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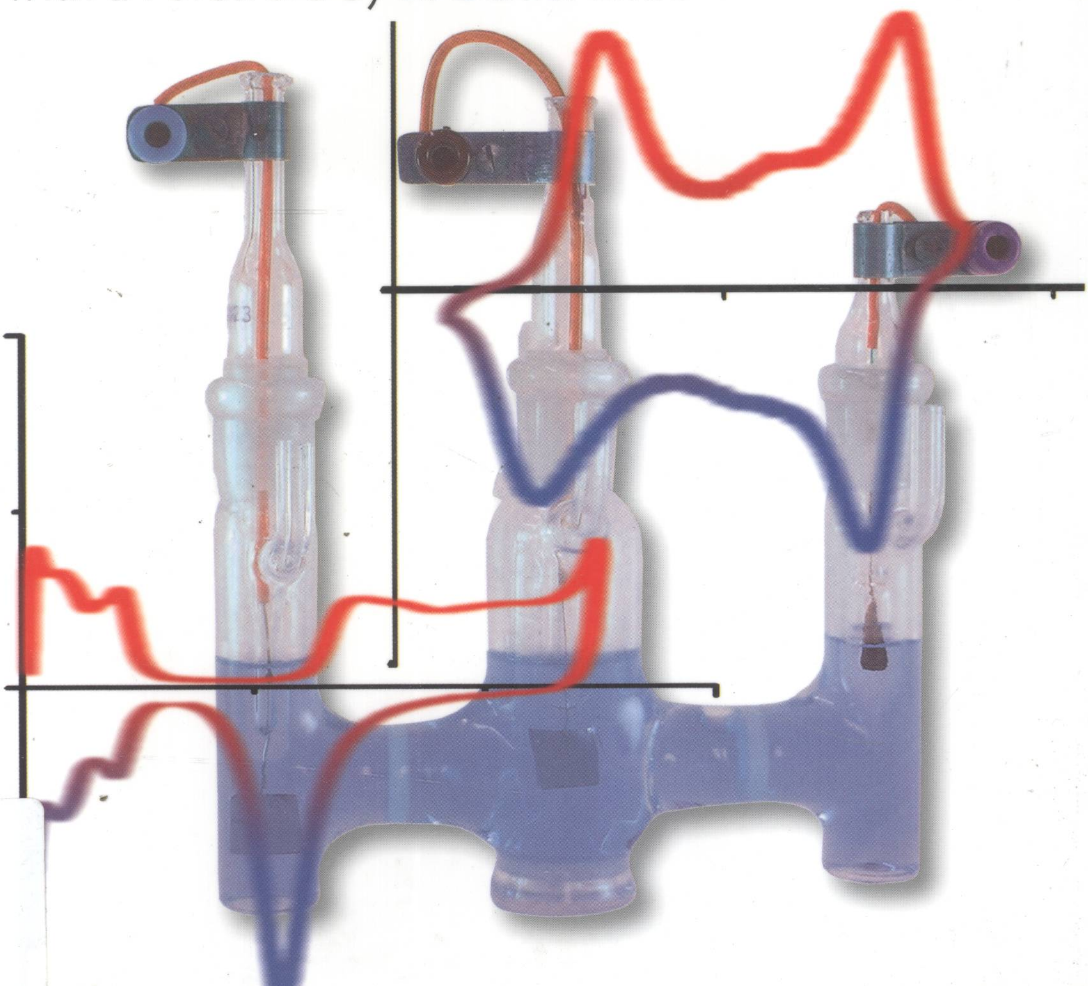
Experimental Electrochemistry

A Laboratory Textbook

With a Foreword by R. Daniel Little



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Preface

Electrochemistry, taught as a subject at all levels from advanced classes in high school to the research of PhD students, is an extremely interdisciplinary science. Electrochemical processes, methods, models, and concepts are present in numerous fields of science and technology. This clearly illustrates the extremely interdisciplinary character of this branch of science. Accordingly, the points of contact with this science are numerous at all levels of education. Being an experimental science, electrochemistry demands the personal experience – the direct hands-on test of a model or a theory is more convincing than anything else. Consequently, at all levels of education, electrochemical experiments of different degrees of complexity are to be found. The intensity of the interaction ranges from the simple application of an electrochemical instrument (e.g., in a pH measurement or the electrolytic generation of hydrogen) up to complete electrochemical laboratory courses as offered in many universities. The increasing importance of the numerous applications of electrochemistry in sensors, surface technology, materials science, microsystems technology, and nanotechnology will certainly help to enhance this importance and omnipresence.

