Electrochemistry: Fundamentals, Cells & Applications

Lecture Notes

Course 529-0659-00L ETH Zürich



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"The Universe is under no obligation to make sense to you."

- Neil deGrasse Tyson, American astrophysicist, author, and science communicator

Title page:

Illustration of the cathode catalyst layer of a polymer electrolyte fuel cell, forming a three-phase region (electronic conductor, ionic conductor, gas phase) where the oxygen reduction reaction (ORR) takes place: $O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$. The size of the carbon and platinum/carbon particles and thickness of the layers are not to scale. A detailed discussion on this this topic can be found in Chapter VII.

Preface

These lecture notes accompany the ETH Zürich course no. 529-0659-00L 'Electrochemistry: Fundamentals, Cells & Applications', comprising 13 lectures of 2 x 45 min plus 1 x 45 min of exercises. The content as well as this text is grouped into an Introduction and 9 Chapters.

The course is aimed at students at the Bachelor or Master level with previous knowledge of physical chemistry and its main teachings on thermodynamics, mixtures, chemical reactions and kinetics. The target audience are not students of a particular degree program, the course is equally suited for chemistry, materials science and engineering students, even physics students with a solid chemical background. Therefore, aside from the language of chemistry, certain chapters or topics will also use concepts from solid-state physics (e.g., the work function) or engineering. Aspects of materials science will be discussed to some extent in the fundamental and especially in the application oriented chapters.

This text is intended to complement the lectures and provide more background and, occasionally, depth to the lecture topics. Ideally, the student prepares for the lecture by reading in advance the corresponding chapter, which will allow him / her to better follow the content. The objective of the course and this text is to develop an understanding of electrochemistry and, in particular, the specific aspects of electrochemical reactions in contrast to chemical reactions. The aim should not primarily be to remember all the different equations and derivations, but to grasp the various conceptual approaches to describe cells, reactions, their limitations, etc., and how electrochemical processes are implemented into applications of technical and thus societal relevance.

This document is based on various textbooks and other educational resources, as well as websites, scientific articles, and reference books. The reader is not required to additionally purchase a textbook to accompany the course, but is of course free to do so to further study certain aspects and deepen the knowledge, or just to understand the derivation of a particular concept or equation.

In the 2023 version of this text some sections have been amended for better understanding, improved clarity, or to correct mistakes and typographical errors.

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Introduction

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It appears to be understood that electrochemistry is perceived as boring. "Elektrochemie ist das Knäckebrot unter den Naturwissenschaften, hart, trocken, unglamourös" (Spiegel, 22. March, 2018) ("Electrochemistry is the crispbread among the natural sciences: hard, dry and unglamorous"), yet it has been conceded in the same article that it will change mobility (in electric vehicles) and therefore our lives fundamentally: "Doch sie wird die Mobilität und damit unser Leben radikal verändern - etwa mit der Autobatterie der Zukunft". This is probably true, but it is not the full story. The statement is also a testimony of the fact that the role and importance of electrochemistry is largely unknown or underestimated by the general public. For example, lead-acid batteries have been essential components in cars for starting, lighting and ignition (SLI) for over 100 years, and industrial electrolytic processes for the production of hydrogen, chlorine, aluminium and many other compounds have been established for even longer ! Also, understanding corrosion and devising protective measures, electroplating, and electrochemical sensors have been around for a long time. Looking into the future, electrochemical devices and conversion processes will likely form integral constituents of our future energy system, e.g. in grid-scale storage, and industry, where traditionally carbon-intensive processes need to be de-fossilized and 'electrified' (Power-to-X concepts). Of course, the electrons used in these processes are expected to be derived from renewable power sources, which have already seen a tremendous growth over the past decade.

This text aims to provide a fundamental understanding of electrochemical reactions and cells, the most important materials classes and components that constitute technically relevant cells, and applications of high importance. The course seeks to establish the essence and essentials of electrochemical reactions, in particular in contrast to chemical reactions, provide the necessary and relevant concepts and tools to describe the reactions and processes, and use those to explain the working principles of selected applications and electrochemical phenomena. We will recognize that electrochemistry offers 'power'ful methods to exploit electricity in combination with chemistry to accomplish a very diverse set of tasks over a wide range of scales, from microelectrodes to full-scale industrial plants.

1 Overview

Electrochemistry is traditionally recognized as a branch of physical chemistry. For the description of the thermodynamics and kinetics of electrochemical cells, similar physical-chemical concepts (e.g., thermodynamic state functions, activation energy) are used as for regular chemical reactions. However, a detailed understanding of the nature and properties of the electrode-electrolyte interface and the mechanisms of electrochemical reactions have only become possible through surface scientific methods and techniques. Especially, spectroscopic methods have greatly helped to

for example in the use of computational methods to predict structure and properties of compounds.

1.1 A very brief historic account

The notion of a potential difference developing between different metals when immersed in an aqueous solution containing ions may have already been around in the ancient world. An archeological relic known as the 'Baghdad battery' (**Figure 0-1a**) could have been built for the purpose of electroplating, but no unequivocal evidence is available. Such or similar devices may have been around in other parts of the world, and the knowledge was lost in time. The birth year of electrochemistry is generally accepted to be 1799, when *Volta* invented the first electrical battery, consisting of a series of two metal discs and brine soaked separators (**Figure 0-1b**), which allowed, for the first time, to produce a continuous electrical current. Before, people used so-called *Leyden jars*¹, electrostatically charged capacitors. Those could provide short discharge bursts of electrical current, which had already been used before Volta's invention to electrochemically split water into hydrogen and oxygen. Volta's discovery did not come out of the blue, though, and notable contributions were made before by other researchers, such as *Galvani*, who experimented with frog's legs and established a bridge between chemical reactions and electricity.



Figure 0-1. (a) Schematic of the 'Baghdad battery', a 2'200-year-old clay jar that is hypothesized to have functioned as a galvanic cell (Source: batteryuniversity.com). (b) The voltaic pile, invented by *Volta* in 1799, was the first electrical battery that could provide a continuous electric current. It consists of stacked pairs of alternating copper (or silver) and zinc discs separated by cloth or cardboard soaked in brine (Source: Wikipedia).

¹ or 'Leiden jars', after the city in the Netherlands.

In the 19th century the scientific understanding of electrochemistry and its technical uses were steadily and greatly advanced, as in other disciplines. A review of the history of electrochemistry is beyond the scope of this text. Important discoveries and developments will be highlighted in the respective chapters on specific topics.

1.2 Technical relevance

Electrochemical cells in practical use come in a wide variety of sizes, configurations, with very different components and materials used. Also, operating conditions can vary greatly. Many cells are used at ambient conditions in an aqueous (e.g., lead-acid batteries) or non-aqueous (such as in lithium-ion batteries) environment, yet processes may also be carried out at high temperature with molten-salt (Al-electrolysis) or ceramic (oxygen sensors in exhaust gas streams) electrolytes. Electrodes can be made of metallic, carbon, ceramic or semiconducting materials, or they may also be liquid (e.g., in sodium-sulfur batteries). Despite the very different settings, there are commonalities among the different electrochemical processes, which can be described with the same suite of concepts and methods, which we will elaborate in the forthcoming chapters. Likewise, the uses of electrochemistry are very diverse. Important applications and the involved cell types will be discussed in the second half of the text, from Chapter VI to IX. Electrochemistry has a number of uses of high technical and economic significance:

• Industrial processes

Production of metals, inorganic and organic chemicals on an industrial scale (e.g., chloralkali process, see Chapter VI); separation and purification processes.

• Electroplating

Galvanization and other surface treatment and forming processes.

• Corrosion

Understanding of metal corrosion processes and implementation of corrosion protection measures (Chapter IX).

• Energy conversion & storage

Electrochemical energy devices, such as supercapacitors, batteries, fuel cells and water electrolyzers (Chapter VII).

Sensors

Potentiometric (e.g. pH electrode, lambda probe) and amperometric sensors; electroanalytical methods (Chapter VIII).

• (Biochemistry)

Key mechanisms sustaining life involve electron transfer processes, such as photosynthesis.

The last topic in the list, biochemistry, is placed in parentheses, as is not a subject of technical relevance as such, but, evidently, charge transfer processes in biological cells¹ are essential to life. As indicated, selected applications will be discussed in this text, yet the following topics will not be treated: bioelectrochemistry, semiconductor electrochemistry and photoelectrochemistry.

2 Electrochemistry Fundamentals

2.1 Quantities and units

Before we study the fundamental principles of an electrochemical cell and establish the relevant terminology, it is useful to introduce the most important physical quantities and their units, which will form the basis for the discussions to follow. **Table 0-1** provides an overview with some explanations. Physical and chemical processes are to a large extent about energy and the conversion of energy from one form to another. We therefore differentiate between different forms of energy, such as *work* (symbol: W) and *heat* (Q). 'Work' mostly describes electrical energy in this text, an essential output of or input to an electrochemical cell. It is inevitable that, given the limited number

Quantity	Symbol	Unit	Comment
Energy	Ε	J (joule)	Capacity of a physical system to perform
		Wh (watt hour)	work or release heat
Work	W	eV (electron volt)	Work is useful energy
Heat	Q	Nm (newton meter)	Heat is the most dispersed form of energy
Power	Р	W (watt) = J/s	Power is energy converted per unit time, i.e.
			the rate of energy conversion
Charge	Q	C (coulomb) = As^a	Charge of 1 mol of e^- : $e \cdot N_A = F = 96'485$ As
		Ah	(F: Faraday constant)
(Electric) potential	Ø, V	V (volt) = J/C	Potential energy of a unit positive charge ^b
	1 - 1		(typically applied to an electron)
Electrode potential	Ε	V	Electric potential of an electrode with respect
_			to a reference electrode
Cell potential	E_{cell}	V	Potential difference ΔE between two
			electrodes
Cell voltage	U	V	Potential difference ΔE between two
			electrodes, used in an engineering context
Current	Ι	A (ampère)	Flow of charge per unit time: $I = dQ/dt$
Resistance	R	Ω (ohm) = V/A	Measure of the difficulty of a component or
		× ,	material to pass an electric current
Capacitance	С	F (farad) = C/V	Ability of a component or material to store
*		· · ·	charge

Table 0-1. List of most important quantities.

^a Since the SI base unit is ampère (A), not coulomb (C), we will mostly use As to represent charge, not C.

^b normally referenced to the vacuum level

¹ The term 'cell' was first used for biological cells, derived from latin *cella*, meaning 'small room', because of their resemblance to cells inhabited by Christian monks in a monastery. They are the basic structural, functional, and biological unit of all known organisms. The term was later adopted for the description of the smallest unit of an electrochemical functional unit: the electrochemical cell.

of letters in the Latin alphabet, some symbols are used for more than one quantity, such as Q for heat as well as electric charge. The symbol E is very common for *energy* in other texts, cf. for example kinetic energy E_{kin} , yet here E is used to mean potential. Still, there is a possible source of confusion here, because E is used for *electrode potential*, measured against a specific reference electrode, but as E_{cell} it is also used to describe the *potential difference* between the two electrodes of an electrochemical cell. This ambiguity also exists in many textbooks. In technical cells, the symbol U is often used to denote the potential difference between the electrodes, which is then called *cell voltage*. We will also adopt this use in the application oriented chapters.



Figure 0-2. Hydraulic analogy to illustrate the meaning of (a) the voltage U as a measure for the potential energy associated with an electrochemical cell, and (b) the current I as a flux of charged particles.

The quantities voltage U and current I deserve a bit more attention, as those are key to describe the operation of an electrochemical cell. For this, we invoke an analogy to the potential energy and the flow of water. In this hydraulic analogy, the voltage U of the cell corresponds to the hydrostatic pressure caused by the water column at the bottom (**Figure 0-2a**). It therefore represents the driving force for water to flow. In the cell the voltage is the driving force for charge to flow. The voltage is measured in volt, which is energy per charge (J/C). This describes the electrical work that is associated with the flow of a unit charge through the cell. The electrical current I in the cell corresponds to the water flux is the mass flow of water per unit time, current is the flow of charge per unit time (C/s = A). Where the flow rate of water is determined by the diameter of the tube, the current is influenced by the electrical resistance R.

2.2 Chemical potential, activity and activity coefficient

The reader of this text and student attending the corresponding course is expected to have a basic knowledge of physical chemistry, in particular thermodynamics and reaction kinetics. While most concepts will be discussed as we go, the topic of *chemical potential* μ , *activity a*, and *activity coefficient* γ , being pivotal notions in thermodynamics, is recalled here. The chemical potential μ_k

(unit: J/mol) of a compound k describes, in a manner of speaking, its 'potential chemical energy' and therefore its tendency to undergo reactions with other compounds (depending on *their* chemical potential and that of the products). It is a function of the dimensionless activity a_k , which can be understood as 'effective concentration', of that compound in the respective phase:

$$\mu_{k} = \mu_{k}^{\circ} + RT \ln(a_{k}) = \mu_{k}^{\circ} + RT \ln(a_{k}^{\text{ideal}}) + RT \ln(\gamma_{k})$$
(0-1)

The activity is expressed as $a = a_{ideal} \cdot \gamma$, where a_{ideal} is the activity under ideal conditions and γ is the activity coefficient, which describes the extent of deviation from the ideal case. μ_k° is the *standard chemical potential*, i.e. the chemical potential of the compound in its standard state, where a = 1, which is explained in **Table 0-2** for the different cases. The symbol 'o' will also be used with other quantities to indicate the standard state. Under ideal conditions, the activity coefficient γ is unity and $a = a_{ideal}$. In particular, a = 1 for pure liquids and solids. Gases with pressures in the range of the standard pressure of $p_0 = 1$ bar can mostly be assumed to follow ideal behavior, described by the ideal gas law: pV = nRT. Therefore, $a_{gas} \cong p/p_0$.

