Electroanalytical Methods

Fritz Scholz
Editor

Electroanalytical Methods

Guide to Experiments and Applications

Second, Revised and Extended Edition

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Electroanalytical Methods

Fritz Scholz dedicates this book to the memory of his late parents Anneliese and Herbert Scholz

Preface to the Second Edition

The authors are pleased to present here the second edition of the book "Electroanalytical Methods. Guide to Experiments and Applications." All chapters have been carefully revised and updated, and a new chapter, devoted to the use of the electrochemical quartz crystal nanobalance, has been added.

Greifswald, Germany, October 2009 *Fritz Scholz*

Preface to the First Edition

Electroanalytical techniques offer a unique access to information on chemical, biochemical, and physical systems. Both the instrumental basis and the theoretical fundamentals have been developed such that non-specialists can easily apply them. However, there is still a considerable lack in acceptance of these techniques by others except those who have experience and training in electrochemistry. The authors of this volume felt that it was time to write a volume that concentrates on the really important techniques together with the most essential information to make them applicable for potential users who do not possess specialist knowledge of electrochemistry. All the authors have a long experience in teaching and know the most frequent experimental pitfalls as well as theoretical misunderstandings and misinterpretations. This book has been written to become a bench book used in the laboratory. The "Electroanalytical Methods" addresses chemists and biochemists who are interested in using electroanalytical techniques to supplement spectroscopic and perhaps theoretical calculations. It also addresses biologists, environmental and material scientists, physicists, medical scientists, and, most importantly, students in all branches of science, who are confronted with the need to apply electroanalytical techniques. In the short first part of the book, entitled "Basic Electrochemistry," the essentials of electrochemical thermodynamics and kinetics are given. The second part, entitled "Electroanalytical Techniques," contains the most frequently utilized techniques, i.e., cyclic voltammetry, pulse and square-wave voltammetry, chronocoulometry, etc. The third part is devoted to electrodes and electrolytes, which are the major constituents of an electrochemical cell. Throughout the book, special attention is given to guide the user to successful laboratory experiments and a sound data evaluation. This book focuses only on modern and widespread techniques. To give the interested reader a key to the historic background, a short list of seminal publications in electrochemistry and electroanalysis is provided in Chap. IV.1.

There are many carefully written monographs on special electroanalytical techniques and textbooks on fundamental electrochemistry available. We refer to this fundamental literature (see Chap. IV.2) for a deeper insight into the subject. The World Wide Web is of steadily growing importance also for electrochemical information. Although it is constantly changing and renewing, some key addresses are provided to make access easier and the search more successful.

Greifswald, Germany, 2001 *Fritz Scholz*

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Index of Symbols and their SI Dimensions

I. Roman Symbols

a	activity
$a_{\mathrm{B}},\ a_{\mathrm{i}}$	relative activity of component B, i
$a_{\pm}$	mean ionic activity
A	absorbance
A	area, m^2, cm^2
A	coefficient of Debye–Hückel equation, $\mathrm{dm}^{3/2}\ \mathrm{mol}^{-1/2}$
A_{real}	real surface area, m^2
b	Tafel slope, V
$b_{\mathrm{a}},\ b_{\mathrm{c}}$	anodic, cathodic Tafel slope, V
B	coefficient of Debye–Hückel equation, $\mathrm{dm}^{1/2}\ \mathrm{mol}^{-1/2}$
c	concentration, $\mathrm{mol\ m}^{-3}$ or $\mathrm{mol\ L}^{-1}$
$c_{\mathrm{B}},\ c_{\mathrm{B}}^{*}$	bulk concentration of component B in solution, $\mathrm{mol\ dm}^{-3}$
$c_{\mathrm{B}}\ (\infty, t)$	bulk concentration of component B at time t , $\mathrm{mol\ dm}^{-3}$
$c_{\mathrm{B}}\ (x = 0)$	concentration of species B at the electrode surface, $\mathrm{mol\ dm}^{-3}$
$c_{\mathrm{B}}\ (0, t)$	concentration of species B at the electrode surface at time t, $\mathrm{mol\ dm}^{-3}$
c_{f}	differential sensitivity of EQCM, $\mathrm{Hz\ g}^{-1}$
c_{O}	concentration of species O (oxidized form), $\mathrm{mol\ dm}^{-3}$
c_{R}	concentration of species R (reduced form), $\mathrm{mol\ dm}^{-3}$
C	capacitance, $\mathrm{F\ m}^{-2}$
C	differential capacitance, $\mathrm{F\ m}^{-2}$
C_{a}	adsorption capacitance, $\mathrm{F\ m}^{-2}$
C_{d}	differential capacitance of the electrochemical double layer, $\mathrm{F\ m}^{-2}$
C_{D}	capacitance of the diffuse double layer, $\mathrm{F\ m}^{-2}$
C_{f}	integral sensitivity of EQCM, $\mathrm{Hz\ cm}^{2}\ \mathrm{g}^{-1}$
C_{g}	geometric capacitance, F
C_{H}	capacitance of the Helmholtz layer, $\mathrm{F\ m}^{-2}$
C_{HF}	high-frequency capacitance, $\mathrm{F\ m}^{-2}$

