reflected intensity of light
R_{CT}	Charge transfer resistance
Rf	Roughness factor
R_{sol}	Electrolyte solution resistance
RHE	Relative hydrogen electrode
T	Absolute temperature
u	Ionic mobility
upd	Underpotential deposit
V	Volume
v	$\mathrm{d}E/\mathrm{d}t$, scan rate in cyclic voltammetry

Part I

Introduction and Overview

1 Introduction

Electrochemistry is an extremely interdisciplinary area of science closely related to chemistry, physics, materials science, biology, surface science and a host of other fields. It is basically devoted to investigations of structures and dynamics as being present at interfaces between phases containing different types of mobile charged particles. Thus the process of electrochemical production of chlorine proceeding at the surface of a metal electrode in contact with a halide-containing solution in chlorine-alkali electrolysis is a typical case of electrochemistry at work. In the electrode the mobile charges are electrons, which are withdrawn from the chloride anions that are the mobile charged species in the solution phase. The interface established between molten iron and the fairly complicated mixture of molten metal oxides floating on top of the molten metal is another example. The stimulation of nerves and the propagation of information along nerves is another, totally different case. One more different case is the delamination of an organic coating applied to a metal surface for corrosion protection that occurs because of processes occurring at the metal-coating interface in the presence of a thin solution film on top of the coating containing small concentrations of electrolyte salts. In all of the examples just mentioned charged particles and large electric fields at interfaces play a pivotal role in establishing the structure at the interface and in controlling the various processes occurring at the interface. These examples share an additional feature that may possibly complicate their investigation: All interfaces are "buried" between two condensed phases (liquid or solid). Electrochemical investigations have focused in recent decades on elucidating their static and dynamic features exactly. The breadth of the few listed examples illustrates the need for intense research. Beyond these aspects of interfacial electrochemistry, the processes and structures within a condensed phase containing ions far away from the interface with their particular properties are the other main topics of electrochemistry. They are related to ionic conduction, thermodynamics of perfect (ideal) and real phases and other topics that are of only peripheral interest within the scope of this book. Initial investigations of electrochemical interfaces were limited to the measurements of electrical and chemical quantities, e.g. current, voltage, potential, charge or concentration. Kinetics could be elucidated by performing these measurements as a function of time, concentration and temperature. Unfortunately the obtained results provided in most cases only a very rough and macroscopic picture. A complete understanding, in particular at the microscopic level, was impossible or only highly speculative. With the increasing importance and breadth of the application of electrochemistry in industry, technology and daily life, this has become a considerable obstacle. Optimization of a given system or process and the understanding of the failure of a product with electrochemical features is possible only based on a deeper understanding of the electrochemical interface.

The advent of a broad variety of methods in vacuum physics, surface and materials science and analytical chemistry has provided a rich zoo of methods that have been converted for use in experimental electrochemistry. In contrast to the experimental methods briefly touched upon before, these methods are summarized as "non-traditional methods".

The overwhelming abundance of available methods is a tremendous possibility and a considerable seduction. Reasonable use of available methods and selection of the most suitable ones is possible only based on at least a minimum knowledge of the available methods, their strengths and weaknesses and their known pitfalls. So far the researcher has to consult either the original literature, including numerous more or less strongly focused reviews, or quite a few books that provide overviews of some subfamilies of the large number of available methods. The present book attempts to provide a broad overview delving into the depth of a certain method only as far as necessary to provide an initial understanding. It attempts to include all known methods of investigation applied to electrochemical interfaces that have arrived at a stage where a useful application has become visible to a broader audience.

In the following chapters and sections this will be done in a way that will hopefully be useful for the researcher looking for a method for his particular problem and for the graduate student looking for possible methods to treat the task of his masters thesis. In the second chapter, the structure and dynamics of electrochemical interfaces will be reviewed briefly. The term "interphase" will be introduced, stressing the fact that the topmost layers or regions of both phases that are in contact at the interface are different from layers and regions within the bulk of the phases. The third chapter pays a closer look at the possibilities of classical electrochemical methods and stresses the limitations beyond which traditional electrochemical methods provide only the basis for speculative interpretation of experimental data.

In Chap. 4, spectroscopic and surface analytical methods that form the bulk of this book are treated in the form of a general overview. This chapter will be of interest for a reader with an already established background in traditional electrochemistry who is looking for a general introduction. Chapter 5 provides the complete picture of spectroscopic methods. Chapters 6 and 7 treat X-ray and surface topographic methods. A brief introduction explains the way methods are assigned to various families. Descriptions of the available methods as known to the author are provided together with instructive examples of their applications. The structure of a description always follows the same scheme. The fundamentals are presented briefly. The electrochemical system properties that can be investigated with the method are indicated. A description of the experimental setup is provided. Some examples serve as illustration. References are provided especially for methods and experimental details that cannot be treated exhaustively within the limited scope of this book. No attempt is made to provide a complete listing of all reported applications of a given technique.