Table 0-2. Standard states, where p is the partial pressure of the gas, and x is the molar fraction of the compound in the mixture. (adapted from Atkins, de Paula, Physical Chemistry, 8^{th} ed., 2006, Table 5.3, p158)

component	standard state	activity	limits
solid or liquid	pure compound	$a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 1$
gas	hypothetical ideal gas ^a at p_0	$a = \gamma p/p_0$	$\gamma \rightarrow 1$ as $p \rightarrow 0$
solvent	pure solvent ^b	$a = \gamma x$	$\gamma \rightarrow 1$ as $x \rightarrow 1$
solute	(1) pure solute ^c	$a = \gamma x$	$\gamma \rightarrow 1 \text{ as } x \rightarrow 0$
	(2) ideal solution at molarity ^d c_0	$a = \gamma c/c_0$	$\gamma \rightarrow 1$ as $c \rightarrow 0$
	(3) ideal solution at molality ^e m_0	$a = \gamma m/m_0$	$\gamma \rightarrow 1$ as $m \rightarrow 0$

^a For gases, instead of activity the term fugacity (symbol: *f*) is often used, and fugacity coefficient (symbol: φ) instead of activity coefficient: $a = \varphi f/p_0$; $p_0 = 1$ bar (Beware that in older literature and thermodynamic tables the standard pressure is 1 atm = 1.10325 bar. IUPAC introduced 1 bar as standard pressure only in 1982). Generally, gases follow ideal behavior at 1 bar with good approximation.

^b same as solid or liquid, Raoult's law

° Henry's law

^d $c_0 = 1 \text{ M} = 1 \text{ mol/L}$

^e $m_0 = 1 \text{ mol/kg}$

For the concentration of dissolved species in a solvent there are different standard states, and we have to make it clear to the reader which one applies. Electrodes undergoing a reaction are often considered to be pure metals, such as copper or zinc, and can therefore be assigned an activity of $1.^{1}$ A typical electrolyte is a solution containing solvated ions, obtained from the dissolution of acid, base or a salt. The concentration of ions is usually given in terms of *molarity* (unit: mol/L) or

¹ In reality, of course, electrodes may be alloys or contain additives. The ideal, pure metal is an approximation in this case.

molality (unit: mol/kg), hence the standard state is a 1 molar solution (1 M = 1 mol/L) or a 1 molal (1 mol/kg) solution of the solute.¹ These are hypothetical standard states (cf. **Table 0-2**), because at the concentrations of c_0 and m_0 most solutions show far from ideal behavior. A sketch of the chemical potential of a solute as a function of its concentration is given in **Figure 0-3**. At low concentration, ideal behavior is asymptotically approached with $\gamma \cong 1$, hence $a \cong c/c_0$. With increasing concentration, the behavior deviates more and more from the ideal case, here shown with $\gamma < 1$, as it is often observed for salt solutions. Therefore, the activity coefficient is a function of concentration, yet it approaches unity at the limit of zero concentration / infinite dilution. As we can see, the ideal behavior at a concentration of 1 M is hypothetical and extrapolated from low concentrations.



Figure 0-3. Chemical potential μ of a dissolved compound in solution, showing an increase with concentration c according to Eq. 0-1. For the ideal solution $a = a_{ideal} = c / c_0$. The standard concentration (molarity) is $c_0 = 1$ M. The real solution shows a deviation from the ideal, characterized by the activity coefficient γ . μ° is the standard chemical potential corresponding to a = 1 under ideal conditions.

It should be noted that activities, also ideal activities, based on molar and molal concentrations are slightly different, hence also the standard chemical potential μ° is different. Consequently, activity coefficients for molarity and molality are also different and sometimes indicated with an index: γ_{c} or γ_{m} .

Example:

Sucrose in water at 25°C at a concentration c = 0.1 M has an activity coefficient of $\gamma = 0.9724$ (J. Chem. Eng. Data 51(5) (2006) 1836). The activity of sucrose is therefore $a = \gamma c/c_0 = 0.9724 \cdot 0.1$ M / 1 M = 0.09724. (The standard state used here is (2), i.e., the hypothetical ideal state at a concentration at 1 M, cf. **Table 0-2**.)

¹ Note that for the molarity (unit: mol/L) the volume refers to the volume of the solution, whereas for the molality (unit: mol/kg) the mass refers to the mass of the solvent only.

The case of dissolved ions, which is of particular importance for electrochemistry, deserves a bit more attention. The chemical potential of ions in solution, written in the following using molalities¹, is as for any other, uncharged species:

$$\mu_{+} = \mu_{+}^{\circ} + RT \ln(a_{+}) = \mu_{+}^{\circ} + RT \ln(\frac{m_{+}}{m_{0}}\gamma_{+})$$
(0-2)

$$\mu_{-} = \mu_{-}^{\circ} + RT \ln(a_{-}) = \mu_{-}^{\circ} + RT \ln(\frac{m_{-}}{m_{0}}\gamma_{-})$$
(0-3)

where + stands for cations and – for anions. The charge of the ion does not enter the expression explicity². There is a catch, however. Electrolyte solutions always contain, for reasons of charge neutrality, balanced amounts of anions and cations. The single-ion activity coefficients γ_+ and γ_- are not experimentally accessible in straightforward manner, because they do not manifest themselves in the general properties of an electrolyte solution. Therefore, for a salt M_pX_q that dissolves into *p* cations and *q* anions, the *mean activity coefficient* γ_+ is defined:

$$\gamma_{+} = \left(\gamma_{+}^{p} \gamma_{-}^{q}\right)^{1/(p+q)} \tag{0-4}$$

In analogy the mean activity a_{\pm} , mean molarity c_{\pm} and mean molality m_{\pm} are defined as follows:

$$a_{\pm} = (a_{\pm}^{p} a_{-}^{q})^{1/(p+q)} \tag{0-5}$$

$$c_{\pm} = (c_{\pm}^{p} c_{-}^{q})^{1/(p+q)} \qquad \qquad m_{\pm} = (m_{\pm}^{p} m_{-}^{q})^{1/(p+q)} \tag{0-6}$$

The (mean) activity of the salt solution is then simply given by $a_{\pm} = \gamma_{\pm} \cdot m_{\pm}/m_0$ or the corresponding expression using molarity. The mean activity coefficient γ_{\pm} of an electrolyte solution can be determined experimentally in an electrochemical experiment. We will learn in Chapter IV that γ_{\pm} is determined by all ions present in an electrolyte, not just the ions of the salt of interest.

For a so-called z-z electrolyte, i.e. a symmetric salt where z is the charge of the ions, such as NaCl(aq) (1-1) or CuSO₄(aq) (2-2), the mean activity coefficient simplifies to $\gamma_{\pm} = \sqrt{\gamma_{\pm}\gamma_{\pm}}$, and the mean molarity c_{\pm} or mean molality m_{\pm} is simply given by the nominal concentration c and m,

¹ Analogous expressions are obtained with molarities, using c/c_0 instead of m/m_0 .

² Implicitly, the influence of the ion charge is 'hidden' in the activity coefficient γ (cf. Debye-Hückel theory, Chapter IV).

Example:

A solution of Na₂SO₄ with a concentration of m = 0.1 mol/kg has a mean activity coefficient of $\gamma_{\pm} = 0.453$ at 25°C (C.H. Hamann, A. Hamnett, W. Vielstich, Electrochemistry, 2nd Edition, Wiley-VCH, 2007, p50). One formula unit of the salt yields 2 Na⁺ ions and 1 SO₄²⁻ ion, hence p = 2 and q = 1. The concentration of dissolved ions is therefore $m_{\pm} = 0.2$ mol/kg and $m_{-} = 0.1$ mol/kg. We calculate the mean molality $m_{\pm} = ((0.2 \text{ mol/kg})^2 \cdot 0.1 \text{ mol/kg})^{1/3} = 0.159 \text{ mol/kg}$. For the mean activity we thus obtain $a_{\pm} = \gamma_{\pm} \cdot m_{\pm} / m_0 = 0.453 \cdot 0.159 \text{ mol/kg} / m_0 = 0.072$.

respectively, of the salt. The chemical potential of a salt M_pX_q in solution is the sum of the chemical potential of the anions M and cations X: $\mu = p \cdot \mu_+ + q \cdot \mu_-$, because the salt dissolves into *p* cations and *q* anions. The chemical potential, expressed with molalities, is then:

$$\mu = p\mu_{+}^{\circ} + q\mu_{-}^{\circ} + (p+q)RT\ln(a_{\pm}) = \mu^{\circ} + (p+q)RT\ln(\frac{m_{\pm}}{m_{0}}\gamma_{\pm})$$
(0-7)

where we have introduced $\mu^{\circ} = p \cdot \mu_{+}^{\circ} + q \cdot \mu_{-}^{\circ}$. For details on the derivation, see **Appendix A**. We can thus express the chemical potential μ_k of the individual ions *k* constituting the salt (*k* = + or –) using the mean activity coefficient γ_{\pm} , a measurable quantity:

$$\mu_{k} = \mu_{k}^{\circ} + RT \ln(a_{k}) = \mu_{k}^{\circ} + RT \ln(\frac{m_{k}}{m_{0}}\gamma_{\pm})$$
(0-8)

Although ions in solution always come in anion-cation combinations, single-ion activities and activity coefficients are of relevance. One of the most fundamental concepts in chemistry, the acidity of a solution expressed with the pH value, is defined based on the activity of protons: $pH = -log(a(H^+))$. The activity and, therefore, the activity coefficient of an individual ion can be measured, for example, with an ion-selective electrode, at least approximately (cf. Chapter VIII). Moreover, single-ion activities at low salt concentrations can be estimated using the *Debye-Hückel* theory, which takes into consideration the coulombic forces between ions in an electrolyte (cf. Chapter IV).

Returning to the definition of the chemical potential, Eq. 0-1, in the analysis of the thermodynamics of an (electro)chemical reaction, we often wish to study the system at temperatures other than room temperature. It is important to note that the temperature dependence of the chemical potential μ is not only given by the $RT \ln(a_k)$ term, but also μ° is temperature dependent, $\mu^{\circ} = \mu^{\circ}(T)$. In conclusion, it is highlighted that the chemical potential of compounds cannot be measured directly. The chemical potential is a conceptual tool. We can, however, measure the change in the chemical potential of a system of compounds undergoing reaction, which is then, at constant temperature and pressure, called the *free energy* or *Gibbs energy G* (unit: J), which is composed of the chemical potentials μ_k of the involved species *k* and their respective amount n_k (unit: mol):

$$G = \sum_{k} n_k \cdot \mu_k \tag{0-9}$$

For dealing with electrochemical reactions, the chemical potential μ will be extended to the electrochemical potential $\tilde{\mu}$ in Chapter III.

2.3 Electrochemical cells: terminology & essentials

Electrochemistry deals with spatially separated redox reactions involving the exchange of electric charges coupled with chemical changes. Electron transfer between compounds undergoing reaction takes place via an external, electrically conducting circuit, while ions are exchanged via the *electrolyte*, an ionically conducting medium. The overall reaction is split into two half-cell reactions taking place on two *electrodes*, one with negative and one with positive polarity (**Figure 0-4a**). More specifically, electron transfer reactions are taking place at the electrode-electrolyte interface. On one side electrons are taken up by the electrode and on the other side electrons are supplied by the electrode. The principle of charge conservation requires that the half-cell reactions at the two electrodes have the same rate during a continuous operation of the cell. An example of a half-cell reaction is:



Figure 0-4. (a) Electrochemical cell, consisting of negative electrode, positive electrode and electrolyte. Electrons are moving in the electrode and outer circuit, ions in the electrolyte. Electron transfer reactions are taking place at the electrode-electrolyte interfaces. U_{cell} is the cell voltage. (b) Illustration of an example electrolytic reaction in an aqueous electrolyte, leading to the formation of gas bubbles at the two electrodes. The cell current is measured in A (ampère), the cell voltage in V (volt).

In principle, the reaction can proceed in forward as well as backward direction. We see that electrons appear in the half-cell reaction, which, depending of the direction of the reaction, are taken up or supplied by the electrode. In the forward direction of the reaction (\rightarrow), the removal of electrons from chloride ions leads to the formation of chlorine, which evolves from the electrode as gas. This is an important reaction in the chemical industry (cf. Chapter VI).

