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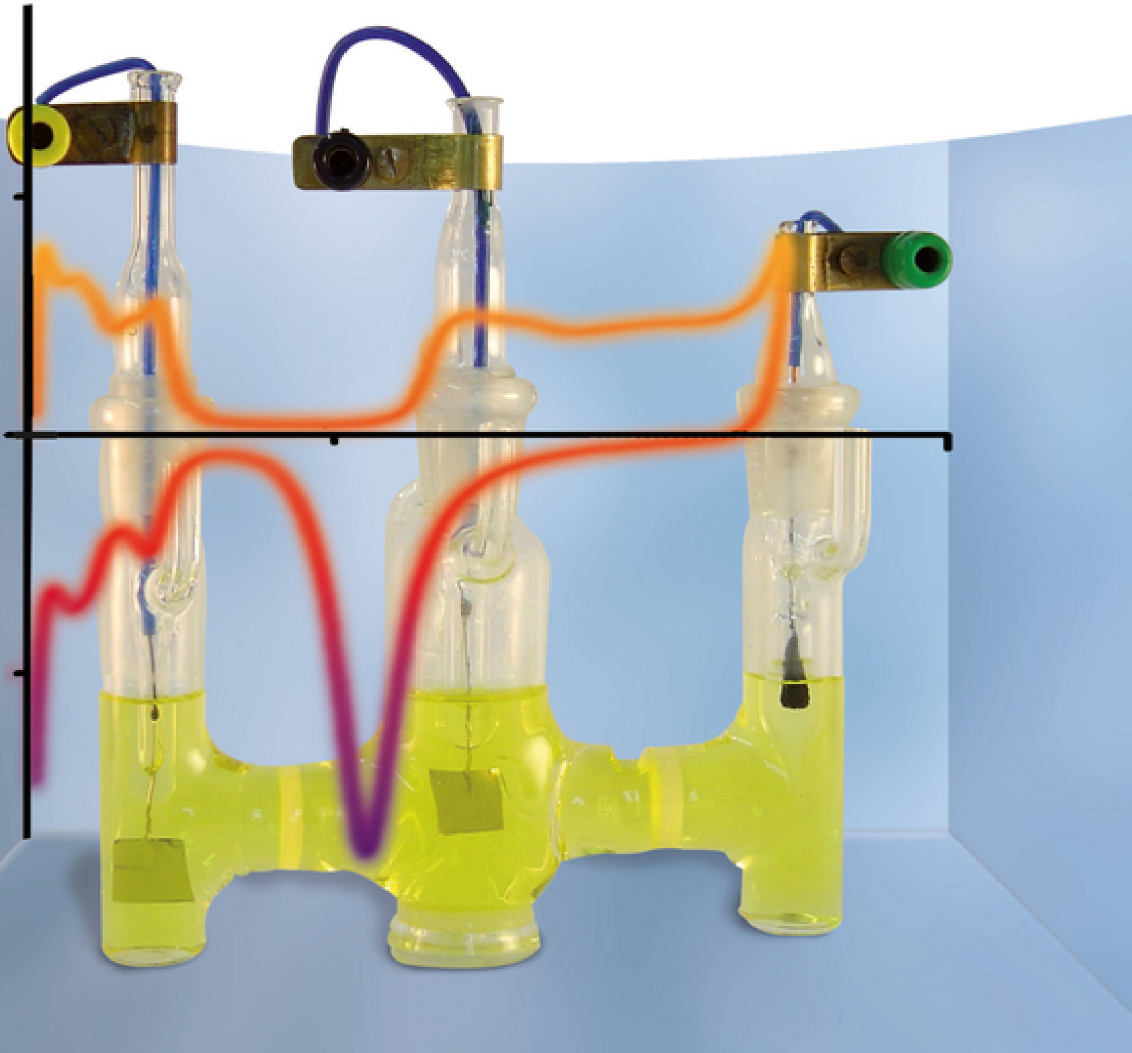
Experimental Electrochemistry