$C_{\mathrm{LF}},\ C_{\mathrm{L}}$	low-frequency capacitance, $\mathrm{F\ m^{-2}}$
d	thickness, m
D	diffusion coefficient, $\mathrm{m^2\ s^{-1}}$, $\mathrm{cm^2\ s^{-1}}$
D_{B}	diffusion coefficient of species B, $\mathrm{m^2\ s^{-1}}$
D_{KA}	diffusion coefficient of electrolyte KA, $\mathrm{m^2\ s^{-1}}$
$D_{\mathrm{O}},\ D_{\mathrm{R}}$	diffusion coefficient of species O, R, $\mathrm{m^2\ s^{-1}}$
e	quantity of charge on the electron (elementary charge), C ($e = 1.60217653(14) \times 10^{-19}$ C)
ΔE	electric potential difference, $\mathrm{V\ m^{-1}}$
E	electromotive force (E_{mf}, emf), V
E	electrode potential, V
$E^{\ominus}$	standard[1] potential of electrochemical half-cell reaction, V
$E^{\ominus}$	standard potential of electrode reaction (standard electrode potential), V
$E_{\mathrm{c}}^{\ominus\prime}$	formal potential, V
E_{cell}	potential of electrochemical cell reaction, V
E_{e}	equilibrium electrode potential, V
E_{F}	Fermi energy (Fermi level), eV
E_{i}	initial potential, V
E_{p}	polarization potential, V
$E_{\mathrm{pa}},\ E_{\mathrm{pc}}$	peak potential (anodic, cathodic in cyclic voltammetry), V
$E_{\mathrm{p/2}}$	half-peak potential, i.e., potential at 1/2 of the peak current (in cyclic voltammetry), V
$E_{3/4}$	potential at 3/4 of the peak current (in cyclic voltammetry), V
$E_{1/4}$	potential at 1/4 of the peak current (in cyclic voltammetry), V
E_{rv}	reversal potential in cyclic voltammetry, V
$E_{1/2}$	half-wave potential, V
E_{r}	rest potential, V
$E_{\sigma=0}$	potential of zero charge, V
E_{ref}	potential of the reference electrode, V
f	F/RT
f	frequency, Hz
f	activity coefficient (molar fraction bases)
$f_{\mathrm{B}},\ f_{\mathrm{i}}$	rational activity coefficient of species B, i
$f_{\pm}$	mean rational activity coefficient
f_0	fundamental frequency, Hz
f_{r}	roughness factor
F	force, N
F	Faraday constant, $\mathrm{C\ mol^{-1}}$ ($F = 9.64853383(83) \times 10^4\ \mathrm{C\ mol^{-1}}$)

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[1] In agreement with the IUPAC suggestions, we are using here the Plimsoll symbol $\ominus$ to indicate standard values. The Plimsoll is a circle with a vertical line, named after Samuel Plimsoll (1824–1898), and originally meant to mark the limit to which a ship may be loaded.