A simple experiment that can be performed at home can illustrate the basic principle of an electrochemical cell and reaction: prepare a glass of lukewarm water, add two table spoons of table salt and dissolve it. Then take two pencils, expose the lead (which is actually graphite) on both ends. Take a 9 V battery and connect each terminal via wires to the pencils using crocodile clips, then immerse the tips of the pencils into the salt-water. Make sure the tips are well-separated and do not touch each other. You will see bubbles forming on the pencil tips. A higher rate of gas evolution is observed at the negative electrode (**Figure 0-4b**). If you collect this gas in a vial and light it with a match, you will recognize it is flammable. This is hydrogen. On the positive electrode, oxygen is formed. Hence, we have split water electrochemically. However, also chlorine is formed at the positive electrode according to reaction 1, which you will recognize from its pungent smell. If you have a multimeter, you can measure the voltage U between the two terminals, it might be around 6 V. If you measure the current *I* passing through the cell, it could be 100 mA. The power *P* supplied by the battery to the electrochemical reaction is given by:

$$P = U \cdot I \tag{0-11}$$

For our experimental cell, we obtain $P = 6 \text{ V} \cdot 0.1 \text{ A} = 0.6 \text{ W}$ (units: $\text{V} \cdot \text{A} = \text{J/C} \cdot \text{C/s} = \text{J/s} = \text{W}$, cf. **Table 0-1**). The experiment can be conducted until the battery is discharged and the gas evolution ceases. To calculate the total electrical energy / work *W* that the battery supplied we write $dW = P \cdot dt$ = $U \cdot I \cdot dt$. Both U and I may be changing with time *t*, so to obtain *W* the expression needs to be integrated over time from the beginning to the end of the experiment: $W = \int U \cdot I \cdot dt$.

The symbols used to denote the type of cell under consideration in this text are indicated in **Figure 0-5**. A generic cell is shown in **Figure 0-5a**. A cell producing electrical output, such as a fuel cell or a battery during discharge, is sketched in **Figure 0-5b**. In this case, electrons are flowing from (-) to (+), like water flowing downhill and turning a mill-wheel. A cell where a reaction is forced to happen is indicated in **Figure 0-5c**. A power source is connected to the terminals and 'pumps' electrons to the (-) terminal and removes electrons from the (+) side. The sketches in **b** and **c** are also used when the cell is at equilibrium and the reaction is infinitely slow (cf. Chapter II).



Figure 0-5. Schematic representation of electrochemical cells: (a) Cell at equilibrium or generic cell. (b) Galvanic cell with spontaneous electrochemical reaction. The symbol O denotes, considering the water analogy, a wheel driven by the cell. (c) Electrolytic cell with driven electrochemical reaction. The symbol \dashv indicates a DC power supply.

It is instructive to look at the key differences between a chemical reaction and an electrochemical reaction. We consider the same overall reaction, as an example we take the reaction of hydrogen and oxygen to form water:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{0-12}$$

Carried out as a chemical reaction, this is the combustion reaction of hydrogen, which we can think of taking place as an explosion (when the gases are mixed in a 2:1 volume ratio in a balloon and then ignited) or in continuous manner in a hydrogen burner (**Figure 0-6a**). Also, think of liquid hydrogen and oxygen being fed to the combustion chamber of a rocket engine. The result of the chemical reaction is the production of heat and volume expansion, it is therefore a thermal process. When the reaction is carried out in an electrochemical manner (**Figure 0-6b**), the half-cell reactions of hydrogen and oxygen are spatially separated and electrons pass between the electrodes through an outer circuit, where they perform electrical work, for example drive an electric motor. The potential difference between the electrodes is \sim 1 V. Through the electrolyte, ions are exchanged between the two electrodes. In this case, the output of the reaction is electrical energy as well as



Figure 0-1. Illustration of key differences between a chemical reaction and an electrochemical reaction for the sample reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$. (a) In the chemical reaction, H_2 is combusted through the reaction with O_2 , which produces heat. (b) In a fuel cell, the reaction is spatially separated into two half-cell reactions taking place at electrodes separated by an electrolyte. Electrons are exchanged via an external circuit and can perform work.

0-13

waste heat. The heat may also be useful, for example to produce warm water. The electrochemical reaction between a fuel and an oxidant is sometimes referred to as 'cold combustion', because it is not a thermal process. The reaction can actually be carried out at room temperature.

At this point, further electrochemical terms of importance are introduced. **Figure 0-7a** depicts a cell where an electrochemical reaction is taking place. The electrode out of which electrons are flowing into the external circuit is called the *anode*. The electrode into which electrons are flowing from the electric circuit is the *cathode*. These terms, as well as 'electrolyte', were established by *Faraday*, but initially introduced by *Whewell*. Electrolyte means 'the decomposing body' and was used because in the studied reactions constituents of the electrolyte were undergoing reaction, for example water during electrolysis to form hydrogen and oxygen. In any case, electrons are flowing from anode to cathode, yet current, defined as the flow of (imaginary) positive charge, is going in the opposite direction, from cathode to anode. In the steady state, the same current *I* is flowing in the electrolyte to maintain charge neutrality, carried by positively charge ions, called *cations*, and negatively charged ions, called *anions*. The rule we can easily remember is: cations flow towards the cathode, anions towards the anode.



Figure 0-7. (a) Electrochemical cell with designated anode and cathode. (b) Sample reaction $Ox + e^{-1}$ Red: per definition, the reduction reaction is taking place at the cathode, the oxidation reaction on the anode.

Let us look more closely at what is happening at the electrode-electrolyte interface (Figure 0-7b). In a cathodic reaction, the electrode is supplying electrons to a half-cell reaction. We can think of a generic half-cell reaction $Ox + e^- \rightarrow Red$, where an oxidized species reacts with an electron to form a reduced species. The electron appears as a reactant in the cathodic reaction. Therefore, the cathode hosts a reduction reaction (mnemonic: RED CAT). In contrast, in an anodic reaction, the electrode is taking up electrons from a half-cell reaction. Our generic half-cell reaction is then Red $\rightarrow Ox + e^-$. Here, the electron appears on the product side in the reaction of a reduced species to an oxidized

one. The anode hosts an oxidation reaction (mnemonic: AN OX). By definition, in a half-cell reaction anodic current is defined as positive (I > 0), cathodic current as negative (I < 0).

2.4 Electron energy in electrode

We take the reaction $Ox + e^{-}$ \Rightarrow Red to be able to proceed in both forward and backward direction. Yet at equilibrium no net flow of electrons is taking place across the interface. Therefore, the energy of the electrons in the electrode at the Fermi level E_F (cf. Chapter III) is equal to the energy of the Ox/Red redox system E_{redox} in the electrolyte (**Figure 0-8a**). If the energy of the electrons in the electrode is increased, for example with a power supply, the electrons start to flow from the higher energy in the electrode to the lower energy in the solution (**Figure 0-8b**). This corresponds to a reduction reaction (the electrode supplies electrons), and the above Ox/Red reaction proceeds in forward (\rightarrow) direction. In the hydraulic analogy, we can imagine the electrode is lowered below E_{redox} , the 'downhill flow' of electrons is from the electrolyte to the electrode (**Figure 0-8c**). The electrode 'drains' electrons from the electrolyte, thus an oxidation reaction is taking place. The Ox/Red reaction is proceeding in backward direction (\leftarrow). At present, these concepts of electron and redox energy levels are not yet familiar to us. This will be studied in detail in Chapter III. It is helpful, however, to think of the behavior of electrons in terms of the hydraulic analogy, as it provides an intuitive understanding of electrode processes.



Figure 0-8. Illustration of the energy of the electron in the electrode, characterized by the energy of the Fermi level E_F , and the energy E_{redox} of a redox couple in solution. (a) At equilibrium, the two energy levels are aligned. (b) In a reduction reaction, the electrode is an electron source (= cathode). (c) In an oxidation reaction, the electrode is an electron sink (= anode).

Appendix A: Chemical Potential of a Salt in Solution

A salt M_pX_q is dissolved to give a solution of p cations and q anions. The chemical potential μ of the dissolved salt is the sum of the chemical potential of the ions:

$$\mu = p \cdot \mu_+ + q \cdot \mu_- \tag{0-A1}$$

 μ_{+} and μ_{-} are the chemical potentials of the cations and anions, respectively, given by:

$$\mu_{+} = \mu_{+}^{\infty} + RT \ln(\gamma_{+}) \qquad \mu_{-} = \mu_{-}^{\infty} + RT \ln(\gamma_{-})$$
(0-A2)

where μ° is the chemical potential under ideal conditions. Inserting into Eq. 0-A1 yields

$$\mu = p \cdot (\mu_{+}^{\infty} + RT \ln(\gamma_{+})) + q \cdot (\mu_{-}^{\infty} + RT \ln(\gamma_{-}))$$
(0-A3)

We define $\mu^{\infty} = p \cdot \mu^{\infty}_{+} + q \cdot \mu^{\infty}_{-}$ and condense the activity coefficient into one ln() term:

$$\mu = \mu^{\infty} + RT \ln(\gamma_{+}^{p} \gamma_{-}^{q}) \tag{0-A4}$$

Recalling the definition of the mean activity coefficient γ_{\pm} , Eq. 0-4, we arrive at

$$\mu = \mu^{\infty} + (p+q)RT\ln(\gamma_{\pm}) \tag{0-A5}$$

We can now express the individual chemical potentials of the ions using the mean activity coefficient γ_{\pm} :

$$\mu_{+} = \mu_{+}^{\infty} + RT \ln(\gamma_{+}) \qquad \mu_{-} = \mu_{-}^{\infty} + RT \ln(\gamma_{+}) \qquad (0-A6)$$

The non-ideality is thus formally 'shared equally' between cations and anions. In reality, this is certainly not the case. The Debye-Hückel theory (cf. Chapter IV), used to estimate the activity coefficient of individual ions, shows $\ln(\gamma_k) \propto (z_k)^2$. The equal splitting of non-ideality between cations and anions is thus merely conceptual in the description of electrolyte solutions.

Chapter I

Redox Reactions & Faraday's Laws

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1-2

1 Redox Reactions

In electrochemical reactions electrons are transferred between species, resulting in some compounds being oxidized and others being reduced. Therefore, they are redox reactions, in which the oxidation number of molecules, atoms, or ions changes by gain or loss of electrons. Many – actually most – chemical reactions are redox reactions. Very prominent examples are combustion reactions, where a compound undergoes reaction with oxygen, for example methane:

$$\begin{array}{c} \text{reduction} \\ \hline -\text{IV} & 0 & +\text{IV} & -\text{II} & -\text{II} \\ \text{CH}_4 + 2 & \text{O}_2 & \rightarrow & \text{CO}_2 + 2 & \text{H}_2\text{O} \\ \hline & & & & & & \\ \text{oxidation} \end{array}$$
(1-1)

1.1 Oxidation numbers

The red, roman numerals denote the *oxidation number* N of the corresponding atoms. The oxidation number of carbon changes from -IV in methane to +IV in carbon dioxide. Therefore, CH₄ undergoes *oxidation* during combustion. Indeed, this is where the term 'oxidation' comes from, meaning 'reacting with oxygen'. Oxygen, on the other hand, is undergoing *reduction*, as N(O)changes from 0 in oxygen to -II in carbon dioxide and water. N(H) does not change here, it is +I in methane as well as water. During oxidation, an element loses electrons, hence its oxidation number increases, LEO: Loss of Electrons = Oxidation. During reduction, it gains electrons and N decreases: GER: Gain of Electrons = Reduction. Therefore, the mnemonic is: LEO says GER !¹ During a redox reaction, the oxidation and redox reactions need to be balanced, meaning that the electrons that are lost by one compound need to be gained by another one. In our above example, the oxidation of CH₄ to CO₂ yields 8 electrons, and since one oxygen atom gains 2 electrons upon reduction to CO₂ and H₂O, 2 molecules of O₂ are required to balance the redox reaction.

Before we look in some more detail at oxidation numbers and how they are determined, it has to be stated that there also non-redox reactions, some of which are very important, even essential ('vital') for life on this planet. An important class of non-redox reactions are hydrolysis reactions, for example the reaction of adenosinetriphosphate (ATP) with water to adenosinediphosphate (ADP) plus a phosphate. This reaction is a universal reaction in living cells that provides energy to drive

¹ There are other mnemonics, for example: Oil Rig - Oxidation involves loss, Reduction involves gain - of electrons.

numerous processes. Further examples of non-redox reactions are acid-base, calcination and precipitation reactions.

The oxidation number, sometimes also called oxidation state, is the hypothetical charge that an atom would have if all its bonds to neighboring atoms were 100% ionic. It is a conceptual tool to establish whether an element is being reduced or oxidized during a reaction. N may be positive, negative or zero. It is often given, as in this text, as roman numerals¹. The procedure to determine oxidation numbers is:

• In covalent bonds: assign the electrons to the more electronegative atom, the formal charge of the atom is the oxidation number. In bonds between identical atoms, distribute the electrons evenly.