A Laboratory Textbook

Second, Completely Revised and Updated Edition



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Contents

Preface to the Second Edition

The first edition of this book has met a friendly welcome. Some errors have been indicated, suggestions for improvements and additions have been made. Electrochemistry as observed in our daily life and current environment is further growing in importance. The number of mobile devices depending on reliable sources of electric energy, the variation of sensors applied in medicine, environmental and process control, corrosion protection for new materials and changed environments, processing of surfaces – the list of things undergoing major developments even in the few years since publication of the first edition in 2009 is impressive. This should be reflected in the new edition presented here. Beyond correcting those flaws indicated above (thanks to the careful readers), new experiments taking into account as far as possible those developments briefly outlined above have been added, and accordingly a major extension can be found in the chapter on electrochemical energy storage and conversion. Unfortunately, some of these developments are hard or impossible to transfer into laboratory experiments suitable for the present textbook and possible in a high school or university chemistry laboratory. Nevertheless, an attempt has been made to update this book as far as possible. The still tremendous growth of helpful entries in the web related to the experiments – old and new described in this book – provides further sources of information, in particular on the background of experiments that could not always be provided to an extent perhaps desired by some readers but going beyond reasonable lengths of text. The author is hoping for the same welcome as extended to the first edition.

A major part of this work was assembled during research stays at Fudan University, Shanghai, China. Yuping Wu's generous hospitality and the supportive environment in his research group provided a stimulating atmosphere for this enterprise.

Chemnitz, November 2018 *Rudolf Holze*

Preface to the First Edition

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 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 continuously, for an update see http://www.tu-chemnitz.de/chemie/elchem/elpra. 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. Dimensions are separated by a slash (quantity calculus); square brackets are only used when necessary to avoid confusion.

Chemnitz, December 2008 *Rudolf Holze*

Foreword to the Second Edition

The first edition of "Experimental Electrochemistry" has proven to be very popular. Based upon commentary from the readership, it is clear that the text has been much appreciated by researchers in industry and in academia, as well as by instructors and students who have used it in the classroom/laboratory. We are grateful to those of you who have pointed out the need for minor corrections; they have been incorporated, with appreciation.

The importance of the text can not be overstated especially when given the renaissance of electrochemistry in electrosynthesis, as well as the critical role it plays in other fields of high current interest and importance. Accordingly, the publisher and author have agreed to extend the selection of experiments into these fields, and new experiments related to energy conversion and storage, materials science and corrosion have been added and have been closely linked to the experiments already present within the text. We are hopeful that the readership will be pleased with these efforts and look forward to both positive feedback and constructive criticism.

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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	molar concentration
c_p	isobar molar heat
c_s	surface concentration
c_V	isochoric molar heat
c_0	bulk concentration
D	diffusion coefficient
d	electrode distance
E	electrode potential
E	electric field strength
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
$E_{\mathrm{Hg_2SO_4}}$	see E_MSE
E_MSE	electrode potential versus a mercurous sulfate electrode, $c_{\mathrm{Hg_2SO_4}} = 0.1\,\mathrm{M}$
E_m	measurement potential
ΔE_p	difference of electrode peak potentials
$E_\mathrm{p,\,ox}$	electrode peak potential of oxidation reaction
$E_\mathrm{p,\,red}$	electrode peak potential of reduction reaction
E_pzc	electrode potential of zero charge
E_red	redox electrode potential
E_ref	reference electrode potential
E_RHE	electrode potential versus relative hydrogen electrode
E_SCE	electrode potential versus 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_D	disk current at a ring–disk electrode
I_diff	diffusion-limited current (also $I_\mathrm{lim,diff}$)
$I_\mathrm{D,\,diff}$	diffusion-limited disk current at a ring–disk electrode
I_p	peak current
I_R	ring current at a ring–disk electrode
$I_\mathrm{R,\,diff}$	diffusion-limited ring current at a ring–disk electrode
I_sc	short circuit current
j	current density
j_ct	charge transfer current density
j_D	disk current at a disk or ring–disk electrode
j_diff	diffusion-limited current density (also: $j_\mathrm{lim,diff}$)
j_lim	limiting current density
j_R	ring current density at a ring–disk 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 analysis: 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	disk radius of a ring–disk electrode
r_2	inner ring radius of a ring–disk electrode
r_3	outer ring radius of a ring–disk 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
ε, ε_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