After publication in 1953 of the ninth and final edition of the book "Elektrochemisches Praktikum", initially published in 1931 by Erich Müller, no textbook in German providing a collection of descriptions of reproducible electrochemical experiments illuminating the whole scope of this science has been published. English textbooks are only slightly more recent. The textbook by N.J. Selley: Experimental Approach to Electrochemistry (Edward Arnold, London 1977) has been out of print for some time. The workbook by J. O'M. Bockris and R.A. Fredlein: A Workbook of Electrochemistry (Plenum Press, New York – London 1973), being a useful supplement from the theoretical point of view though without any experiments described in it, has met the same fate. Thus there seems to be a considerable need for a textbook containing a collection of descriptions of reproducible experiments suitable for course work at all levels from advanced high school to graduate school at university. The Eurocurriculum Electrochemistry developed by the Federation of European Chemical Societies as approved in 1999 called (so far without success) for descriptions of laboratory exercises supplementing the numerous already available textbooks. This curriculum was taken as a guideline. The selection presented here is based on an extensive

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collection of experiments developed and installed as part of laboratory courses for students of chemistry, materials science, and other sciences also. In addition it contains experiments developed for teachers at various levels in school where pupils will encounter electrochemistry for the first time. Because the whole range of electrochemistry can hardly be present as a whole at a single place and in one research group, experiments and their descriptions as supplied by instructors from other universities are included. Thus, special thanks are due to F. Beck, H. Schäfer, J.-W. Schultze, M. Paul, K. Banert, H. J. Thomas, R. Daniel Little and E. Steckhan†. The development of the described experiments and the corresponding instructions in the author's group would have been impossible without the enthusiastic cooperation of creative students and researchers. W. Leyffer, K. Pflugbeil, J. Poppe, and M. Stelter have provided invaluable support by careful evaluation and optimization of experimental concepts; numerous students in laboratory courses have provided results and further input; this is gratefully acknowledged. Finally, E. Rahm has tested many descriptions for practical applications; without her, many minor and perhaps even some major defects would have made it into print. Part of the manuscript was prepared during a stay at St. Petersburg State University: the generous hospitality of my host V. Malev and the stimulating environment as well as a travel stipend of DAAD are gratefully acknowledged.

The scope of electrochemistry is not only illustrated by the diversity of methods and concepts; it is also demonstrated by the range of instruments and tools employed. The experiments described here range from simple tests easily performed at school to complex investigations requiring spectrometers and other large instruments most likely feasible only in a university laboratory. Thus, the author hopes to provide some stimulating input for teachers at both limits of the range: the high school teacher looking for an experiment demonstrating ionization as well as the university professor extending his physical or organic chemistry laboratory course.

In all descriptions emphasis is placed on clear, well-defined, and lucid descriptions, including all details needed for successful repetition of the experiment. Unnecessary details are avoided. Practical details of an experimental setup and instruction for manufacturing are added only if really necessary. Safety instructions and suggestions for safe experiments are provided only in case of particular dangers. Complete lists of dangers, risks, and safety instructions, which are very likely present in every chemistry laboratory are not given. Instrument manufactures are not mentioned or suggested as this might cause undesirable reluctance in installing a given experiment. Only specific characteristics of an instrument required for, e.g., a spectroscopic experiment, are stated.

The present book cannot supplement a textbook of electrochemistry. Any attempt would have resulted in a book of excessive size, which in addition would be hard to use. Instead, brief introductions and some background are provided at the beginning of every description, supplemented by references to the textbook by C.H. Hamann, A. Hamnett, and W. Vielstich: Electrochemistry, Second edition, (Wiley-VCH, Weinheim 2007), quoted as EC and the respective page number. If necessary, further references to textbooks, review articles, and research papers are added.

A collection of experiments and their descriptions as provided following is a "work in progress". Further experiments related to new or less popular areas of electrochemistry will be added continuosly, for an update see http://www.tu-chemnitz.de/chemie/elchem/elpra. Further illustratins of experiments described in this book including short videos demonstrating visible changes of the system under investigation will be made available at the publishers website.

Symbols and descriptions in figures are used according to suggestions by IUPAC (Pure Appl. Chem. **37** (1974) 499). When compared with older textbooks this might occasionally result in minor confusion; the list of symbols, acronyms, and abbreviations will help (p. XV). Dimensions are separated by a slash (quantity calculus); square brackets are only used when necessary to avoid confusion.

Chemnitz, December 2008 Rudolf Holze

Foreword

Electrochemistry is everywhere in our daily life: It powers our cell phones, notebook computers and many other electronic devices, it provides the power to start our cars in the morning, it is undesirably present in corrosion, but also in metal winning and refining and the list goes on and on and...