Examples: $H-Cl \rightarrow H(+I)$, Cl(-I); $NO_3^- \rightarrow N(+V)$, O(-II); $H_2O_2 \rightarrow H(+I)$, O(-I)

• The oxidation number of elements is zero:

Examples: Fe(0), $N \equiv N \rightarrow N(0)$

in monoatomic ions, the oxidation number is the charge of the ion:
 Examples: NaCl → Na(+I), Cl(-I), Fe₃O₄ → Fe²⁺(+II), 2 x Fe³⁺(+III), 4 x O²⁻(-II)²

Table 1-1 provides some rules for determining oxidation numbers. The formalism can also be used in organic chemistry. In C₁ compounds, for example, the oxidation number of carbon can vary between -IV in CH₄ to +IV in CO₂.³ In molecules with more than one carbon atom, the electrons need to be assigned to atoms, as described above, according to their electronegativity. Many other elements show a variety of different oxidation numbers, such as nitrogen (from -III in NH₃ to +Vin NO₃⁻) or chlorine (from -I in HCl to +VII in ClO₄⁻), and, obviously, most transition metal ions.

Compound	Oxidation number	Example
elements	0	S ₈ , Pt , H ₂
monoatomic ion	charge of ion	Ca^{2+}, S^{2-}
Н	+I, except in hydrides (-I)	H(+I)Cl, LiH(-I)
0	usually –II, –I in peroxides	$H_2O(-II), H_2O_2(-I)$
alkali metals	+I	\mathbf{K}^+
alkaline earth metals	+II	Mg(+II)Cl ₂
halogens in binary compounds	-I	HBr(-I)
neutral compound	$\Sigma = 0$	$H_2S \rightarrow H(+I), S(-II)$
polyatomic ion	$\Sigma =$ charge of ion	$CN^{-} \rightarrow C(+II), N(-III)$

Table 1-1.	Rules for	determining	oxidation	numbers.

1-3

¹ Zero '0', strictly speaking, actually does not belong to the family of roman numerals.

 $^{^2}$ This compound, magnetite, is admittedly a bit tricky. It is a spinel with the general formula AB₂O₄, where the A and B cations both happen to be Fe, yet in different oxidation states !

³ Carbon dioxide is actually not an organic compound, we consider it here as an 'end product' of the oxidation of any organic compound.

1.2 Electrochemical reactions

Before we discuss specific characteristics of electrochemical reactions, we look at an example of a chemical redox reaction. If we immerse a zinc strip into a solution containing copper(II) ions, such as $CuSO_4(aq)$, the following reaction takes place:

$$Zn(s) + Cu^{2+}(aq) + SO_4^{2-}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) + SO_4^{2-}(aq)$$
 (1-2)

Zn metal is oxidized and going into solution as Zn^{2+} ions, whereas Cu^{2+} ions are reduced and deposited as Cu metal onto the Zn strip. Some of the copper particles may not stick to the zinc and settle on the bottom of the beaker. During the reaction, 2 electrons are transferred from Zn atoms to Cu^{2+} ions. This so-called metal displacement reaction is shown schematically in **Figure 1-1a**.



Figure 1-1. Reaction between Zn and Cu^{2+} as given in Reaction 1-2, carried out as (a) a chemical reaction, or (b) as an electrochemical reaction. In the latter case, the half-cell reactions are taking place in separate compartments, which are ionically connected via a salt bridge. In the absence of current, the potential difference between the two electrodes is ~1 V. Upon connecting the electrodes, a current starts to flow.

We now turn this reaction into an electrochemical one by separating the overall redox reaction into two half-cell reactions, an anodic one (oxidation) and a cathodic one (reduction). For this, we make two half-cell compartments, with Zn metal dipping into $ZnSO_4(aq)$ solution on the left and Cu metal dipping into $CuSO_4(aq)$ solution on the right (**Figure 1-1b**). The two electrolyte compartments are ionically connected via a *salt bridge* (see Chapter IV for details), which prevents mixing of the solutions to avoid the direct chemical reaction. A potential difference (= voltage) of ~1 V establishes between the Zn and the Cu electrode, and if the two electrodes are electrically connected, a current will flow. The half-cell reactions taking place at the two electrodes are:

(-)/anode:
$$\operatorname{Zn} \to \operatorname{Zn}^{2+} + 2 e^{-}$$
 (1-3)

$$(+) / \text{cathode:} \quad Cu^{2+} + 2e^{-} \rightarrow Cu \tag{1-4}$$

We see that the overall reaction is the same as in the chemical reaction (1-2), only that in the case of the electrochemical reaction, the electrons travel from the Zn electrode to the Cu electrode via the outer electrical circuit, where they can perform useful electrical work, for example drive a small motor. As in the chemical reaction, Zn metal is oxidized to Zn^{2+} ions, thereby slowly dissolving the Zn electrode, and Cu^{2+} ions are reduced to Cu metal, which deposits on the Cu electrode¹. The Zn/Cu cell is called *Daniell cell*, invented by John Frederic Daniell in 1836. Later in the 19th century this type of cell was widely used in telegraphy. In fact, with a power supply we can drive the reaction in the other direction, $Zn^{2+} + Cu \rightarrow Zn + Cu^{2+}$, and thereby 'charge' the Daniell cell. It can, therefore, be used to build a rechargeable battery.

In summary, a half-cell reaction is either an oxidation or a reduction reaction occurring at an electrode, and electrons appear in the half-cell reaction equation, either on the reactant side (reduction reaction) or on the product side (oxidation reaction).

1.3 Balancing half-cell reactions

The electrons transferred in half-cell reactions of an arbitrary electrochemical process are subject to the conservation of charge. If we are combining half-cell reaction equations to the overall cell reaction, we have to ensure that the electrons on both sides of the equation cancel. This is called 'balancing of half-cell reactions'. As an example, we take the hydrogen fuel cell reaction with oxygen to form water (cf. Reaction 0-12 in the Introduction, and **Figure 1-2**).



Figure 1-2. Schematic of a H_2/O_2 fuel cell in (a) acidic electrolyte, and (b) alkaline electrolyte. H_2 and O_2 are fed from outside to the Pt electrodes.

¹ Instead of copper, we could also use an inert metal on the right side, such as silver. The cathodic reaction would then lead to the formation of a layer of copper on the silver electrode.

To start with, we look at the reaction under acidic conditions (**Figure 1-2a**). Under acidic conditions, the ions involved in the reaction are protons $(H^+)^1$. The oxidation of one molecule of hydrogen yields 2 electrons (and 2 protons) in the anodic reaction. For the reaction of one molecule of oxygen in the cathodic reaction, 4 electrons (and 4 protons) are required. To combine the 2 half-cell reactions to the overall reactions, we have to balance them as follows:

Acidic electrolyte:

anode (oxidation)	H_2	\rightarrow	2 H ⁺ + 2 e ⁻	(1)
cathode (reduction)	$O_2 + 4 H^+ + 4 e^-$	\rightarrow	$2 H_2O$	(2)
overall	$H_2 + \frac{1}{2} O_2$	↑	H ₂ O	$(1) + \frac{1}{2}(2)$

We thus obtain the well-known stoichiometry of hydrogen and oxygen in this reaction. The number of electrons transferred per formula unit is 2. Alternatively, we could have added 2 (1) + (2) to obtain 2 H₂ + O₂ \rightarrow 2 H₂O. Here, 4 electrons are exchanged per formula unit. We can also consider the reaction to take place under alkaline conditions (**Figure 1-2b**). In this case, hydroxide ions, OH⁻, enter the half-cell reaction equations:

Alkaline electrolyte:

anode (oxidation)	$H_2 + 2 OH^-$	\rightarrow	$2 H_2O + 2 e^{-1}$	(1)
cathode (reduction)	$O_2 + 2 H_2O + 4 e^-$	\rightarrow	4 OH-	(2)
overall	$H_2 + \frac{1}{2}O_2 + H_2O_2$	→	$\frac{2}{2}$ H ₂ O	$(1) + \frac{1}{2}(2)$

We see that under alkaline conditions water is a reactant (on the cathode side) as well as a product (on the anode side) in the half-cell reactions. In the overall reaction, we can therefore cancel 'excess' water molecules on the two sides of the equation and, hence, arrive at the same overall reaction as under acidic conditions. It is important to realize, though, that the type of species, i.e. water, protons or hydroxide ions, involved in an electrode process is essential to understand the half-cell reaction mechanism (cf. Chapters V and VII). In any case, the stoichiometry of the overall reaction is independent on the type of electrolyte used. In Chapter VII, we will also encounter half-cell reactions written for an oxide ion conducting ceramic used as electrolyte in a solid oxide fuel cell.

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Evidently, protons do not exist in 'naked' form as H⁺ in water or an aqueous solution, they are generally bound to water to form hydronium ions, H₃O⁺. We could therefore also write the half-cell reactions using H₃O⁺ instead of H⁺.

2 Faradaic Processes

An electrochemical reaction taking place in continuous manner in an electrochemical cell requires a steady flow of electrons across the electrode-electrolyte interface. In the external circuit, we measure this charge flow as current. The invention of Volta in 1799, consisting of a stack with alternating discs of Zn and Cu separated by a brine-soaked cloth or paper¹, later named in his honor 'voltaic pile', is a key milestone in electrochemistry. His 'electrical battery' allowed, for the first time, the continuous production of electrical current, which ushered in a prolific era of discoveries enabled by this device, such as the preparation of elemental potassium, sodium and calcium by Davy in 1807/08. The quantitative understanding of the relation between the charge passed through a cell and the extent of chemical change was developed later, in the 1830s, by Faraday. Therefore, a reaction where electrons flow across an electrode-electrolyte interface to elicit chemical change is called *faradaic reaction* or *faradaic process* (Figure 1-3a). Before the advent of the voltaic pile, people had already been experimenting widely with electricity, yet the devices they used were only capable of supplying short 'bursts' of electric charge. The Leiden jar is such a device. It is essentially a capacitor, which stores high-voltage electric charge from an external source. There is no charge transfer reaction occurring in a Leiden jar, and the capacitive accumulation of charge at an electrodeelectrolyte interface is referred to as a non-faradaic process (Figure 1-3b). A capacitor cannot sustain a continuous flow of charge (\equiv current).



Figure 1-3. A faradaic process describes a sustained electrochemical reaction involving the transfer of electrons across the electrode-electrolyte interface. In a non-faradaic process charges are accumulating at the electrode-electrolyte interface, without charge transfer reactions taking place. It is a capacitive process that cannot sustain a continuous current.

2.1 Faraday's laws

Faraday not only popularized terminology we use today, such as 'anode', 'cathode', 'electrode' and 'electrolysis' (cf. Introduction), but also provided a quantitative description of the mass m of an element deposited on an electrode and the charge Q passed through the electrochemical cell. For

¹ He carried out numerous experiments with different metals and solutions, some of which also worked. The Volta Temple in Como (Italy) features his experimental arrangements, and is worth a visit.

example, if Zn^{2+} ions from solution are plated as Zn metal onto an electrode in a cathodic reaction, the mass of zinc is proportional to the charge that passed through the cell over a given period of time Δt . At constant current *I*, the charge *Q* is given by $Q = I \cdot \Delta t$. The relationship discovered by Faraday is¹:

1 - 8

$$Q = \int I(t)dt = zFn = zF\frac{m}{M}$$
(1-5)

where *n* is the amount of substance (unit: mol) electrochemically converted, *z* the number of electrons involved in the reaction per unit of substance (e.g., 2 for Zn^{2+} reduced to Zn). It can also be regarded as the stoichiometric coefficient of the electrons in the half-reaction in question ($Zn^{2+} + 2e^- \rightarrow Zn$). *F* is a constant named after Faraday, the Faraday constant, which is the charge of 1 mol of electrons: $F = e \cdot N_A = 96'485$ As/mol. Obviously, the mass of substance *m* is related to its amount *n* by the molar mass *M*.

Eq. 1-5 describes the charge passed and substance converted over a certain period of time. For a current that is varying over time, I(t), we arrive at the charge through integration over time. Alternatively, we can also take the derivative with respect to time on both sides and since I = dQ/dt the *rate* of reaction $\dot{n} = dn/dt$ (unit: mol/s) or $\dot{m} = dm/dt$ (unit: kg/s) can be related to the current I: $I = zF\dot{n} = zF\dot{m}/M$.

Example:

A water electrolysis cell is operated for 7 days at a current of 1'200 A. How many kg of hydrogen are produced ? First, we calculate the total charge passed: $Q = I \Delta t = 7.26 \cdot 10^8$ As. Next, we write down the cathodic water splitting half-cell reaction, the hydrogen evolution reaction: $2 \text{ H}^+ + 2 \text{ e}^- \rightarrow \text{H}_2$. We have assumed acidic conditions, we may as well have used alkaline conditions. The important thing to know is the number of electrons required per molecule of H₂: z = 2. We can now insert the numerical values into Eq. 1-5 and solve for $m(\text{H}_2)$. With $M(\text{H}_2) = 2$ g/mol we obtain $m(\text{H}_2) = 7.52$ kg.