$\lambda_{\mathrm{eq}}^{+}$	equivalent ionic conductivity of cations
$\lambda_{\mathrm{eq}}^{-}$	equivalent ionic conductivity of anions
$\lambda_{\mathrm{mol}}^{+}$	molar ionic conductivity of cations
$\lambda_{\mathrm{eq}}^{-}$	molar ionic conductivity of anions
λ_{0}^{-}	molar ionic conductivity of cations at infinite dilution
λ_{0}^{+}	molar ionic conductivity of anions at infinite dilution
η	overpotential
η_{ct}	charge transfer overpotential
η	dynamic viscosity
θ	degree of coverage
ρ	specific resistance or resistivity
τ	drop time of a dropping mercury electrode in seconds; transition time
ξ	extent of reaction
ω	angular velocity

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 conceivable selection of possible experiments intended as an illustration of this width and 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, that is, 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, for example, 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, for example, 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 nontraditional, 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 instruments. Electrochemical methods of energy conversion and storage are of utmost practical importance, and numerous first personal interactions with electrochemistry deal with these devices. They combine applied aspects of equilibrium (i.e., thermodynamic) electrochemistry and

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[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, for example, with synthetic electrochemistry); sometimes it means application of electrochemical methods in analytical chemistry – as intended here.

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electrochemical kinetics; consequently, in this chapter only those experiments are collected where these aspects are not dominant. Electrochemical methods in industrial (synthetic) chemistry applied in the production of base chemicals, for example, chlorine or sodium hydroxide, and in synthetic procedures are subject of some experiments in the final chapter, the difficulties of the transfer of a large-scale industrial process into a simple laboratory experiment limit the selection.

The following descriptions of experiments are organized according to a general scheme. A brief statement of the experimenter's task and the aim of the experiment are followed by a condensed description of the theoretical foundations, essentially for understanding the experiment. This information cannot replace the respective parts of a textbook or the original reports in the primary literature. Besides references to primary sources, the respective sections of C.H. Hamann, A. Hamnett, and W. Vielstich, *Electrochemistry*, Wiley-VCH Verlag GmbH, Weinheim, 2007, are quoted as EC and the respective page number: EC:xx. Some methods such as polarography and cyclic voltammetry are employed in several experiments; nevertheless, their fundamentals are described only once when the method is introduced first. No attempt is made in the descriptions to list all conceivable applications of the method used in this experiment. The tempting concept to arrange experiments according to difficulty or complexity of the experimental apparatus was discarded soon as being too personal and subjective. Instead, the readers and users of this book will easily select experiments according to their personal interests and intentions; the comparison of available and necessary equipment can subsequently been performed easily as well as the estimate of the required knowledge for successful execution.

The description of the execution of an experiment starts with a list of necessary instruments and chemicals. Possible alternative instrumentations are highlighted; the subsequent description is nevertheless limited to one experimental way only. The description contains – if necessary – a schematic circuit diagram of the setup and sketches of the construction of the apparatus or parts of it. The execution of the suggested measurements is briefly outlined. Potential pitfalls and unusual details are indicated. The way from the raw data to the desired results is sketched. Final questions including those pertaining to the practical execution help to confirm the newly acquired knowledge. Extensive calculation training examples are not included, these can be found in the textbook by J.O'M. Bockris and R.A. Fredlein. Typical results are displayed without cosmetic tidying up, this will encourage the user, it also demonstrates the level of skill needed to obtain satisfactory agreement between literature data (always quoted according to bibliographic standards from generally available textbooks for comparison) and one's own results.

Practical Hints

In most experiments aqueous solutions are used. If not stated otherwise, ultrapure water (sometimes called 18 MΩ-water because of the typical specific resistance value of this water) is used. It can be obtained by after-purification of deionized water by various commercially available purification systems. As an alternative, doubly distilled (bidistilled) water can be used. In some experiments, simple deionized water can be used. Because especially in demanding conductivity[2] and potentiometric measurements, traces of impurities present in deionized water may cause erroneous results, blind tests are required, in particular when water of less than ideal purity is used. In some cases, not only the desired concentration of a necessary solution but also the amount of the selected chemicals needed for preparing the requested amount of solution is given for ease of preparation. When cells or other experimental setups with volumes different from the suggested setup are used, these numbers must obviously be corrected. Purification of organic solvents has been thoroughly described by C.K. Mann (*Nonaqueous Solvents for Electrochemical Use, Electroanalytical Chemistry 3* (A.J. Bard, ed.), Marcel Dekker, New York, 1969, p. 57); further information on electrolyte solutions based on organic solvents has been collected by H.J. Gores and J.M.G. Barthel (*Pure Appl. Chem.*, **67** (1995) 919).