g	interaction parameter
G	Gibbs free energy, J
ΔG	change of Gibbs free energy, J
ΔG_{ads}	Gibbs free energy of adsorption, J
ΔG_{s}	Gibbs free energy of solvation, J
$\Delta^{\ddagger}G$	Gibbs free energy of activation, J
$\Delta^{\ddagger}G^{\ominus}$	Standard Gibbs free energy of activation, J
h	hydration number
h	Planck constant, J s
H	enthalpy, J
H_0	Hammett-acidity function
ΔH	enthalpy change, J
ΔH_{s}	solvation enthalpy change, J
I	electric current, A
I	ionic strength, mol kg^{-1}, mol dm^{-3}
I_{a}	anodic current, A
I_{c}	cathodic current, A
I_{d}	diffusion current, A
I_{L}	limiting current, A
I_{m}	migration current, A
I_{m}	amplitude of sinusoidal current, A
I_0	exchange current, A
j	electric current density, A m^{-2}
j_0	exchange current density, A m^{-2}
$j_{\mathrm{a}}, j_{\mathrm{c}}$	anodic, cathodic current density, A m^{-2}
j_{D}	diffusion current density, A m^{-2}
j_{L}	limiting current density, A m^{-2}
J	flux, mol m^{-2} s^{-1}
J_{B}	flux of species B, mol m^{-2} s^{-1}
k	rate constant for reaction of the n -th order $\left(\mathrm{m}^3\ \mathrm{mol}^{-1}\right)^{n-1}\ \mathrm{s}^{-1}(n = 1,2,\ldots)$
k	rate constant of heterogeneous reaction, m s^{-1}
k_{a}	rate constant of adsorption, m s^{-1}
$k_{\mathrm{a}n}$, $k_{\mathrm{c}n}$	anodic, cathodic rate constants for n -th order reactions, A m$^{(3n\text{ -}2)}$ mol^{-n}
k_{B}	Boltzmann constant, J K^{-1} (k_{B}= 1.3806504(24) × 10^{-23} J K^{-1})
k_{d}	rate constant of desorption, mol s^{-1} cm^{-2}
k_{d}	rate constant of diffusion mass transport, m s^{-1}
k_{m}	mass transport rate constant, m s^{-1}
k_{ox}	heterogeneous rate constant for oxidation, m s^{-1}
k_{red}	heterogeneous rate constant for reduction, m s^{-1}
k_{s}	standard heterogeneous rate constant, m s^{-1}

K	equilibrium constant
K_a	thermodynamical equilibrium constant
K_c	conditional equilibrium constant
L	thickness, length, distance, m
m	mass, g, kg
m_e	mass of the electron, kg
m_i	molarity of species i, mol kg^{-1}
M	molar mass, kg mol^{-1}
M_i	relative molar mass of species i
n	charge number of electrochemical cell reaction
n	reaction order
n	refractive index
n_i	number of density of species i, mol
N_A	Avogadro constant, mol^{-1} ($6.02214179(30) \times 10^{23}$mol^{-1})
p	pressure, Pa
pH	negative decadic logarithm of the relative activity of H_3O^+ ions
pK_a, pK_b	negative decadic logarithm of acidity and base constant resp.
P	pressure, Pa
Q	charge, C
Q	constant phase element (CPE) coefficient
r	radius, m
r	inhomogeneity factor
r_i	radius of species i, m
r_{kr}	crystallographic radius of species i, m
r_0	radius of a disc microelectrode, m
r_{st}	Stokes radius, m
R	gas constant, J mol^{-1} K^{-1} (8.314472(15) J mol^{-1} K^{-1})
R_a	adsorption resistance, Ωm^2
R_b	cell resistance, Ω
R_{ct}	charge transfer resistance, Ω
R_d	diffusion resistance, Ω
R_e	Reynolds number
R_m	metal wire resistance, Ω
R_p	polarization resistance, Ω
R_s	solution resistance, Ω
R_{sa}	relative surface area ($R_{sa} = A_{3D}/A_{2D}$), A_{3D} is the “real surface area, ”A_{2D} is the projected surface area
R_u	uncompensated ohmic resistance, Ω
R_Ω	ohmic resistance, Ω
S	entropy, J K^{-1}
t	time, s
t_i	transport number of species i

T	(thermodynamical or absolute) temperature, K
u_i	mobility of ion i, $\mathrm{m}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$
u_0	linear velocity of the liquid, $\mathrm{m\ s}^{-1}$
U	internal energy, J
U	electric potential, potential difference, V
U_m	amplitude of sinusoidal voltage, V
v	potential scan rate, $\mathrm{V\ s}^{-1}$
v	rate of a chemical reaction, $\mathrm{mol\ s}^{-1}$, $\mathrm{mol\ s}^{-1}\ \mathrm{cm}^{-3}$
v_a	rate of adsorption, $\mathrm{mol\ s}^{-1}\ \mathrm{cm}^{-2}$ (variable)
v_b	rate of homogeneous reaction, $\mathrm{mol\ s}^{-1}\ \mathrm{cm}^{-3}$
v_d	rate of desorption, $\mathrm{mol\ s}^{-1}\ \mathrm{cm}^{-2}$ (variable)
$\bar{v}_\mathrm{i}$	mean velocity of species i, $\mathrm{m\ s}^{-1}$
v_ox	rate of oxidation, $\mathrm{m\ s}^{-1}\ \mathrm{cm}^{-2}$
v_red	rate of reduction, $\mathrm{m\ s}^{-1}\ \mathrm{cm}^{-2}$
$v(x)$	velocity of the volume element of a fluid in x direction $\mathrm{m}^3\ \mathrm{s}^{-1}$, $\mathrm{kg\ s}^{-1}$
V	volume, m^3
w_el	electrical work, J
W	Warburg impedance, Ω
x_h	thickness of the Prandtl layer, m
x_H	thickness of the Helmholtz layer, m
x_i	molar fraction of species i
y_i	activity coefficient of component i (concentration basis)
$y_\pm$	mean ionic activity coefficient
Y	admittance, $\mathrm{S\ m}^{-2}$
z_i	charge number of an ion i
Z	impedance, Ω, $\Omega\mathrm{m}^2$
Z'	real part (in-phase) impedance Ω, $\Omega\mathrm{m}^2$
Z''	imaginary part (out of phase) impedance, Ω, $\Omega\mathrm{m}^2$
Z_dl	impedance of the double layer, $\Omega\mathrm{m}^2$
Z_el	electrode impedance, $\Omega\mathrm{m}^2$
Z_F	Faraday impedance, $\Omega\mathrm{m}^2$
Z_R	solution impedance, $\Omega\mathrm{m}^2$