In fact, there are two laws (hence 'Faraday's laws') (cf. Wikipedia page 'Faraday's laws of electrolysis'):

^{1.} The mass *m* of an element deposited at an electrode is proportional to the charge *Q* that was passed through the cell: $m \propto Q$

^{2.} For a given value of Q, the mass m of the substance liberated / deposited at the electrodes is proportional to their 'electro-chemical equivalent', which is the molar mass M divided by the number of electrons per species $z: m_1 : m_2 : m_3 ... \propto (M_1/z_1) : (M_2/z_2) : (M_3/z_3) ...$

2.2 Faradaic efficiency

It happens that in practice faradaic reactions are not always 100 % efficient, meaning that there is a deviation from Eq. 1-5, for which there may be several reasons. In general, the *faradaic efficiency* $\varepsilon_{\rm F}$, which sometimes is also referred to as *coulombic efficiency*¹, for a reaction is defined as the ratio of the desired output to the invested input:

$$\varepsilon_{\rm F} = \frac{\{\text{desired output}\}}{\{\text{input}\}} = \frac{\overbrace{n(e^-)}^{\text{galvanic cell}}}{n(\text{reactant})} \text{ or } \frac{\overbrace{n(\text{product})}^{\text{electrolytic cell}}}{n(e^-)}$$
(1-6)

where $n(e^-) = Q/zF$. For a galvanic cell, where a spontaneous electrochemical reaction is taking place (cf. Chapter II), the desired output is electrons, i.e., charge, and the input the reactants. In an electrolytic cell, on the other hand, the desired output is a product of the electrochemical reaction, and the input is the 'invested' number of electrons supplied by a power source. Evidently, the faradaic efficiency is always equal to or lower than 100 %. In our example from above, for the reaction $Zn^{2+} + 2e^- \rightarrow Zn$ there may be hydrogen evolution $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ as a side reaction. This means that some of the electrons supplied to the cathode 'end up' in H₂ instead of Zn.

Instead of considering a reaction over a certain period of time, we can also determine the instantaneous faradaic efficiency of a process by taking derivatives with respect to time in the numerator and denominator of Eq. 1-6, yielding $\dot{n}(e^-) = I/zF$ and the rate of chemical turnover \dot{n} . It may well be that for a given process the faradaic efficiency changes as a function of cell current.

Example:

Chromium is electroplated from Cr³⁺ onto a steel workpiece for improved corrosion resistance. A current of 1.5 A is passed through the cell. After 10 min the mass of the workpiece increases by 100 mg. How much is the faradaic efficiency of this electroplating process ? The molar mass of chromium is 52.0 g/mol. The desired output is the plated chromium, the input the electrons provided by a power source. The charge passed through the cell in 10 min is $Q = I \Delta t = 900$ As. With this, theoretically Q/3F = 3.11 mmol Cr can be plated. The amount of plated Cr is n(Cr) = m(Cr) / M(Cr) = 0.1 g / 52.0 g/mol = 1.92 mmol. Therefore, the faradaic efficiency of this chrome plating process is $\varepsilon_{\text{F}} = 1.92 \text{ mmol} / 3.11 \text{ mmol} = 62\%$.

¹ because one is counting the charge / no. of Coulombs.

Generally, the following sources of faradaic efficiency loss can be identified:

• Occurrence of unwanted *side reactions*:

In an electrolytic cell, several products may be formed, but only one is desired. For example, in the chlor-alkali process Cl_2 is produced in the anodic half-cell reaction, yet some O_2 is evolved as well. Typically the faradaic efficiency of the chlorine evolution reaction is around 98% (cf. Chapter VI). In a galvanic cell, a reactant may be consumed in a parasitic reaction, such as in the direct methanol fuel cell, where methanol (the fuel) diffuses from the anode compartment through the electrolyte membrane to the cathode to react there directly with oxygen (see also Chapter VII).

• *Recombination* of formed products:

For example, in an electrolyzer water is electrochemically split into H_2 and O_2 , yet these gases can diffuse through the electrolyte to the opposite electrode and recombine there to again form water.

• A finite electronic conductivity of the electrolyte, leading to an *internal short circuit*: Some oxide ion conducting ceramics also display a non-zero electronic conductivity (cf. Chapter IV). This leads to a 'leakage' of electrons through the electrolyte, which thereby do not pass through the external electronic circuit.

Chapter II

Equilibrium Electrochemistry

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This chapter is dedicated to the study of electrochemical cells under *equilibrium* conditions. Before we immerse ourselves in the topic and throw about expressions with thermodynamic functions, it is worthwhile to consider what is meant by 'equilibrium'. In thermodynamics, the notion of an equilibrium implies that the (electro)chemical reaction under consideration is not taking place at a finite rate, only with infinitely slow rate. The deviation from equilibrium is therefore *infinitesimal*, and the reaction is said to be a *reversible process*. This means that its direction can be reversed without leaving any changes in the reaction system or the surroundings. Perfectly reversible processes are impossible, obviously, they are at best quasi-reversible.

1 Chemical Thermodynamics

The concept of a reaction being 'at equilibrium' is somewhat different for a chemical and an electrochemical reaction. The key thermodynamic quantity used to characterize this at constant temperature and pressure¹ is the *Gibbs free energy of reaction* (or just 'free energy' or 'Gibbs energy') $\Delta_r G$. It is a thermodynamic state function², which describes 'how far away from equilibrium' the system under study is. That is, it describes the thermodynamic driving force towards equilibrium. To understand the differences in the description of the equilibrium condition, we look at both cases in the following, starting with the case of a chemical reaction.

1.1 Chemical equilibrium

The Gibbs free energy of reaction $\Delta_r G$ for a chemical system at given temperature *T* depends on the composition of the reaction mixture in the following way.

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q \tag{2-1}$$

R is the gas constant with the value 8.314 J·mol⁻¹·K⁻¹ and *Q* is the reaction quotient defined as:

$$Q = \prod_{k} (a_{k})^{\nu_{k}} = \frac{\prod_{k} (a_{k})^{\nu_{k,p}}}{\prod_{k} (a_{k})^{|\nu_{k,r}|}}$$
(2-2)

¹ Other thermodynamic state functions have to be used in other cases, such as the Helmholtz free energy ΔF (sometimes also called ' ΔA ') at constant temperature and volume of the system.

² The value of a thermodynamic state function, which characterizes a system at a given set of conditions, such as its composition and temperature, is independent of the path chosen to reach that state. Therefore, a thermodynamic state function is also called 'thermodynamic potential'.

 a_k is the activity of compound k and v_k its stoichiometric factor in the reaction equation. The stoichiometric factor is negative for reactants and positive for products. Therefore, the activity coefficients of the products (p) appear in the numerator of Q, the ones of the reactants (r) in the denominator. $\Delta_r G^\circ$ is the free energy at standard state, indicated by the symbol '°', of the compounds involved, corresponding to $a_k = 1$, which leads to Q = 1 and $\ln(Q) = 0$. $\Delta_r G^\circ$ is actually temperature dependent, as we shall see below (Section 1.4). To indicate the temperature, we write the temperature in parenthesis, e.g. $\Delta_r G^\circ(573 \text{ K})$. Sometimes, as in some textbooks, we indicate the value of the temperature as a subscript number, omitting the 'K', for example $\Delta_r G^\circ_{573}$ for the free energy at 573 K = 300°C. In case the temperature is not indicated, it is implicit from the context or assumed to be the standard temperature of 25°C¹.

The reaction is at equilibrium if the following condition is fulfilled: $\Delta_r G = 0$ (cf. Appendix A for details how we arrive at this expression). Therefore, from Eq. 2-1 we obtain the following important relationship for a chemical reaction at equilibrium:

$$\Delta_{\rm r}G^{\circ} = -R \cdot T \ln(K) \tag{2-3}$$

The reaction quotient Q has been replaced by the corresponding expression at equilibrium, the equilibrium constant K. This is the *law of mass action*, which provides a relationship between the activities of the reactants and products for a chemical reaction at equilibrium.

Example:

We study the thermolytic water splitting reaction $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ at 1'000°C. The standard free energy is $\Delta_r G^{\circ}(1273 \text{ K}) = 177 \text{ kJ/mol}$. With Eq. 2-3 we obtain $K_{1273} = \exp(-\Delta_r G^{\circ}_{1273}/RT) = 10^{-7.3}$. The equilibrium is therefore strongly on the side of the reactant, H_2O , and no significant water (steam) thermolysis takes place at 1'000 °C. Since we are dealing with gases here, we insert partial pressures for the activities in *K* and obtain

$$K = \frac{p(H_2) / p_0 \cdot \sqrt{p(O_2) / p_0}}{p(H_2O) / p_0}$$

with $p_0 = 1$ bar. If we assume $p(H_2O) = 1$ bar $= 10^5$ Pa, then we obtain $p(H_2) = 1.8$ Pa and $p(O_2) = 0.9$ Pa. In fact, we have to go to significantly higher temperatures above 3'000°C to observe notable concentrations of hydrogen and oxygen in equilibrium with steam. We will see that using electrolysis, we only need a voltage of a bit more than 1 V to electrochemically split water.

¹ The standard temperature of 25°C corresponds to 298.15 K on the Kelvin scale. In this text, we will omit the '.15' from the numbers in K for convenience, thus 25°C ≈ 298 K.

1.2 Equilibrium of an electrochemical reaction

To describe an electrochemical reaction at equilibrium, we imagine an electrochemical cell (cf. Introduction, Figure 2-4a) where the two half-cell reactions at their respective electrodes are at equilibrium and the cell is at open circuit, i.e. there is no external electronic connection between the electrodes. We shall take the fuel cell reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O(1)$ as an example (cf. Chapter I, Figure 2-2). Pt electrodes are used, which are inert and allow the half-cell reactions to establish their respective equilibrium. Also, we make sure that the two redox pairs are well-separated by the electrolyte to prevent a direct chemical reaction¹. Since electrons are involved in a half-cell reaction, an equilibrium potential will be established in the electrode, which depends on the chemical nature of the redox pair (A more in-depth description of this process will be given in Chapter III). Hence, owing to the different half-cell reactions, the two electrodes will have a dissimilar potential. With a voltmeter, the potential difference² between the electrodes can be measured, which is called the *cell* potential E_{cell} , sometimes also ΔE_{cell} to stress that it is a potential difference. Another common terminology is thermodynamic or ideal cell voltage, which is therefore also referred to as reversible *cell voltage* U_{rev} , indicating that the cell is at equilibrium. In most of this text, the term cell voltage with the symbol U will be used to describe the potential difference between electrodes, be it at equilibrium or not, to avoid confusion with the electrode potential E, which is measured against a certain reference electrode (see below, Section 2.2). In our cell, owing to the absence of an electronic connection between the two electrodes, electrons cannot be exchanged and the overall reaction can therefore not reach the chemical equilibrium. Consequently, the relationship $\Delta_r G = 0$ does not hold for an electrochemical reaction (except, of course, if the half-cell reactions at the two electrodes are the same...).

The next question to address is: how does the Gibbs energy of reaction $\Delta_r G$ relate to the reversible cell voltage U_{rev} ? We describe the theoretical electrical work W_e (unit: J/mol) associated with an electrochemical reaction by imagining that an amount of charge Q is allowed to pass between the two electrodes in reversible manner, i.e. infinitely slowly. Therefore, the cell voltage will not deviate from its theoretical value U_{rev} . The electrical work (unit: J) delivered to the surroundings is $Q \cdot U_{rev}$ and, consequently, the work done on the system is $-Q \cdot U_{rev}$. Thermodynamically, the electrical work

¹ Although H₂ and O₂ will not undergo reaction if just mixed at room temperature, in the presence of a noble metal catalyst, such as Pt, the reaction will be catalyzed and will proceed.

² An old term used for potential difference is *electromotive force* (EMF), but it is somewhat outdated, as it does not have the unit of force. It can, at best, be thought of as a 'driving force' for an electrochemical reaction to take place.
Chapter II

 W_e is non-volume work, which is given by $\Delta_r G$ under reversible conditions (cf. Appendix B for the derivation).¹ With Faraday's law (cf. Chapter I), Q = zFn, we obtain:

$$\Delta_{\rm r}G = W_{\rm e} = -\frac{Q}{n}U_{\rm rev} = -zFU_{\rm rev}$$
(2-4)

where n is the amount (unit: mol) of substance converted (per formula unit). We rearrange to obtain the following key equation in electrochemistry:

$$U_{\rm rev} = -\frac{\Delta_{\rm r}G}{zF}$$
(2-5)

How do we determine $\Delta_r G$ for a given reaction ? The most straightforward approach is to look up the *standard Gibbs free energies of formation* $\Delta_f G^\circ$ ('f' = formation) of the involved compounds k= 1...N in thermodynamic tables and then calculate $\Delta_r G^\circ$ from the stoichiometry of the reaction:

$$\Delta_{\rm r}G = \sum_{k} \nu_k \cdot \Delta_{\rm f}G_k \tag{2-6}$$

where v_k is the stoichiometric factor of compound k. The Gibbs energies of formation for elements in their standard state are defined as zero at all temperatures. We will see below (Section 1.3) how values of the reaction free energy $\Delta_r G$ at arbitrary temperature and non-standard conditions are calculated.