Electrodes

As suggested by W. Nernst, the term electrode should always be applied to a specific combination of an electronically conducting material (e.g., metal, graphite, semiconductor) and an ionically conducting phase in contact with this material (e.g., an aqueous solution, a polymeric electrolyte, a molten salt). The need for this use will be neatly illustrated in Experiment 3.12 with lead being in contact with various electrolyte solutions; quite obviously, the term lead electrode becomes ambiguous. In daily life, the term electrode mostly refers to the electronically conducting component only. This well-established usage will not be completely suppressed in this book; nevertheless, the possible confusion will be addressed repeatedly.

In some experiments, electrodes of special shape and construction prepared from selected materials are needed; details are provided in the descriptions of the experiments. In many experiments, electrodes of a fairly general type and construction will be used. Because they can be prepared easily in a glassblower's shop or even without any expert help, some suggestions are given below.

Frequently, metal sheets (of noble metals such as platinum or gold) are used as working and counter electrodes. These electrodes can be manufactured easily by spot welding a metal wire to a piece of sheet metal (about 0.1–0.2 mm thick). After extending the metal wire with a piece of copper wire connected with hard solder (i.e., silver solder; soft solder is not recommended because it will most

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[2] Meaning and use of the terms conductance and conductivity and their respective reciprocal relative resistance and resistivity are slightly confusing and frequently inconsistent. According to the standard reference works, conductance applies to the conducting power of matter without requiring specific dimensions of the sample, whereas conductivity refers to the conductance of a sample with unit dimensions, that is, it refers to specific conductance. The frequently employed term "specific conductivity" might thus be popular, but it remains a pleonasm or tautology. In this book, the standard terms conductivity meter or conductivity measurements are employed – although in most cases only conductances are measured.

likely melt in the subsequent glassblowing operation; in addition soft solder forms alloys with gold making a reliable connection impossible), the noble metal wire is sealed into a glass tube. Glass with low melting point is preferred because the low viscosity of the molten glass obtained even at moderate temperatures provides a tight glass–metal seal. With platinum, borosilicate glass of higher melting point can be used. Particularly useful even for silver wires are lead dioxide-based glasses. The glassblowers must avoid reducing conditions when operating their blowtorch. Unfortunately, these glasses are hard to get. When a spot welding machine is not available, simple metal wire spirals can be used instead of sheet electrodes. Instead, with a glass–metal seal, the wire can also be fixed with epoxy glue; unfortunately, this connection is mechanically and chemically less stable, may not be exposed to some aggressive cleaning solutions, and, in addition, may release traces of contaminants into the electrolyte solution.

In the case of a very simple preparation of a microelectrode, this epoxy glue is essential as shown in Figure 1.1. A glass tube is heated until its end almost collapses and a very narrow opening remains. A carbon fiber is fed through the opening. The opening is closed with epoxy. By pulling and pushing the fiber gently, it is coated with epoxy and completely surrounded with the glue. After curing the epoxy, an electric connection to a copper wire is provided on the inside with conductive silver or graphite cement.

As reference electrode mostly hydrogen or metal ion electrodes are used. Saturated calomel and silver chloride electrodes (EC:99) are particularly popular. Figure 1.2 shows typical constructions.

Various aqueous as well as nonaqueous electrolyte solutions can be used; in all cases the high chloride concentration may result in contamination of the electrolyte solution in the electrochemical cell because of halide diffusion

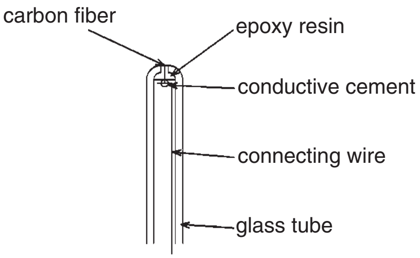


Figure 1.1 Cross section of a simple microelectrode.