A generous list of acronyms is provided, giving the reader access to fast explanations of the myriad of examples of the modern letter soup omnipresent in scientific papers. The subject index will serve as a fast access lane especially for those readers searching for information about a particular method.

2 Structure and Dynamics of Electrochemical Phase Boundaries

In our environment surfaces, phase boundaries and interfaces are omnipresent. A living cell, a crystal of salt, a living organism, a cutting tool or a sheet of metal are separated from the surroundings by surfaces—and thus interfaces are established. At a first glance this may be accepted as a trivial and obvious fact of life without much importance. The properties and activities of a biological cell are presumably controlled by its structure and the processes occurring in its interior; density and the chemical and physical properties of a crystal depend on the chemical identity of its constituents and their arrangement in the crystal. The same may be said of the other examples. A closer look at this understanding leaves a number of open questions, because many processes of central importance are occurring at the interface. By just looking at the bulk properties of the adjacent systems these properties may be understood improperly or, sometimes, not at all.

This quickly becomes evident when we take another look at our examples: The exchange of all materials (nutrients, water, waste, etc.) of a cell with the environment occurs via the membrane enclosing the cell, wherein a liquid/liquid interface is established. The permeability of the membrane is of vital importance for a proper functioning of these transport processes. It depends upon the structure of the membrane itself and the structure and composition of the interface between the membrane and the surrounding atmosphere. The selective permeability for toxins of the cells and membranes constituting an animal's skin may be a reason for the massive die-off among amphibians. The practical applicability and the many mechanical properties of a cutting tool certainly depend on the bulk properties of the used raw material. But the durability of the cutting edge, its hardness and stability even under demanding operating conditions, depend mostly upon the chemical composition and structure of its surface, which basically forms a solid/gas interface. Surface hardening or treatment by, for example, ion implantation or galvanic deposition of additional material, may considerably change and improve the bulk material's initial properties. The corrosion stability of the metal sheet depends of course upon the chemical identity or, in the case of an alloy, the composition of the metal. But corrosion takes place only on the outermost layer of the sheet, and consequently the surface properties once more control the process occurring at this solid/liquid interface.

These apparently unrelated examples have one feature in common: Structure or dynamics or even both at the interface are strongly influenced by electronic charges that are present as ions in the liquid around the membrane or the corroding metal. Sometimes the participation of charged particles in chemical processes as necessary in the surface treatment of the cutting tool is essential. The investigation of the structure and dynamics of interfaces influenced by electric charges or by charged particles is the task of electrochemists. Traditional methods and their limits will be reviewed briefly in the following chapter.

3 Scope and Limitations of Classical Electrochemical Methods

The experimental tools of electrochemists were, until a few years ago, mainly rather simple measurements of electrical, physical and chemical quantities. Using a broad variety of experimental methods today called "classical electrochemical methods", they were able to provide models of electrified interfaces with respect to both structure and dynamics. Unfortunately their results were in many cases of a very macroscopic nature, any interpretations of the model with respect to the microscopic structure and mechanistic aspects of the dynamics and reaction were only more or less reasonable derivations. This gap, which caused many misunderstandings of puzzling features in electrochemical processes and interfaces, has started to close. The use of an enormous variety of spectroscopic and surface analytical tools in investigations of these interfaces has considerably broadened our knowledge. In many cases microscopic models based on the results of these studies with "non-traditional electrochemical methods" have enabled us to understand many hitherto strange phenomena in a convincing way.

The "traditional methods" generally are based upon measuring the potential of a working electrode and the current necessary to establish this potential. In many cases the registration of these data is done as a function of time, concentration or some other additional experimental variable. The relationship between current and potential, in particular the deviation of the actual electrode potential established during the flow of a current from the rest potential at nil current, can be explained by assuming a variety of hindrances impeding the flow of current or increasing the electrode potential actually necessary to obtain the desired current. This difference of potentials is called overpotential and the various contributing hindrances are named according to the cause of the hindrance: A charge transfer overpotential is caused by a sluggish charge transfer needing additional activation energy in order to proceed at appreciable rates. The slow mass transport caused by limited rates of diffusion, convection or migration generates a concentration overpotential (sometimes it is more precisely called "diffusion overpotential"). The name implies that an insufficient concentration of a reactant needed in the electrochemical reaction is the cause. Of course a small concentration of the reactant in the bulk of the solution enhances this effect. Slow removal of reaction products will also result in diffusion overpotentials. Chemical reactions preceding or following the charge transfer as heterogeneous reactions on the electrode surface or as homogeneous reactions in the solution phase produce reaction overpotentials. As both transport and reaction tend to impede the overall rate of the electrochemical reaction by limiting either the supply of reactants or the removal of products, they are sometimes summarized as concentration overpotentials. Finally, adsorption or desorption of reactants and crystallization in the case of metal deposition or dissolution may be slow, resulting in adsorption or crystallization overpotentials. Numerous electrochemical methods have been used to separate these various overpotentials in order to get a handle for further improvements of the reaction rate for practical applications or to get a better understanding of the reaction kinetics. Of course, it was always tempting to deduce mechanistic models describing the reaction on a molecular-microscopic level. Unfortunately, such deductions must be mostly tentative because they generally are not based on direct molecular or atomic evidence of the actual identity of the species proposed as participants in the electrochemical reaction sequence.