Example:

For the fuel cell reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O(I)$, we calculate the Gibbs free reaction energy for simplicity at 25°C and standard conditions. The stoichiometric factors are -1 for H_2 , -0.5 for O_2 and +1 for H_2O . Using Eq. 2-6: $\Delta_r G^\circ = -1 \cdot \Delta_f G^\circ(H_2) - 0.5 \cdot \Delta_f G^\circ(O_2) + 1 \cdot \Delta_r G^\circ(H_2O) = -237$ kJ/mol. Since $\Delta_f G^\circ \equiv 0$ for H_2 and O_2 , $\Delta_r G^\circ$ happens to be identical to $\Delta_f G^\circ(H_2O)$ (which we can find in thermodynamic tables). We use Eq. 2-5 to calculate the theoretical voltage U_{rev}° of this fuel cell. The number of exchanged electrons *z* per formula unit is 2. We obtain: $U_{rev}^\circ = +237$ kJ/mol / $(2 \cdot 96'485$ As/mol) = 1.23 V.

¹ $\Delta_r G$ is the maximum amount of energy that can be 'freed' from the system to perform useful work, i.e. work other than that associated with the expansion of the system, for example electrical work. In fact, the use of the term 'energy' for $\Delta_r G$ is misleading, as it lacks one of the most important attributes of energy: it is not conserved.

Thermodynamics teaches us that a reaction with a negative $\Delta_r G$ characterizes a spontaneous process. This means that the reaction will take place if allowed to, like in the example of our H₂-O₂ fuel cell reaction with $\Delta_r G^\circ = -237$ kJ/mol at 25°C. Therefore, according to Eq. 2-5 an electrochemical cell hosting a thermodynamically 'downhill' process has a positive U_{rev} . This is referred to as a *galvanic* (or voltaic) *cell*, as it releases electricity like in the experiments of *Galvani* and *Volta*¹ (Figure 2-1). A positive $\Delta_r G$, on the other hand, is indicative of a non-spontaneous reaction, i.e. a thermodynamically 'uphill' process. Its U_{rev} is negative, and the cell is called an *electrolytic cell*. It needs to be supplied with electrical energy from a power source to drive the reaction. An obvious example is the reverse reaction of the H₂-O₂ fuel cell, water electrolysis, for which evidently $\Delta_r G^\circ = +237$ kJ/mol.



Figure 2-1. Schematic of a galvanic cell and an electrolytic cell with indicated key differences, with a reaction at equilibrium that can be slightly 'tipped' in both directions. Note that the designation of anode and cathode switches upon changing the direction of the reaction (anode = electron source, cathode = electron sink).

Let us analyze the situation in **Figure 2-1** in a bit more detail. The cells are sketched with the negative electrode on the left and the positive electrode on the right, according to the convention in this text. Our reaction $H_2 + \frac{1}{2} O_2 \leftrightarrows H_2O$ may be considered to take place in forward (\rightarrow , fuel cell) as well as backward (\leftarrow , water electrolysis) direction. The negative electrode is the hydrogen electrode, where hydrogen is consumed (fuel cell) or evolved (water electrolysis), and the positive electrolysis). In the galvanic cell mode, H_2 is oxidized, hence the negative electrode becomes the anode, and O_2 is reduced, which makes the positive electrode the cathode. In the water splitting (electrolysis) mode, cathode and anode switch sides, because now H_2 is evolved (reduction reaction)

¹ We have encountered the experiments of Volta already (see Chapter I). A few years earlier, Galvani observed that the muscles of a (dead) frog twitched when touched with wires made of different metals.

at the negative electrode, which makes it the cathode, and O_2 is evolved (oxidation reaction) at the positive electrode, thus becoming the anode.

We consider the reaction $H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O$ to be at equilibrium. We can now imagine that the reaction is 'tipped' towards the right (\rightarrow) by an infinitesimal amount, such that the conditions of reversibility are maintained. This triggers the fuel cell reaction, hence $U_{rev} > 0$. If we 'tip' the reaction towards the left (\leftarrow), the water splitting reaction takes place, and $U_{rev} < 0$. So, does this mean that the measured cell voltage actually flips from positive to negative ?! If we were to attach a voltmeter to the cell we would always measure a voltage of 1.23 V (or -1.23 V, depending on how we connect the cables) at 25°C under ideal conditions¹ during infinitesimal deviations from the equilibrium towards the right and the left. The difference in the sign of U_{rev} for a galvanic and an electrolytic cell has to do with how U_{rev} is supposed to be measured according to the convention. It is defined as the potential of the cathode minus the potential of the anode (cf. Section 2.2). Therefore, the sign of U_{rev} flips when we switch from galvanic to electrolytic mode, and vice-versa (**Figure 2-1**). Actually, this means that when we measure the cell voltage in an experiment, we should flip the cables of the voltmeter when we are changing the direction of the reaction. The difference in the sign of U_{rev} depending on the direction of reaction is admittedly a bit awkward and it seems unpractical, yet it is a necessary requirement for reasons of thermodynamic consistency.

The Gibbs energy of reaction is given in energy per formula unit. Taking the reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O(1)$ at 25°C as an example, $\Delta_r G^\circ$ is -237 kJ/mol. If we were to double the number of species, $2 H_2 + O_2 \rightarrow 2 H_2O(1)$, $\Delta_r G^\circ$ would double to -474 kJ/mol, yet U_{rev} , given by Eq. 2-5, would be the same for both cases, namely 1.23 V, because doubling the amount of species also doubles the number *z* of transferred electrons from 2 to 4.

1.3 Thermodynamic state functions

The fundamental difference between an electrochemical reaction and a chemical reaction in terms of how energy is converted to electricity or/and heat can only be understood by looking at two other important thermodynamic state functions, the *reaction enthalpy* $\Delta_r H$ and the *reaction entropy* $\Delta_r S$, and how they relate to $\Delta_r G$:

$$\Delta_{\rm r}G = \Delta_{\rm r}H - T \cdot \Delta_{\rm r}S \tag{2-7}$$

2-7

¹ We will see in Chapter VII that practically it is very difficult to attain the value of 1.23 V in an experimental setup, because the oxygen electrode is not behaving as ideally as presumed. The setting here is that of a *gedankenexperiment* to understand the concept of electrochemical cells at equilibrium.

The reaction enthalpy $\Delta_r H$ is the total heat of reaction. It tells us whether the reaction leads to an overall heat release to or to heat absorption from the environment. This is independent of whether the reaction is carried out in a chemical or electrochemical manner (because the enthalpy is a state function). For example, the reaction H₂ + $\frac{1}{2}$ O₂ \rightarrow H₂O(1) is exothermic, $\Delta_r H^\circ = -286$ kJ/mol at 25°C, as we know well. Endothermic reactions ($\Delta_r H > 0$) absorb heat from the environment, such as the calcination of lime, $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. Entropy is a quantity that is a bit more difficult to grasp. It measures the extent of energy dispersal of a system, sometimes also somewhat sloppily described as 'state of order / disorder'. The sign of the reaction entropy $\Delta_{\rm P}S$ can be estimated using a few rules of thumb. Gases have much higher entropy than liquids, which have higher entropy than solids. If the number of gas molecules decreases during a reaction, there are less possibilities for energy dispersal, hence the entropy decreases and the reaction entropy is negative. This is the case for our sample reaction of H₂ and O₂ to water, $\Delta_r S^\circ = -163 \text{ J/(mol·K)}$ at 25°C. We can now combine the reaction enthalpy and entropy to obtain $\Delta_r G^\circ = \Delta_r H^\circ - T \cdot \Delta_r S^\circ = -237 \text{ kJ/mol}$, a value we have already encountered. For the corresponding reverse reaction, the water splitting reactions, the values of $\Delta_r H^{\circ}$, $\Delta_r S^{\circ}$, and $\Delta_r G^{\circ}$ are the same but with inverted sign: the reaction is endothermic $(\Delta_r H^\circ > 0)$, leads to more disorder $(\Delta_r S^\circ > 0)$, and needs to be driven $(\Delta_r G^\circ > 0)$.



Figure 2-2. Thought experiment to assess the heat ΔQ generated by the reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O(1)$ when carried out as (a) a chemical reaction (combustion), (b) an electrochemical reaction with the electric output being dissipated in a resistor, and (b') the same, but with separate analysis of the heat dissipated by the resistor and the cell, where we assume the cell to be at reversible conditions ($U = U_{rev}$).

Next, we compare the reaction being carried out as a chemical reaction in one case, and the same reaction being carried out electrochemically in another case to understand what the introduced thermodynamic state functions are telling us. Again, we take the reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O(1)$ at 25°C as an example. The chemical reaction is the hydrogen combustion reaction. In this case, an amount of heat of 286 kJ/mol is released to the environment under standard conditions, since $\Delta_r H^\circ = -286$ kJ/mol (**Figure 2-2a**). This heat can be used, for example, for cooking or to propel a rocket.

The reaction entropy and Gibbs energy of reaction are not 'visible' in this case, except that we know that the reaction is spontaneous ($\Delta_r G^{\circ} < 0$). In case of the electrochemical reaction mode (in a fuel cell), we assume that a resistor is inserted between the electrodes, which dissipates the electricity produced by the cell as heat (Figure 2-2b). The overall heat released by the system is (has to be !) the same as in the case of the chemical reaction: 286 kJ/mol of heat is released to the environment. In a refinement of the gedankenexperiment, we analyze the heat released by the cell and the resistor separately (Figure 2-2b'). If the reaction in the cell proceeds reversibly, the voltage across the resistor is U_{rev} . Therefore, according to Eq. 2-5, the energy dissipated by the resistor as heat is 237 kJ/mol, because $\Delta_r G^\circ = -237$ kJ/mol. Consequently, since $\Delta_r H = \Delta_r G + T \cdot \Delta_r S$ (see Eq. 2-7) the difference of 286 kJ/mol – 237 kJ/mol = 49 kJ/mol, which corresponds to $|T \Delta_r S|$, is released by the cell itself as heat to the environment. Therefore, since $\Delta_r S < 0$ for our sample reaction, this means that even under reversible conditions, the cell releases 'waste heat' of magnitude $T\Delta_r S$ to the environment. $T \Delta_r S$ is therefore also referred to as 'reversible heat'. This furthermore means that the theoretical (i.e., maximum possible) efficiency of electricity generation of this type of cell is less than 100 % (cf. Chapter VII). On the other hand, if we choose a fuel cell reaction with $\Delta_r S > 0$, the cell absorbs heat from the environment under reversible conditions, and therefore the theoretical efficiency of electricity generation is >100 % !¹ If the cell reaction were to be carried out at finite rate, the cell would no longer be at equilibrium and the cell voltage would drop below U_{rev} . Less heat would be dissipated by the resistor and more by the cell², but the sum would still be 286 kJ/mol. In the extreme case, the cell would be shorted and all of the heat given by the reaction enthalpy would then be released by the cell.

In electrochemistry we are often interested in calculating the theoretical cell voltage U_{rev} for a reaction of interest, which we can calculate from $\Delta_r G$ according to Eq. 2-5. The free energy of reaction under standard conditions $\Delta_r G^{\circ}$ can, as already mentioned, be calculated from the standard free energies of formation $\Delta_f G^{\circ}$ (Eq. 2-6). It can also be calculated from the values of $\Delta_r H^{\circ}$ and $\Delta_r S^{\circ}$ according to Eq. 2-7. This will make it easier to calculate $\Delta_r G^{\circ}$ at temperatures other than 25°C (see Section 1.4). The temperature dependence of $\Delta_r H$ and $\Delta_r S$ is not very pronounced. Values of $\Delta_r H$ and $\Delta_r S$ can be obtained, in analogy to $\Delta_r G$, from the *formation enthalpies* $\Delta_r H$ and *entropies* S of the compounds k involved in the reaction with their respective stoichiometric factors v.

¹ This does not constitute a violation of the 1st law of thermodynamics, of course. The reversible heat $T \cdot \Delta_r S$ absorbed by the cell has to come from somewhere, for example from a combustion reaction, for which, again, we need some fuel. So overall, energy is conserved.

² We would need to cool the cell to prevent it from overheating (cf. Chapter VII).

$$\Delta_{\rm r}H = \sum_{k} \nu_k \cdot \Delta_{\rm f}H_k \tag{2-8}$$

$$\Delta_{\mathbf{r}}S = \sum_{k} v_k \cdot S_k \tag{2-9}$$

The standard formation enthalpy $\Delta_t H^\circ$ of substances can be found in thermodynamic tables, mostly given at 25°C. Note that $\Delta_t H^\circ \equiv 0$ for elements in their most stable state at all temperatures. The entropy is tabulated as *standard entropy* S° of compounds at 1 bar and 298 K. The 3rd law of thermodynamics states that the entropy of a substance in the form of a perfect crystal at T = 0 is zero. Therefore, the entropy is the only thermodynamic potential for which we can calculate an absolute value. In particular, the values are non-zero for the elements at 25°C, unlike in the case of the formation enthalpy. **Table 2-1** lists the $\Delta_t H^\circ$ and S° values for our example reaction, where we have also added the values for water vapor.