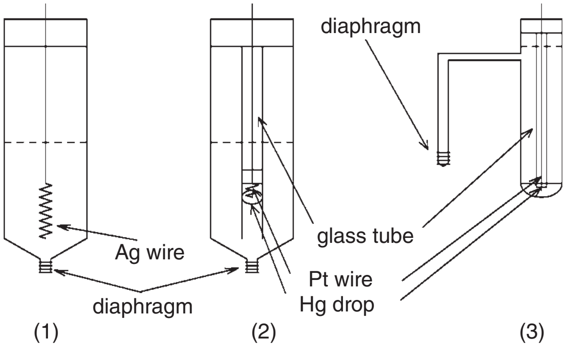
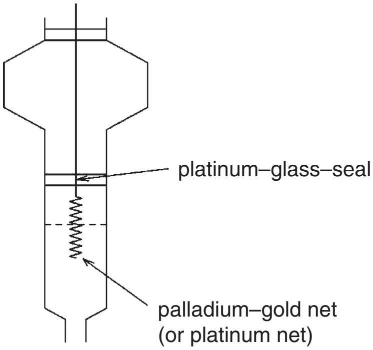


Figure 1.2 Cross sections of various types of reference electrodes. (1): Silver/silver chloride electrodes. (2 and 3): Calomel or mercurous sulfate electrode. Dotted lines indicate solution filling level.

Figure 1.3 Hydrogen electrode according to Will.



through the separating diaphragms and so on. In alkaline solution, disproportionation of calomel may occur.

A particularly simple design of a hydrogen electrode,[3] as suggested by F.G. Will and H.J. Hess (*J. Electrochem. Soc.*, **120** (1973) 1; *J. Electrochem. Soc.*, **133** (1986), 454), is shown in Figure 1.3.

Platinum wire net (better: a palladium or palladium–gold wire net) is spot welded to a platinum wire. This assembly is fixed inside the glass tube drawn into a capillary with a glass–metal seal. The active surface area of the net is enlarged by electrolytic coating with platinum black. Using the electrolyte solution of the planned experiment, an auxiliary electrode (e.g., platinum wire) as anode, and a DC power supply (a few volts will be enough), the metal net inside the capillary is charged with hydrogen by cathodic reduction of protons until a hydrogen gas bubble is formed. The bubble may stay in place for several weeks when the glass–metal seal is sufficiently tight; accordingly, the electrode potential remains stable. In the case of organic compounds dissolved in the electrolyte solution, which may react at the platinum surface, potential shifts may occur as a consequence of electrode poisoning; in the case of neutral electrolyte solution, the potential is also less stable because the exchange current density of the hydrogen electrode reaction is pH dependent (EC:344). The activity of protons in the solution filled into the hydrogen electrode will be unity only in rare cases. Consequently, this electrode may not be called a standard hydrogen electrode (SHE) (the term normal hydrogen electrode (NHE) should be avoided altogether because the term normal may be taken as designation of a certain concentration); because the hydrogen electrode potential is related to the proton activity, this hydrogen electrode is sometimes called relative hydrogen electrode (RHE).

With nonaqueous electrolyte solutions, the use of reference electrodes containing aqueous electrolyte solutions is still possible with salt bridges (see below)

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[3] Sometimes hydrogen electrodes are called reversible or relative hydrogen electrodes (RHE). The former term is obviously redundant. The term reversible implies the presence of a reversible reaction: An electrode reaction proceeds on the same reaction pathway in both directions at significant rates; without this, no stable electrode potential would be established. Alternatively, the term might imply reversible in a thermodynamic sense – being at equilibrium. Because a reference electrode is always used without any flow of current, it is in equilibrium. The term relative refers to the fact that a nonstandard proton concentration may be present, thus the electrode is not a standard electrode.