Consequently electrochemistry is a prominent subject in science and technology. Being an experimental science, progress in electrochemistry strongly depends on the close interplay between theory and practice. This interplay should start in education and teaching as early as possible. The present book illustrates this suggestion nicely: It contains a wide collection of experiments covering almost all areas of experimental electrochemistry ranging from simple, basic experiments for classes in high school to elaborate ones for advanced students at universities. The book fills a gap that has existed for some time as indicated in the electrochemistry curriculum of the *International Society of Electrochemists*: There are numerous textbooks on electrochemistry, but a book on electrochemical experiments is completely missing. The broad selection of experiments, carefully and reproducibly described, offers numerous possibilities useful in different educational environments depending on local traditions in teaching, safety regulations and curricula; it favorably complements existing textbooks on this subject (without repeating their content in undue length). The obvious relationship between theory and experiment is consistently presented, and as an interesting feature of the book, the practical importance in our daily life is highlighted also in many experiments.

This book will hopefully be a helpful companion for everyone teaching and studying electrochemistry at all levels thus providing a deeper understanding of those numerous phenomena and processes that are associated with the science of electrochemistry.

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Symbols and Acronyms

A	Area
a	Activity
a_i	Debye length
C	Cell constant of a conductivity measurement cell
CV	Cyclic voltammogram
C_D	Double layer capacity
C_{diff}	differential double layer capacity
C_{int}	integral double layer capacity
c_p	isobar molar heat
c_V	isochoric molar heat
c	molar concentration
c_s	Surface concentration
c_0	Bulk concentration
D	Diffusion coefficient
d	Electrode distance
E	Electrode potential
E	electric field strength
ΔE_p	Difference of electrode peak potentials
E_0	Electrode potential at equilibrium with no flow of current, formal potential
E_{00}	Standard electrode potential
E_a	Energy of activation in a chemical reaction
E_F	Fermi energy, Fermi edge
$E_{Hg_2SO_4}$	see E_{MSE}
E_{MSE}	Electrode potential vs. a mercurous sulphate electrode, $c_{Hg_2SO_4} = 0.1$ M
E_m	Measurement potential
E_{pzc}	Electrode potential of zero charge
$E_{p,ox}$	Electrode peak potential of oxidation reaction
$E_{p,red}$	Electrode peak potential of reduction reaction
E_{red}	Redox electrode potential
E_{ref}	Reference electrode potential
E_{RHE}	Electrode potential vs. relative hydrogen electrode

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E_{SCE}	Electrode potential vs. saturated calomel electrode SCE
e_0	Elementary charge
F	Force
F	Faraday constant
f	Measurement error, standard deviation; frequency, fugacity of a gas i ($f_i = \gamma_i p_i$)
ΔG	Gibbs energy (change); Gibbs energy of ion-solvent interaction
$\Delta H_{\mathrm{Ion\text{-}LM}}$	Enthalpy of ion-solvent interaction
HOMO	Highest occupied molecular orbital
HRE	Hydrogen reference electrode
I	Ionic strength
I	Current (total current), also flow of species
I_a	Current transported by anions
I_c	Current transported by cations
I_C	Capacitive current
I_{ct}	Charge transfer current
I_{diff}	Diffusion-limited current (also: $I_{\mathrm{lim,diff}}$)
I_D	Disc current at a ring-disc electrode
$I_{\mathrm{D,diff}}$ D	iffusion limited disc current at a ring-disc electrode
I_p	Peak current
I_R	Ring current at a ring-disc electrode
$I_{\mathrm{R,diff}}$	Diffusion limited ring current at a ring-disc electrode
I_{sc}	Short circuit current
j	Current density
j_{ct}	Charge transfer current density
j_{diff}	Diffusion limited current density (also: $j_{\mathrm{lim,diff}}$)
j_{lim}	Limiting current density
j_R	Ring current density at a ring-disc electrode
j_D	Disc current at a disc or ring-disc electrode
K	Equilibrium constant
K_c	Concentration equilibrium constant, also: dissociation (equilibrium) constant
K_s	Dissociation (equilibrium) constant
k	Kohlrausch constant, rate constant
L	Conductance, electrical conductance; also: solubility product
LUMO	Lowest unoccupied molecular orbital
M	Molarity
M	Molar mass, atomic mass
m	Molality, flow rate of mercury at the dropping mercury electrode in $\mathrm{mg \cdot s^{-1}}$
N_A	Avogadro's number (see also: N_L)
N_L	Loschmidt number (see also: N_A)
n	Number of mols
n	Electrode reaction valency