Table 2-1. Thermodynamic data at standard conditions and 25°C of compounds for the reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$, listing both liquid water and water vapor. (Source: P.W. Atkins, Physikalische Chemie, 1990)

Compound	$\Delta_{\rm f} H^{\rm o}$ S°	
	(kJ·mol⁻¹)	$(J \cdot mol^{-1} \cdot K^{-1})$
H ₂	0	130.7
O ₂	0	205.1
$H_2O(1)$	-285.8	69.9
$H_2O(g)$	-241.8	188.8

The reaction enthalpy $\Delta_r H^\circ$ corresponds to the formation enthalpy $\Delta_f H^\circ$ of water, because in the reaction it is formed from the elements H₂ and O₂. With the values of S° , we obtain the reaction entropy $\Delta_r S^\circ = -163 \text{ J/(mol·K)}$ for liquid water and -44.5 J/(mol·K) for water vapor as product. This indicates, in agreement with our intuition, that the decrease in entropy is more pronounced when the product is liquid water rather than water vapor.

It has to be mentioned that Eq. 2-7 only holds for reaction quantities, and not for individual compounds: $\Delta_f G^\circ \neq \Delta_f H^\circ - T \cdot S^\circ$. This is because the formation enthalpy ($\Delta_f H \equiv 0$ for elements at all *T*) and the entropy (S $\equiv 0$ at T = 0) have different 'reference points'. The reaction quantities $\Delta_r H$ and $\Delta_r S$ are differences, thus different reference points cancel in the calculation.

The thermodynamic tables provide data at standard conditions, such as ideal gases with a partial pressure of 1 bar and concentration of dissolved species of 1 M in an ideal solution (cf. Introduction), generally at 25°C. What about non-standard conditions, such as gas partial pressures higher or lower than 1 bar? For this we return to Eq. 2-1. The reaction quotient Q (Eq. 2-2) contains the expressions for the concentration, activity, or partial pressure of the species involved in a

chemical reaction. To calculate the reversible cell voltage U_{rev} under non-standard conditions, we insert Eq. 2-1 into Eq. 2-5 and obtain

$$U_{\rm rev} = U_{\rm rev}^{\circ} - \frac{RT}{zF} \ln(Q) = U_{\rm rev}^{\circ} - \ln(10) \frac{RT}{zF} \log\left(\prod_{k} (a_k)^{\nu_k}\right)$$
(2-10)

This is the *Nernst equation*, one of the most important expressions in electrochemistry. In practice it is often more convenient to use base-10 logarithms, which yields the factor $\ln(10) \approx 2.303$ upon change of the base from *e* to 10. At room temperature (T = 298 K), we obtain the well-known factor $\ln(10) \cdot RT/F = 59.2$ mV.

Example:

Again, we consider the fuel cell reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O(1)$, which has a standard reversible voltage of $U_{rev}^{\circ} = 1.23$ V at 25°C (see above). Now we wish to calculate U_{rev} for the case where air is used instead of oxygen as reactant at 1 bar. For hydrogen we assume a partial pressure at 1 bar. The reaction quotient is $Q = a(H_2O) / (a(H_2) \cdot a(O_2)^{\frac{1}{2}})$. Pure, liquid water has an activity of one, and for the activities of the gases we insert the partial pressures p/p_0 , with $p_0 = 1$ bar. For hydrogen we have $a(H_2) = 1$ and for oxygen $a(O_2) = 0.209$. Inserting everything into Eq. 2-10, remembering that z = 2, yields $U_{rev} = 1.23$ V + 0.059 V / 2 $\cdot \log((0.209)^{\frac{1}{2}}) = 1.22$ V. The difference to the standard value is only around 10 mV.

1.4 Temperature dependence of U_{rev}

The reversible cell voltage U_{rev} is, because it is given by $\Delta_r G$, temperature dependent. The main nfluence of temperature comes from the $T \cdot \Delta_r S$ term in Eq. 2-7. The derivative of $\Delta_r G$ with respect to temperature *T* at constant pressure *p* is:

$$\left(\frac{\partial \Delta_{\rm r}G}{\partial T}\right)_p = -zF\left(\frac{\partial U_{\rm rev}}{\partial T}\right)_p = -\Delta_{\rm r}S \tag{2-11}$$

With this, we also have the temperature dependence of U_{rev} . For example, for the above fuel cell reaction to liquid water, U_{rev}° decreases by ~0.8 mV per degree. It is important to note that also $\Delta_r H$ and $\Delta_r S$ show a temperature dependence, albeit a small one. Nonetheless, Eq. 2-11 still holds in this case. Why ? For the explanation, we look at how enthalpy and entropy are defined. The enthalpy change of a compound with temperature is $dH = c_p \cdot dT$, and that of the entropy $dS = c_p/T \cdot dT$, where

 c_p is the heat capacity of the compound at constant pressure. With these definitions, the derivative with respect to temperature in Eq. 2-7 yields Eq. 2-11.¹

With this knowledge, we can calculate the values of the thermodynamic state functions and the reversible cell voltage as a function of temperature. For the hydrogen fuel cell reaction, this is shown in Figure 2-3 up to a temperature of 1'000°C, which covers the operating temperature range of the various types of fuel cell (cf. Chapter VII). The transition at 100°C from the product being liquid water to water vapor is clearly discernible. The drop in reaction enthalpy at 100°C is due to the enthalpy of vaporization of water $\Delta_{vap}H^{\circ} = 40.7$ kJ/mol, which is identical to the change in $T \cdot \Delta_{vap}S^{\circ}$, so the entropy of vaporization is $\Delta_{vap}S^{\circ} = 109.1 \text{ J/(mol·K)}$. The free energy of reaction $\Delta_r G^{\circ}$ and reversible cell voltage U_{rev}° are continuous, and at 100°C liquid water and water vapor of 1 bar pressure are at equilibrium with $U_{rev}^{\circ} = 1.167$ V. The stronger drop in U_{rev}° in the liquid water regime compared to the temperature range >100°C is a result of the different reaction entropies. With water vapor, U_{rev}° changes with ~0.2 mV/K. In first approximation, the temperature dependence of $\Delta_r G^{\circ}$ and U_{rev}° can be calculated assuming constant $\Delta_r H^{\circ}$ and $\Delta_r S^{\circ}$ in the respective regimes. At high temperatures, however, this leads to significant deviations, and for a more accurate calculation the temperature dependence of the enthalpy and entropy of reaction, which are defined based on the heat capacity c_p of the compounds involved, as outlined above, needs to be taken into account. For yet more accurate values, the temperature dependence of the heat capacity c_p itself needs to be considered, which increases with temperature. For a detailed analysis and explanations, the reader is referred to Appendix C.



Figure 2-3. Temperature dependence of thermodynamic state function and the reversible cell voltage for the indicated reaction. For the calculation, temperature dependent values of the heat capacities c_p are taken to calculate $\Delta_r H^{\circ}$ and $\Delta_r S^{\circ}$ at temperature T (cf. Appendix C), then $\Delta_r G^{\circ}$ and U_{rev}° are calculated via Eq. 2-7 and 2-5, respectively.

¹ For differentiation of Eq. 2-7 we remember the product rule: $(f \cdot g)' = f \cdot g + f \cdot g'$. This yields: $\partial \Delta_r G / \partial T = \partial \Delta_r H / \partial T - \partial / \partial T (T \cdot \Delta_r S) = \partial / \partial T \int \Delta c_p dT - (\Delta_r S + T \cdot \partial / \partial T \int \Delta c_p / T dT)$ $= \Delta c_p - \Delta_r S - T \cdot \Delta c_p / T = -\Delta_r S$, where $\Delta c_p = \sum v_k c_{p,k}$. We see that the temperature dependencies of $\Delta_r H$ and $\Delta_r S$ cancel.

1.5 Cell diagram

Electrochemistry allows us to separate chemical reactions into two half-cell reactions. Also, one particular half-cell reaction, e.g. $Zn \rightarrow Zn^{2+} + 2 e^-$, may be combined with a variety of different half-cell reactions on the opposite electrode, e.g. $Cu^{2+} + 2 e^- \rightarrow Cu$ (Daniell element, cf. Chapter I), or $O_2 + 2 H_2O + 2 e^- \rightarrow 4 OH^-$ (Zn-air battery, cf. Chapter VII). For an efficient schematic representation of an electrochemical cell, a shorthand notation is used, which lists the compounds involved in the reaction and uses specific symbols to represent boundaries between different phases or compartments (**Table 2-2**). The Daniell element, for example, is written as follows:

$$Zn | Zn^{2+}, SO_4^{2-} (aq) || Cu^{2+}, SO_4^{2-} (aq) | Cu$$
(2-12)

On the outside are the metal electrodes zinc and copper, dipping into solutions of $ZnSO_4(aq)$ and $CuSO_4(aq)$, respectively. The two electrolyte compartments are separated by a salt bridge (cf. Chapter I, **Figure 2-1**). The generic representation of a cell with salt bridge is M' | S' || S | M, where M and M' are the (metal) electrodes, S and S' the electrolyte solutions. We may also have a cell with a common electrolyte: M' | S | M. An example is the H₂ fuel cell with sulfuric acid electrolyte encountered in Chapter I: Pt | H₂ | H₂SO₄(aq, 2 M) | O₂ | Pt, where we have specified the concentration of the acid. The gases, being a different phase, are separated from the electrodes and the electrolyte by a '|' symbol.

Table 2-2. Symbols used in the shorthand notation of cells to separate different phases and compartments.

Symbol	Meaning	Example
	phase boundary	Metal Electrolyte
	salt bridge	KCl(aq) gelified with agar-agar
	liquid junction	glass frit
H	semipermeable membrane	ion exchange membrane

In some textbooks (e.g., Atkins), it is stated that the cell diagram is written such that the anode is on the left side and the cathode on the right side. So far, this has also been the convention used here, but obviously, if we do not know *a priori* which half-cell reaction is which, this rule cannot be followed strictly.

2 Half-Cell Reactions

A redox couple establishing a half-cell reaction equilibrium at an electrode leads to the formation of a defined potential of that electrode. We can describe the electron energy in the electrode in the hydraulic analogy as 'electron pressure' (cf. detailed elaboration in Chapter III). The potential of an electrode characterizes the tendency for an oxidation or reduction reaction to proceed on it. However, the potential of a single electrode cannot be measured ('you cannot clap with one hand'), because in practice we need a second electrode against which we can measure the potential of the electrode in question as a potential difference¹. The study of the reaction at a single electrode is therefore performed by measuring its potential against a *reference electrode*, which is designed to have a defined and stable potential.

2.1 The hydrogen electrode

In electrochemistry, the hydrogen electrode has been selected as a universal reference. The half-cell reaction that defines the equilibrium is:

$$2 H^{+}(aq) + 2 e^{-} \leftrightarrows H_{2}(g)$$
 (2-13)

The choice of the hydrogen electrode appears somewhat arbitrary. In fact, the use of a hydrogen reference electrode in experiments is somewhat impractical, and normally more 'user-friendly' reference electrode types are used, such as the calomel electrode (cf. Chapter III). The hydrogen electrode is a preferred reference, though, because the equilibrium of Eq. 2-13 is easily established using a platinum electrode. Hence, its potential is very stable when in contact with H₂, which is bubbled over the electrode. The standard electrode potential $E_{\rm H}^{\circ}$ of the hydrogen electrode, or, to be more precise, the standard half-cell potential of the H⁺/H₂ redox couple, is set by definition as 0 V at all temperatures (not only at 25°C !):

$$E_{\rm H}^{\circ} \equiv E^{\circ}({\rm H}^+/{\rm H}_2) \equiv 0 {\rm V}$$
 (2-14)

The symbol '*E*' stands for electrode potential here. Being a standard potential, Eq. 2-14 requires H_2 and H^+ to be at their standard state to yield unit activity. For H_2 , this corresponds to a partial pressure

¹ With considerable effort and dedicated surface scientific experiments, the absolute potential of an electrode can be defined in a suitable reference framework and experimentally determined (cf. Chapter III), but the approach is far from being practical.

of 1 bar.¹ At this pressure, non-ideality of hydrogen gas can be neglected. A proton activity of 1 corresponds to a pH of 0 according to the definition $pH = -log(a(H^+))$. A corollary of the definition of $E_{\rm H}^{\circ} \equiv 0$ is $\Delta_{\rm f}G^{\circ}({\rm H}^+) \equiv 0,^2$ since we also have $\Delta_{\rm f}G^{\circ}({\rm H}_2) \equiv 0$. This electrode is called the *standard hydrogen electrode* (SHE). It defines the origin of the electrochemical potential scale, and the half-cell potential of other reactions is often quoted 'versus SHE', even when in practice the measurement was done against another reference electrode, which has a defined offset from the SHE.

It is important to realize that the SHE is a theoretical, ideal electrode that, although well-defined, cannot be created through any possible experiment, because the protons are supposed to have no interaction with other ions, a condition that is not physically attainable at a finite acid concentration (cf. Discussion on chemical potential in the Introduction, and Debye-Hückel theory in Chapter IV). In the concentration range of 1 M, acid solutions show far from ideal behavior. Moreover, different acids show different extents of non-ideality.³

Before the SHE was introduced as a standard the *normal hydrogen electrode* (NHE) was used as an empirical hydrogen reference electrode, where an acid with concentration of 1 M of H⁺ is used and H₂ at a pressure of 1 atm. The difference to the SHE is ~6 mV at 25°C if HCl(aq) is used as acid. Other hydrogen reference electrode types are in use today. The *reversible hydrogen electrode* (RHE) is a practical hydrogen reference electrode immersed in the electrolyte solution actually used in an experiment, for example a solution with a certain pH. The benefit is that no salt bridge is needed between the reference electrode compartment and the working electrode compartment. In the *dynamic hydrogen electrode* (DHE) no hydrogen gas needs to be supplied to the electrode, as it produces its own 'cushion' of H₂ by passing a small cathodic current through the electrode, which leads to hydrogen being evolved. Therefore, the potential of the DHE is about 5 to 20 mV below that of an RHE in the same electrolyte.