providing the ionically conducting connection. The diffusion potentials created at the phase boundaries between the various solutions may cause considerable experimental errors if not corrected properly. In addition, the slow diffusion of solution components (including of course water) into the nonaqueous electrolyte solution may cause undesirable chemical reactions or other experimental artifacts. Thus, electrolyte solutions employing nonaqueous solvents are an attractive option. Unfortunately, electrodes of the second kind (e.g., silver/silver chloride, for details see above) are prone to disproportionation and finally decomposition resulting in reference electrode potential drift. In addition, the potential of these electrodes depends on the employed solvent and thus comparison between experimental results obtained with different solvents may be unreliable. Redox systems with a formal potential E_0 defined as the midpoint potential between their respective oxidation and reduction peak potentials as observed in a cyclic voltammogram ($E_0 = E_{\mathrm{p,\,red}} + (E_{\mathrm{p,\,ox}} - E_{\mathrm{p,\,red}})/2$, for details see Experiment 3.18) have been employed as point of reference repeatedly provided that the value of E_0 does not depend on the solvent. Ferrocene (see Experiment 3.18) has been suggested as a candidate (R.R. Gagné, C.A. Koval, and G.C. Lisensky, *Inorg. Chem.*, **19** (1980) 2854) because the iron ion at the center of the two cyclopentadienyl ligands seems to be shielded fairly well from the solvent. Unfortunately, it has turned out that upon oxidation of ferrocene, most of the charge is removed from the ligand; the actual charge on the iron is changed only by about 1/10th of an electron charge. As a substitute decamethyl ferrocene or decaphenyl ferrocene have been suggested; for a review, see I. Noviandri, K.N. Brown, D.S. Fleming, P.T. Gulyas, P.A. Lay, A.F. Masters, and L. Phillips, *J. Phys. Chem. B*, **103** (1999), 6713. In an actual experiment, a reference electrode of the second kind filled with a nonaqueous electrolyte solution may be used; at the end of the experiment, some ferrocene is added, a cyclic voltammogram is recorded, and all electrode potentials are converted to this reference (e.g., the ferrocene) scale. Only in this way can results obtained with different solvents at different places be made compatible and comparable and comparisons be made possible.

Although a large selection of electronic reference voltage sources with a precision sufficient for calibration purposes are available (for a suggested circuit, see Appendix), electrochemical reference cells are still in use. The only infrequently encountered Clark cell ($\mathrm{Zn|ZnSO_{4,(aq.,\,sat.)}|ZnSO_{4,\,sol.} + Hg_2SO_{4,\,sol.}|Hg}$) has been replaced by the Weston cell ($\mathrm{Cd|CdSO_{4,(aq.,\,sat.)}|CdSO_{4,\,sol.} + Hg_2SO_{4,\,sol.}|Hg}$). The cell reaction of the latter has significantly lower entropy of reaction, resulting in a smaller temperature coefficient of the cell voltage.

Measuring Instruments[4]

Apart from special instruments typical of certain experimental methods (e.g., polarographs for polarography), simple electronic instruments are frequently

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[4] A complete setup including a potentiostat built as plug-in for a standard desktop PC, a cell, several electrodes, and software suitable for running several of the experiments described below, including a workbook is offered by Sycopel Scientific Instruments, Washington, Great Britain.

needed, in particular for the measurement of voltage and current. Standard analog or digital multimeters are sufficient in most cases. During measurements of electrode potentials performed as the measurement of the voltage between a reference electrode and the working electrode under study, the flow of electric current must be avoided. Ideally this has been done using a compensation circuit. This procedure is cumbersome and today of only limited practical importance. Voltmeters with very high input resistance ($R_i > 10^{12}$ Ω) are sufficiently close to this ideal method. During selection of instruments for precision measurements, this input resistance merits particular attention. Budget-priced multimeters are frequently built with a voltage divider circuit for range selection at the input, resulting in fairly low input resistance values; these should be used in appropriate respect. With commercially available digital voltmeter modules (no input voltage divider added) with a 2 V range, a powerful instrument for potential measurements can be built at low cost. Measurements of current–potential curves require current meters with a very small measuring (shunt) resistor; ideally its value should be zero. This can be realized with simple circuits based on operational amplifiers (current followers), which are particularly helpful during measurements with electrochemical cells providing only small output voltages (fuel cells, batteries). Because of lower price and apparently higher precision, digital instruments are frequently preferred. During experiments wherein a voltage has to be adjusted to a certain value, an analog instrument may be better because trends in the measured signal can be discerned more clearly. Digital instruments with an additional bar graph display may be a compromise; it may be difficult to become accustomed to the flickering bar graph display.