This lack of evidence has stimulated intense efforts to modify known methods in order to comply with the specific requirements of measurements in the presence of an electrolyte solution or other specifics of electrochemical investigations.

At any given interface between two phases the properties of both phases close to the interface and, in particular, those of the topmost layers are different from those in the bulk. In order to separate this special portion of a system from both bulk phases the term interphase has been coined for this quasi-phase in between the bulk phases. This term considerably expands the two-dimensional view of the phase boundary as a simple interface between two completely homogenous phases. The particular properties of these interphases are of pivotal importance for their behavior in many areas of science and technology. In applied sciences an improvement of these properties is possible only with knowledge of these properties that is as broad and deep as possible. In electrochemistry the interphase properties are further complicated by the involvement of charged particles and extremely high electric fields. A broader overview of the electrochemical interface will identify further adjacent domains:

- The electrolyte solution
- Diffusion and/or reaction layers
- The electrochemical double layer comprised of the diffuse (Gouy-Chapman) and the inner (Helmholtz) layer
- Space charge layers and surface states (with semiconducting electrodes)
- Adsorbed species on the electrode surface
- Molecular or polymer films
- The bulk of the electrode material

Properties of interphases relevant for an understanding of structures and dynamics therein can be grouped into atomic (microscopic) and macroscopic ones. Nevertheless the close relationships between both types of properties have allowed us to infer conclusions with respect to atomic models from macroscopic information. Investigations of these properties have gained tremendously in recent years from the application of a broad variety of spectroscopic methods. Certainly many properties, in particular macroscopic ones, can be studied by measuring surface properties (like conductivity, hardness, etc.) with non-spectroscopic methods. In most cases the results will be rather general and a complete understanding of relationships between the surface properties of interest, any structural features of the surface and the interphase on an atomic level will not be accessible. This will seriously obstruct further improvements of the knowledge of these properties.

4 Spectroscopy and Surface Analysis at Interfaces Between Condensed Phases

The need for further methods to study electrochemical interfaces and interphases has been indicated in the preceding chapter. Spectroscopic methods in particular were suggested as suitable tools [1–3]. The major advantage was considered to be their capability to provide information on a microscopic level by probing the subject of interest, resulting in signals that contain the desired information specifically from the place of interest. In this chapter a first overview is given of available methods and possible approaches for a typical selection of experimental tasks, which are taken predominantly from electrochemical investigations. All methods will be dealt with in detail in the sections of the following chapters; thus the immediately following text is addressed preferably at the reader looking for a general introduction.

The broad variety of methods suitable for spectroscopy at surfaces and other kinds of surface analysis has been touched upon already in the preceding chapter. The term "surface" referred mostly to solids being exposed to a vacuum or even ultra high vacuum environment. Few methods can be used under ambient conditions and at atmospheric pressure or even in the presence of condensed phases as encountered in electrochemical systems because of the strong interactions between several probes and signals with particles in condensed phases or in the gas phase at ambient temperature and pressure. The same line of argument applies to the interface between immiscible liquids.

The application of spectroscopic methods to surface studies always involves a probe used to stimulate or perturb the interphase in a well-defined way. This causes a signal to be emitted from the interphase. In many cases the signal is simply the modulated probe. Special care has to be exercised in order to obtain information exclusively from those parts of the interface as close as possible to the interface. Many techniques are essentially surface sensitive (i.e. selective). In some cases methods or sample systems have to be modified in order to achieve this surface sensitivity.

The broad range of energies (or wavelengths, frequency or any other equivalent unit) as depicted in Fig. 4.1 provides ample opportunities to develop methods.

Various probes available for surface studies are depicted in Fig. 4.2. Electromagnetic radiation ($h \cdot \nu$), neutral atom beams (i^0), ion beams ($i^{\pm}$), magnetic (H) or electric (E) fields and thermal excitation (W) can be used as probes.

Because of the numerous different types of interactions and resulting signals, the possible combinations of probes and signals are myriad. A simple matrix indicating some of these combinations and the resulting methods is provided in Table 4.1.