II. Greek Symbols

α	degree of dissociation
α	transfer coefficient (electrochemical)
α	real potential, V
α_a, α_c	anodic, cathodic transfer coefficient
α_f	constant phase element (CPE) exponent
δ	thickness of diffusion layer
δ_i	thickness of diffusion layer related to species i, m
γ	surface tension, J m^{-2}
γ_i	activity coefficient of species i (molality basis)
$\gamma_{\pm}$	mean ionic activity coefficient
Γ_i	surface (excess) concentration of species i, mol m^{-2}
$\Gamma_{i(H_2O)}$	surface (excess) concentration of species i related to water (solvent), mol m^{-2}
ε	molar (decadic) absorption coefficient, m^2 mol^{-1}, or L mol^{-1} cm^{-1}
ε	dielectric permittivity, Fm^{-1} $\left(C\ V^{-1}\ m^{-1}\right)$
ε_0	permittivity of vacuum, F m^{-1} ($8.8541878176 \times 10^{-12}$ F m^{-1})
$\varepsilon_{0(\omega \to 0)}$	static relative permittivity
$\varepsilon_{\infty(\omega \to \infty)}$	optical relative permittivity
ε_r	relative permittivity
ϑ	phase angle, °, rad
η	overpotential, V
η	dynamic viscosity, P (g $cm^{-1}s^{-1}$)
η_{diff}	diffusion overpotential, V
Θ	surface coverage
Θ_i	surface coverage of species i
χ	conductivity, S m^{-1}
χ	surface electric potential, V
χ	transmission coefficient
χ^{-1}	radius of ionic atmosphere, Debye length, m
λ_i	molar ionic conductivity of ion i, S m^2 mol^{-1}
λ_B	absolute activity of species B
Λ	molar conductivity of an electrolyte, S m^2 mol^{-1}
Λ^0	molar conductivity at infinite dilution, S m^2 mol^{-1}
μ	electric dipole moment, C m
μ_i	chemical potential of species i, J mol^{-1}
$\mu_i^{\ominus}$	standard chemical potential of species i, J mol^{-1}
$\tilde{\mu}_i$	electrochemical potential of species i, J mol^{-1}
ν	kinematic viscosity, m^2 s^{-1}
ν_i	stoichiometric number of species i

ρ	density, kg dm^{-3}, g cm^{-3}
ρ	charge density, C m^{-3}
ρ	resistivity, Ω m
σ	surface charge density, C m^{-2}
σ	Warburg coefficient, Ω cm^2 $s^{-1/2}$
τ	characteristic time, relaxation time, s
φ	potential, V
$\Delta\varphi_{\mathrm{diff}}$	junction (diffusion) potential, V
ϕ^{α}	inner electric potential of phase α, V
$\Delta\phi$	Galvani-potential difference, V
Φ	work function $\Phi = E - E_{\mathrm{F}}$, eV
Ψ^{α}	outer electric potential of phase α, V
$\Delta\Psi$	Volta potential difference (contact potential), V
ω	angular frequency $\omega = 2\pi f$, Hz
ω_{r}	angular velocity, rad s^{-1}