Electrochemical Cells

In addition to specific cells designed just for a certain experiment as described in the text related to it, some generally used types of electrochemical cells have come into practice. A simple beaker will be sufficient only in a few cases because operation with inert gas atmosphere above the electrolyte solution and sufficient purging of the solution itself are impossible with this arrangement. In addition, reliable and reproducible mounting of electrodes can be done only with additional holders and so on. For cyclic voltammetry, a cell, depicted in Figure 1.4, commonly called H-cell (because of its shape) is frequently used.

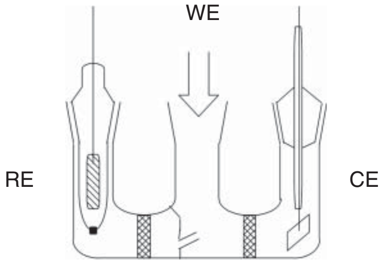

Figure 1.4 Cross section of an H-cell for electrochemical experiments, WE: working electrode; RE: reference electrode; CE: counter electrode.

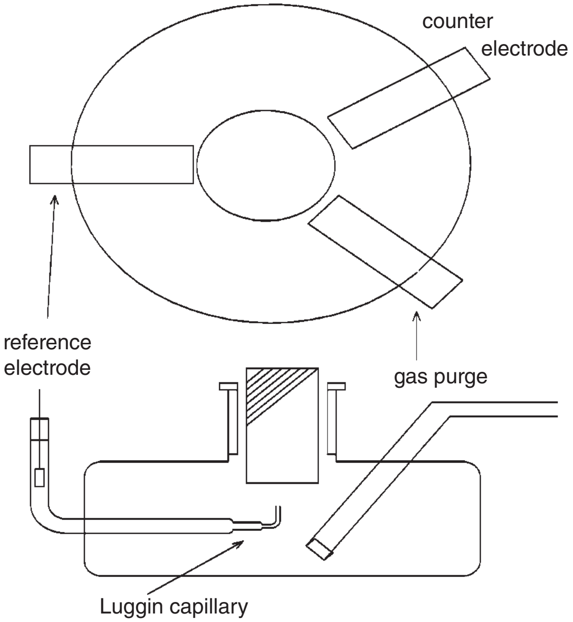

Figure 1.5 Cross section of an electrochemical cell for AC measurements and rotating disk electrode studies.

For electrochemical impedance measurements and further experiments with AC modulation of the electrode potential, spherical working electrodes or circular disk-shaped electrodes embedded in an inert material mounted in the center of a symmetric cell vessel are advantageous. Additional ground glass feedthroughs hold glass tubes for gas purge of the electrolyte solution and the counter and reference electrodes. Reduced exchange of electrolyte solution between the interior of the latter tubes and the main compartment of the cell can be achieved by closing the tubes with porous glass or ceramic frits. This type of cell can also be employed in studies with a rotating disk electrode as shown in Figure 1.5.

In precision studies[5] and in experiments, where mixing of electrolyte solutions must be prevented, "salt bridges" (Figure 1.6) are needed. They provide electrolytic connection between cell compartments without bringing the electrolyte solutions in these compartments into direct contact. In a very simple design, a piece of plastic tube filled with a suitable electrolyte solution and closed with cotton wool plugs or plugs made of filter paper may be sufficient. The electrolyte could be 1 M KNO_3, both ions having similar mobility (P.W. Atkins, J. de Paula, *Physical Chemistry*, 8th ed., Oxford University Press, Oxford, 2006, p. 1019), which results in an approximate compensation of diffusion potentials (P.W. Atkins, J. de Paula, *Physical Chemistry*, 8th ed., Oxford University Press, Oxford, 2006, p. 216; EC:112;146) generated at the interfaces of the cell solutions. In addition, both ions show only minor interference with most electrochemical processes and cell reactions. More reliable and stable are ground glass diaphragms

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[5] For example, measurements of standard electrode potentials or cell voltages wherein diffusion potentials must be either avoided or precisely known.