n_A	Number of mols of anions
n_C	Number of mols of cations
n^+	Stoichiometric coefficient of cations
n^-	Stoichiometric coefficient of anions
p. A.	pro analysi: pure for analysis, degree of purity of a substance
Q_{DL}	Electrical charge needed for double layer charging
q_e	Charge of an electron
q^-	Charge transported by anions
q^+	Charge transported by cations
R	Electrical resistance, gas constant
R_{ct}	Charge transfer resistance
R_f	Roughness factor
R_{sol}	Electrolyte solution resistance
RHE	Relative Hydrogen Electrode
r_i	Ionic radius
r_1	Disc radius of a ring-disc electrode
r_2	Inner ring radius of a ring-disc electrode
r_3	Outer ring radius of a ring-disc electrode
SOMO	Semioccupied molecular orbital
T	Absolute temperature
t	Transference number
t^+	Transference number of cations
t^-	Transference number of anions
t	Student's t-factor
U	Electrical voltage, difference of two electrode potentials
U_0	Electrical voltage at equilibrium ($I=0$), difference of two electrode potentials at equilibrium ($I=0$),
U_d	Decomposition voltage
u	Ionic mobility, $u=v/E$
V	Volume
v	Traveling velocity of ions; rate of mercury flow at a dropping mercury electrode
v	dE/dt, scan rate in cyclic voltammetry
v	Kinematic viscosity
x	Mole fraction
z	Ionic charge number

Greek symbols

α	Degree of dissociation, symmetry coefficient
χ	Surface potential
δ	Diffusion layer thickness
δ_N	Nernst diffusion layer thickness
$\varepsilon, \varepsilon_r$	Dielectric constant, relative dielectric constant
γ	Activity coefficient
φ	Volta potential
φ	Electrostatic potential
κ	Specific conductance
Λ_{eq}	Equivalent conductivity
Λ_0	Equivalent conductivity at infinite dilution
Λ_{mol}	Molar conductance
λ_{eq}^+	Equivalent ionic conductivity of cations
λ_{eq}^-	Equivalent ionic conductivity of anions
λ_{mol}^+	Molar ionic conductivity of cations
λ_{mol}^-	Molar ionic conductivity of anions
λ_0^-	Molar (equivalent) ionic conductivity of cations at infinite dilution
λ_0^+	Molar (equivalent) ionic conductivity of anions at infinite dilution
η	Overpotential
η_{ct}	Charge transfer overpotential
η	Dynamic viscosity
θ	Degree of coverage
ρ	Specific resistance
τ	Drop time of a dropping mercury electrode in s; transition time
ξ	Extent of reaction
ω	Angular velocity

Contents

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1
Introduction – An Overview of Practical Electrochemistry

Students in natural sciences as well as professionals in numerous areas will meet electrochemical methods, concepts, and processes in many fields of science and technology. Accordingly, any a conceivable selection of possible experiments intended as an illustration of this width, the numerous possibilities of electrochemistry, and an introduction to the subject has to be similarly broad. According to the book's purpose and intention this will be achieved by the width of the selection of experiments, the scope of the practical (instrumental) requirements, and the necessary level of knowledge. Convenient use of the book and logical arrangement of the essentials of the theoretical introduction suggest a rational arrangement of experiments. As already proposed and executed elsewhere (R. Holze: Leitfaden der Elektrochemie, Teubner, Stuttgart 1998 and Elektrochemisches Praktikum, Teubner, Stuttgart 2000), electrochemistry in equilibrium, i.e. without flow of current and conversion of matter, is followed by electrochemistry with flow of current. In the first chapter, measurements of electrode potential and their application in, e.g., the determination of thermodynamic data are treated. The second chapter deals with all kinds of experiments where an electrical current crosses the electrochemical interface. Applications of electrochemical methods (both without and with flow of current) are handled in a chapter on electrochemical methods of analytical chemistry[1]. This chapter also contains experiments helpful in elucidating, e.g., mechanisms of electrode processes (a somewhat broader meaning of analytical) if the focus of the experiment is not on the experimental method itself, thus suggesting its inclusion in one of the preceding chapters. According to the growing impact of non-traditional, in particular spectroscopic, methods in electrochemistry a small section of experiments from this branch follows; unfortunately, the feasibility of these experiments depends crucially on the presence of mostly expensive instrument. Electrochemical methods of energy conversion and storage are of utmost practical importance, and numerous first personal interactions with electrochemistry

1) The term analytical electrochemistry is neat and seemingly well-defined, but unfortunately in daily life its use is somewhat confusing: The term "analytical" is sometimes applied to qualify a certain branch of electrochemistry (in contrast, e.g., with synthetic electrochemistry); sometimes it means application of electrochemical methods in analytical chemistry – as intended here.

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