Part I
Basic Electrochemistry

Chapter I.1
The Electrical Double Layer and Its Structure

Zbigniew Stojek

I.1.1 Introduction

At any electrode immersed in an electrolyte solution, a specific interfacial region is formed. This region is called the double layer. The electrical properties of such a layer are important, since they significantly affect the electrochemical measurements. In an electrical circuit used to measure the current that flows at a particular working electrode, the double layer can be viewed as a capacitor. Figure I.1.1 depicts this situation where the electrochemical cell is represented by an electrical circuit and capacitor C_d corresponds to the differential capacity of the double layer. To obtain a desired potential at the working electrodes, the double-layer capacitor must be first appropriately charged, which means that a capacitive current, not related to the reduction or oxidation of the substrates, flows in the electrical circuit. While this capacitive current carries some information concerning the double layer and its structure, and in some cases can be used for analytical purposes, in general, it interferes with electrochemical investigations. A variety of methods are used in electrochemistry to depress, isolate, or filter the capacitive current.

Although many models for the double layer have been published in the literature, there is no general model that can be used in all experimental situations. This is because the double-layer structure and its capacity depend on several parameters such as electrode material (metals, types of carbon, semiconductors, material porosity, the presence of layers of either oxides or polymeric films or other solid materials at the surface), type of solvent, type of supporting electrolyte, extent of specific adsorption of ions and molecules, and temperature.

The composition of the double layer influences the electron transfer rate (see Sect. I.3.1.5). Some ions and molecules specifically adsorbed at the electrode surface enhance the rate of the electrode process. In such a situation, we talk about heterogeneous electrocatalysis. On the other hand, there are numerous compounds that, after adsorption, decrease the electron transfer rate and therefore are simply

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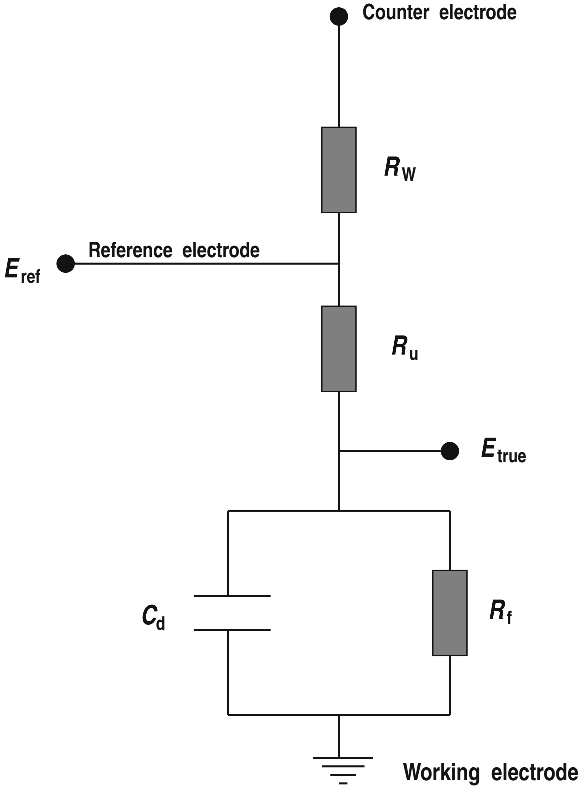
Fig. I.1.1 A simple electronic scheme equivalent to the electrochemical cell. R_u, resistance uncompensated in the regular three-electrode system; C_d, differential capacity of the double layer; R_f, resistance to faradaic current at the electrode surface; R_Ω, solution resistance compensated in the three-electrode system



inhibitors. Some surface-active compounds can be very strongly adsorbed. This may lead to the total isolation of the electrode surface and, finally, to the disappearance, or substantial decrease, of the voltammetric peaks or waves.

An imposition of a potential from an external source (potentiostat/voltammograph) to a metallic electrode results in generation of a charge, σ_M, on the metal, and a charge σ_S in the solution. The charge at the electrode is related directly to the interfacial (double-layer) capacity or capacitance. There are two ways to describe the capacity of an electrode:

- the differential capacitance, C_d, which naturally is at the minimum for the potential of zero charge and which is represented by Eq. (I.1.1):

$$C_d = \frac{\partial \sigma_M}{\partial E} \tag{I.1.1}$$

- and the integral capacitance, C_i, described by Eq. (I.1.2).

$$C_{\mathrm{i}} = \frac{\sigma_{\mathrm{M}}}{E - E_{\sigma=0}} \tag{I.1.2}$$

The excess charge on the metallic electrode, σ_{M}, is a function of the electrode potential. The simplest equation that describes the charge on the metal is given for mercury electrodes. This is because the excess charge strongly affects the surface tension of mercury, and the latter can be easily measured experimentally. One simple method to measure the surface tension vs. potential is to measure the drop time of a mercury-dropping electrode immersed in an electrolyte solution. The surface tension of mercury plotted vs. potential usually gives a parabolic curve. The maximum of this curve is located at the potential of zero charge, $E_{\sigma = 0}$, since

$$-\sigma_{\mathrm{M}} = \frac{\partial \gamma}{\partial E} \tag{I.1.3}$$

and the derivative of the surface tension equals 0 at the maximum. The differential capacity, C_{d}, reaches its minimum also at the potential of zero charge, a fact that can be concluded from a simple inspection of Eq. (I.1.1).

I.1.2 Double-Layer Models

The concept of the existence of the double layer at the surface of a metal being in contact with an electrolyte appeared in 1879 (Helmholtz). That first theoretical model assumed the presence of a *compact layer* of ions in contact with the charged metal surface. The next model, of Gouy and Chapman, involves *a diffuse double layer* in which the accumulated ions, due to the Boltzmann distribution, extend to some distance from the solid surface. In further developments, Stern (1924) suggested that the electrified solid–liquid interface includes both the rigid Helmholtz layer and the diffuse one of Gouy and Chapman. Specific adsorption of ions at the metal surface was pointed out by Graham in 1947. In consecutive developments, the role of the solvent has been taken into account (Parsons, 1954; Bockris, 1963). It soon became clear that in dipolar solvents, such as water, the dipoles must interact with the charged metal surface. It is also worth noting here that these interactions are promoted by the high concentration of the solvent, which is usually at least several moles per liter, and, in particular, for water it is around 55.5 M. In his theory, Parsons recognized that the dielectric constant of the solvent in the compact layer of adsorbed molecules is much lower compared to the outer region and approaches the limiting Maxwell value. A detailed description of the double-layer models mentioned above can be found in the literature [1–4].

A classic, simplified model of the double layer formed at the metal electrode surface is presented in Fig. I.1.2. There is a layer of adsorbed water molecules on the electrode surface. Since it has been assumed that there is excess of negative charge at the metal phase, the hydrogen atoms of adsorbed water molecules are oriented toward the metal surface. However, it is not a prerequisite that all water molecules

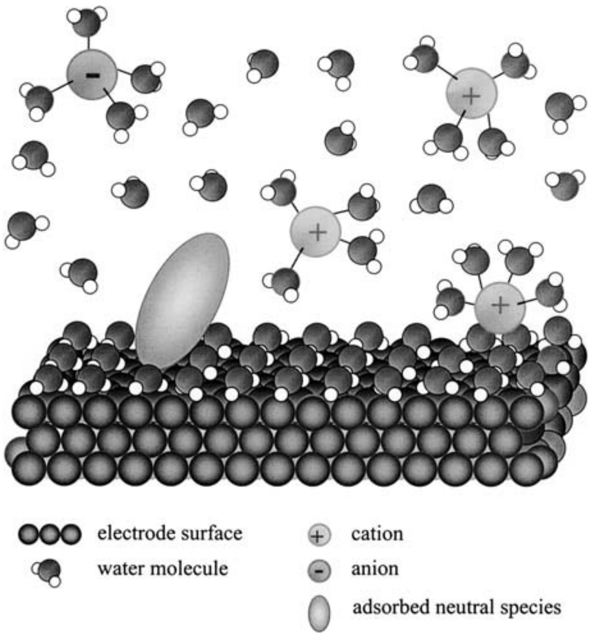


Fig. I.1.2 General representation of the double layer formed at the metal–electrolyte interface

at a particular electrode potential and the corresponding excess charge have the same orientation. For excess of positive charge at the metal surface, the dipoles of water will have a different orientation: the oxygen atoms of adsorbed water molecules will be oriented toward the metal surface. A specifically adsorbed large neutral molecule is also shown in Fig. I.1.2. Note that this molecule has removed some water molecules from the surface. The situation is different when a hydrated cation is present at the surface: it has not removed surface water and therefore cannot be considered as specifically adsorbed.

Two planes are usually associated with the double layer. The first one, the inner Helmholtz plane (IHP), passes through the centers of specifically adsorbed ions (compact layer in the Helmholtz model), or is simply located just behind the layer of adsorbed water. The second plane is called the outer Helmholtz plane (OHP) and passes through the centers of the hydrated ions that are in contact with the metal surface. The electric potentials linked to the IHP and OHP are usually written as Ψ_2 and Ψ_1, respectively The diffuse layer develops outside the OHP. The concentration of cations in the diffuse layer decreases exponentially vs. the distance from the electrode surface. The hydrated ions in the solution are most often octahedral complexes; however, in Fig. I.1.2. they are shown as tetrahedral structures for simplification.

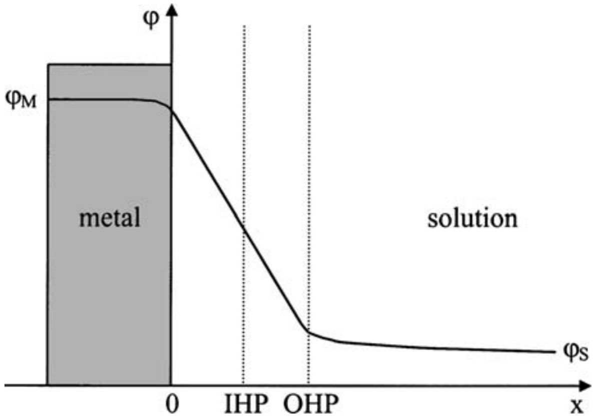


Fig. I.1.3 Potential profile in the double layer formed at a metallic electrode charged negatively

The change in the electric potential within the double layer is illustrated in Fig. I.1.3. It is assumed that the electrode is charged negatively. The electric potential, ϕ_{M}, is virtually constant throughout the metallic phase except for the layers of metal atoms located next to the solution, where a discontinuity in the metal structure takes place and the wave properties of the electron are exposed (the jellium model [1, 3]). This effect is much stronger in semiconductor electrodes, where the accessible electronic levels are more restricted [5].

At carbon electrodes, which are widely used in electrochemistry, the double layer develops too; however, these electrodes have some specific interfacial properties. The two main types of carbon electrodes, glassy carbon and highly oriented pyrolitic graphite (HOPG) and the recently introduced boron-doped diamond, differ much in the bulk and the surface structure. They also differ in electrochemical activity. Particularly big differences exist for the two surfaces of highly oriented pyrolitic graphite: the basal (hexagonal) plane and the edge one. At the edge plane, the electrode processes are usually much faster. An additional important factor for the electron transfer rate is the presence of oxygen at the surface. Oxygen easily chemisorbs on sp^2 carbon present in graphitic materials. This leads to the formation of many functional groups, mainly carbonyl, phenolic, and carboxylate, to an increase in the electrode differential capacity, and to an increase in the rate of the electrode processes. To reverse the chemisorption of oxygen, and to obtain, reproducibly, oxygen-free surfaces, is not easy. Neither is it easy to keep the surface oxygen-to-carbon ratio constant in the consecutive experiments. A positive aspect of the presence of the functional groups at the graphitic surfaces is that they make the chemical modification of the electrodes easier.

Details of the properties of carbon electrodes can be found in the literature [6]. For the effect of the double-layer structure on the electrode reaction rate see Sect. I.3.2.5.

I.1.3 Thickness of the Electric Double Layer

The thickness of the double layer is usually given as being approximately 1.5 κ^{-1}, where κ^{-1} is the Debye–Hückel length:

$$\kappa^{-1} = \left(\varepsilon_r \varepsilon_0 k_B T / 2c^0 z_i^2 e^2\right)^{1/2} \tag{I.1.4}$$

where c^0 is the bulk concentration of the $z{:}z$ electrolyte, ε_r is the relative dielectric permittivity of the solvent, ε_0 is the permittivity of the vacuum, k_B is the Boltzmann constant, T is the temperature, z is the ion charge, and e is the elementary charge. For $z = 1$, the approximate κ^{-1} values calculated for electrolyte concentrations of 1×10^{-3}, 1×10^{-5}, and 1×10^{-7} M are 10 nm, 100 nm, and 1 μm, respectively. The thickness of the double layer also depends on the potential: the larger the difference between the electrode potential and the potential of zero charge (the potential at which the excess charge on the electrode equals zero), the smaller the Debye–Hückel length.

I.1.4 Recent Developments

There is still much to do to be able to predict the behavior and the capacitance of the double layer in the entire available potential window and under all conditions. The introduction of rigorous theories that can take into account the various chemical and electrochemical properties of electrode materials, the specific adsorption of ions and neutral molecules, and the dynamics of adsorbed solvent molecules and other adsorbates is not trivial. In consequence, there is still no satisfactory agreement between the experimental and theoretical data regarding capacitance of the double layer. Hopefully, the new experimental techniques, such as atomic force and scanning tunneling microscopies [7], and scanning electrochemical microscopy [8], will allow electrochemists to learn more about the structure of the double layer at the atomic level. On the theoretical side, the new digital methods of calculations provide a possibility to simulate, in time, all the changes within the double layer. The recent progress in the research on the solid–liquid electrochemical interfaces is given in, e.g., [9] and [10].

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Chapter I.2
Thermodynamics of Electrochemical Reactions

Fritz Scholz

I.2.1 Introduction

The wish to determine thermodynamic data of electrochemical reactions and of the involved compounds is one of the most important motivations to perform electrochemical measurements. After calorimetry, electrochemistry is the second most important tool to determine thermodynamic data. Although ab initio quantum chemical calculations can be used for the calculation of thermodynamic data of small molecules, the day is not yet foreseeable when electrochemical experiments will be replaced by such calculations. In this chapter we provide the essential information as to what thermodynamic information can be extracted from electrochemical experiments and what the necessary prerequisites are to do so.

The first step in this discussion is to distinguish between the thermodynamics and kinetics of an electrochemical reaction. Thermodynamics only describes the changes in energy and entropy during a reaction. The interplay between these two fundamental state functions determines to what extent a reaction will proceed, i.e., what the equilibrium constant is. Nothing can be said about the rate at which this equilibrium state can be reached, and nothing can be said about the mechanism of the proceeding reaction. In general, thermodynamic information can only be obtained about systems that are in equilibrium, or at least very near to equilibrium. Since electrochemical reactions always involve the passage of current, it is in many cases easy to let a reaction proceed near to the equilibrium by limiting the current, i.e., the passage of charge per time, which is nothing else but the reaction rate.

In this chapter, no attempt is made to provide a comprehensive account of electrochemical thermodynamics; but rather a survey of what is essential to understand the thermodynamic information provided by electroanalytical techniques. The fundamentals of electrochemical thermodynamics are available elsewhere [1].

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I.2.2 The Standard Potential

The electroanalytical techniques considered in this volume are such that one always measures an electrode potential–current relationship, which is determined by the electrochemical reaction proceeding at one electrode only, i.e., the so-called working electrode. Of course, the same current must flow through the counter, or auxiliary, electrode as well; however, the experiments are designed in such a way that the process at the counter electrode is not rate determining. To give an example, when a platinum disc electrode of 1 mm diameter is used as the working electrode and the counter electrode is a sheet of platinum with a surface area of 4 cm^2, and the solution contains 10^{-3} mol L^{-1} $\mathrm{K_4[Fe(CN)_6]}$ and 0.1 mol L^{-1} $\mathrm{KNO_3}$, the dependence of current on electrode potential will be determined by the following electrochemical reaction only:

$$\left[\mathrm{Fe\,(CN)_6}\right]^{4-} \rightleftarrows \left[\mathrm{Fe\,(CN)_6}\right]^{3-} + \mathrm{e}^- \tag{I.2.1}$$

Of course, on the counter electrode, another electrochemical reaction proceeds, the nature of which remains usually unknown. Let us assume that we measure a cyclic voltammogram (Fig. I.2.1), so that, in the first potential scan going in the positive direction, the hexacyanoferrate(II) ions are oxidized at the working electrode to hexacyanoferrate(III). The counterbalancing reaction at the second (auxiliary) electrode is not known; however, it is probable that hydronium ions of the water are reduced to hydrogen. In the following scan to negative potentials, the hexacyanoferrate(III) ions formed in the first scan are reduced back to hexacyanoferrate(II). Here the counterbalancing reaction on the auxiliary electrode may be an oxidation of the adsorbed hydrogen or the oxidation of the hexacyanoferrate(II) ions, which are also present at the auxiliary electrode (provided that this electrode is, as normally, in the same solution as the working electrode). The fact that we do not know what happens at the counter electrode, and, even worse, the fact that *different* processes may occur on the counter electrode, would make it very hard to use such electrode potential–current relationships for the determination of thermodynamic data, if we could not provide conditions where only the current at the working electrode is determining the measured response: this is achieved by using a working electrode having a surface area which is much smaller than that of the auxiliary electrode. Such ratio of electrode surface areas assures that the electrode reaction at the working electrodes limits the measured currents. Further, it is advantageous to control the electrode potential of the working electrode always versus the potential of an electrode having a fixed and stable reference potential; therefore, such measurements are nowadays always performed in a three-electrode arrangement: A third electrode, the so-called reference electrode (see Chap. III.2), is in electrolytic contact with the solution to be studied, only for the purpose to control the potential of the working electrode throughout the experiment. Practically no current is allowed to flow through the reference electrode and its construction is such that its potential is constant (equilibrium potential) under all conditions, in particular, independent of the composition of the solution being studied. Since