¹ Note that prior to 1982, the standard pressure was 1 atm = 1.01325 bar. Therefore, in many tables and reference documents, one can still find values of thermodynamic quantities given at 1 atm instead of 1 bar.

² Free energies of formation of single ions cannot be determined experimentally, because there are always at least two types of ion present in a solution. The definition of $\Delta_{\rm f} G^{\circ}({\rm H}^+) \equiv 0$ is therefore equally arbitrary as $E_{\rm H}^{\circ} \equiv 0$.

³ As an illustration of the problem, consider the different mean activity coefficient for binary acids at a concentration of 1 M: for HCl(aq) $\gamma_{\pm} = 0.830$, for HNO₃(aq) $\gamma_{\pm} = 0.766$.

2.2 Half-cell potentials

Having defined the hydrogen electrode as reference, we can now measure or theoretically calculate the potential of any arbitrary half-cell reaction against it. For our example of the Daniell element (Zn-Cu cell), say we wish to determine the standard half-cell potential of the copper electrode. Conceptually, we replace the zinc electrode by a hydrogen electrode and obtain the cell Pt | H₂ | H⁺(aq) || Cu²⁺(aq) | Cu (**Figure 2-4a**), assuming an ideal salt bridge (cf. Chapter IV). Having in mind the rule from Section 1.5 we take the left side to be the anode and the right side the cathode, which gives us the following reaction: H₂ + Cu²⁺ \leftrightarrows 2 H⁺ + Cu.¹ For the calculation of the standard free energy of this reaction at 25°C, only the free energy of formation of Cu²⁺ is non-zero, thus we have $\Delta_r G^\circ = -\Delta_f G^\circ(Cu^{2+}) = -65.5$ kJ/mol, with which, using Eq. 2-5 and z = 2, we obtain $U_{rev}^\circ = 0.34$ V. This is the reversible voltage of the H₂-Cu cell, given by the potential difference between the Cu²⁺/Cu electrode at standard conditions and the SHE.



Figure 2-4. (a) Schematic representation of a H₂-Cu cell for the derivation of the definition of the electrode potential of the Cu^{2+}/Cu redox couple, using a hydrogen reference electrode. (b) Generic representation of the cell configuration to express the electrode potential of the redox couple Ox/Red.

For the general description of a half-cell potential, the copper half-cell is replaced by an arbitrary half-cell reaction $Ox + z \cdot e^- \leftrightarrows Red$ (Figure 2-4b), for which we can write the schematic

Pt
$$| H_2 | H^+(aq) || Ox, Red | (M)$$
 (2-15)

where (M) is a suitable electrode material that easily allows the Ox/Red half-cell reaction to establish equilibrium. Based on this configuration, the *electrode potential* or *half-cell potential* E(Ox/Red) of the Ox/Red redox couple vs SHE is defined as:

¹ We take the reaction to be at equilibrium, indicated by the symbol ' \Rightarrow ', but for the calculation of the free energy of reaction we consider the reaction to proceed (infinitely slowly) in forward ' \rightarrow ' direction.

$$U_{\rm rev} = E_{\rm cell} = E(\rm Ox/Red) - E_{\rm SHE}$$
(2-16)

The determined standard reversible voltage of the H₂-Cu cell of 0.34 V therefore corresponds to the standard electrode or half-cell potential $E^{\circ}(Cu^{2+}/Cu)$ of the Cu²⁺/Cu redox couple at $a(Cu^{2+}) = 1$ and 25°C¹.

2.3 The electrochemical series

The equilibrium electrode potential for any given half-cell reaction can be determined either by experiment or through calculation via $\Delta_r G$. In this way, we can rank the oxidative / reductive strength of redox couples according to their half-cell potential. This leads to the *electrochemical potential series*, a list that contains the standard electrode potentials of half-cell reactions in ascending or descending order. Selected values can be found in **Table 2-3**, a more comprehensive list is available at https://ecl-lecture.web.psi.ch/public/elc_std-potentials.pdf.

Table 2-3. Selected half-cell reactions of the electrochemical series, written as reduction reactions, and corresponding standard reduction potentials E° vs. SHE at 25°C.

Half-cell reaction	l	E°
		(V)
$F_2 + 2 e^-$	→ 2 F ⁻	+2.87
$Cl_2 + 2e^-$	→ 2 Cl ⁻	+1.36
$O_2 + 4 H^+ + 4 e^-$	\rightarrow 2 H ₂ O	+1.23
$Fe^{3+} + e^{-}$	\rightarrow Fe ²⁺	+0.77
$Cu^{2+} + 2 e^{-}$	→ Cu	+0.34
$2 H^+ + 2 e^-$	\rightarrow H ₂	0.00
$Fe^{2+} + 2 e^{-}$	→ Fe	-0.44
$Zn^{2+} + 2 e^{-}$	→ Zn	-0.76
$Li^{+} + e^{-}$	→ Li	-3.05

The listed values are *reduction potentials*. This means that we 'build' a conceptual cell with the half-cell reaction in question written as a reduction reaction, for example $Ox + z e^- \rightarrow Red$, and the reaction of the SHE as a correspondingly balanced oxidation reaction, i.e. $z \cdot \frac{1}{2} H_2 \rightarrow z H^+ + z e^-$, leading to the overall reaction $Ox + z \cdot \frac{1}{2} H_2 \rightarrow Red + z H^+$. If the resulting reversible cell voltage U_{rev} calculated via Eq. 2-16 is positive, it means that, according to Figure 2-1, the reaction is spontaneous. It is a convention to use reduction potentials, in theory one could also use oxidation potentials (see Appendix D for an elaboration). Consequently, all the half-cell reactions in Table 2-3 with a potential >0 V undergo a spontaneous reaction in the indicated cathodic direction when combined with the hydrogen half-cell reaction in anodic direction, i.e. when H₂ is oxidized to H⁺. Take for example the O₂ reduction reaction to water with $E^o(O_2/H_2O) = +1.23$ V. The combination

¹ Although the potential of the SHE is defined as zero for all temperatures, the standard potential of any half-cell reaction is temperature dependent, because its free energy of reaction is a function of temperature.

with the hydrogen reaction yields the well-known fuel cell reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ with $U_{rev}^{\circ} = 1.23$ V. On the other hand, half-cell reactions with E < 0 V yield $U_{rev} < 0$ when combined as cathodic half-cell reaction with the hydrogen reaction in anodic direction, thus the reaction is non-spontaneous in this direction. If the reaction direction is reversed, the reaction becomes spontaneous and $U_{rev} > 0$. For example, if we expose metallic zinc to acid, it is oxidized to Zn^{2+} and protons are reduced to H_2 . Therefore, from a thermodynamic point of view, all metals with E < 0 theoretically evolve hydrogen in acid.

The electrochemical potential series allows us to assess whether the combination of two half-cell reactions yields a spontaneous process or not, and calculate the reaction's standard reversible cell voltage. We choose one half-cell reaction as a cathodic reaction with reduction potential E_{ca} and another half-cell reaction as an anodic reaction with reduction potential E_{an} and calculate the reversible cell voltage as follows:

$$U_{\rm rev} = E_{\rm ca} - E_{\rm an} \, (+E_{\rm LL}) \tag{2-17}$$

It may be that there is a liquid junction in the cell between electrolyte compartments, which will lead to the formation of a liquid junction potential E_{LJ} (cf. Chapter IV for a detailed treatment of the topic). In general, this will affect the theoretical cell voltage. With a salt bridge, liquid junctions can be minimized (but not completely avoided). For both half-cell reactions we choose the reduction potential listed in **Table 2-3** or take the value from another, more comprehensive resource. In the electrochemical series, the half-cell reactions with high E° have strong oxidizing agents (and poor reducing agents), and the ones with low negative E° have strong reducing agents (and poor oxidizing agents). For example, elemental fluorine, F_2 , is one of the strongest oxidizing agents known, because $E^{\circ}(F_2/F^-) = +2.87$ V, and metallic lithium, Li, is one of strongest reducing agents, because $E^{\circ}(Li^+/Li) = -3.05$ V. The electrochemical series, therefore, provides a kind of 'pecking order' of oxidative or reductive strength of redox couples.

Some compounds undergo a number of different electrochemical reactions. For instance, we see in **Table 2-3** two reactions listed involving iron: (1) $Fe^{2+} + 2e^- \rightarrow Fe(s)$ with $E^{\circ}(Fe^{2+}/Fe) = -0.44$ V, and (2) $Fe^{3+} + e^- \rightarrow Fe^{2+}$ with $E^{\circ}(Fe^{3+}/Fe^{2+}) = +0.77$ V. This triggers the question what the standard half-cell potential $E^{\circ}(Fe^{3+}/Fe)$ of the reaction (3) $Fe^{3+} + 3e^- \rightarrow Fe(s)$ is. Reaction (3) is obtained by adding reactions (1) and (2). Therefore $\Delta_r G_3 = \Delta_r G_1 + \Delta_r G_2$. With $\Delta_r G = -zFE$ (this relationship also works for half-cell potentials) we obtain $z_3FE_3 = z_1FE_1 + z_2FE_2$ and thus $E_3^{\circ} = -0.037$ V. In general, we have to keep in mind that for a combination of reactions, we have to sum the free energies of reaction, taking into consideration the factors a_k for the linear combination of reactions 1 to n:

$$\Delta_{\mathbf{r}}G = a_1 \Delta_{\mathbf{r}}G_1 + a_2 \Delta_{\mathbf{r}}G_2 + \dots + a_n \Delta_{\mathbf{r}}G_n = \sum_{k=1}^n a_k \Delta_{\mathbf{r}}G_k$$
(2-18)

This translates into the following expression for the half-cell potentials:

$$-(a_1z_1 + a_2z_2 + \dots)FE = -a_1z_1FE_1 - a_2z_2FE_2 - \dots = -F\sum_{k=1}^n a_kz_kE_k$$
(2-19)

Rearrangement yields the following relationship:

$$E = \frac{\sum a_k z_k E_k}{\sum a_k z_k}$$
(2-20)

The table of electrochemical potentials lists the values at standard condition, yet we often want to know the value of the potential at another activity or concentration of the reactants and/or products. To develop the corresponding relationship and expression, we go back to the example of the arbitrary electrode reaction $Ox + z e^- \rightarrow Red$, written as reduction, paired with the hydrogen reaction, balanced for *z*, written as oxidation, $z \cdot \frac{1}{2} H_2 \rightarrow z H^+ + z e^-$, to yield the overall reaction $Ox + z \cdot \frac{1}{2} H_2 \rightarrow Red + z H^+$. The Nernst equation gives the following reversible cell voltage (remember, activities of products are in the numerator, those of reactants in the denominator):

$$U_{\text{rev}} = U_{\text{rev}}^{\circ} - \frac{RT}{zF} \ln(\frac{a(\text{Red}) \cdot a(\text{H}^{+})^{z}}{a(\text{Ox}) \cdot a(\text{H}_{2})^{z/2}})$$
(2-21)

We can now replace U_{rev}° by $E^{\circ}(Ox/Red) - E_{H}^{\circ}$ (Eq. 2-16) and 'distribute' the terms in the logarithm to the respective half-cell reaction:

$$U_{\rm rev} = \left(E^{\circ}(\text{Ox/Red}) + \frac{RT}{zF}\ln(\frac{a(\text{Ox})}{a(\text{Red})})\right) - \left(E^{\circ}_{\rm H} + \frac{RT}{F}\ln(\frac{a(\text{H}^+)}{\sqrt{a(\text{H}_2)}})\right)$$
(2-22)
$$\underline{E(\text{Ox/Red})} = \underline{E_{\rm H}}$$

With this, we have derived the concentration dependence of the half-cell potential E:

$$E = E^{\circ} + \frac{RT}{zF} \ln(\frac{\{a(\mathrm{Ox})\}}{\{a(\mathrm{Red})\}}) = E^{\circ} + \ln(10)\frac{RT}{zF}\log(\frac{\{a(\mathrm{Ox})\}}{\{a(\mathrm{Red})\}})$$
(2-23)

This is the *Nernst equation* for a half-cell reaction. Here, the curly brackets indicate activities of compounds on the oxidized and reduced side of the half-cell reaction, respectively. Remember that activities need to be raised to the power of the stoichiometric coefficient v in a general expression: a^{v} (cf. Eq. 2-2).

Example:

We calculate the electrode potential for the Cl₂/Cl⁻ redox couple, corresponding to the half-cell reaction 2 Cl⁻ \rightarrow Cl₂ + 2 e⁻, at a Cl₂ pressure of 1 bar and a chloride concentration of 0.01 M (we assume an ideal solution) at a temperature of 25°C. The Nernst equation is:

$$E(Cl_2/Cl^-) = E^{\circ}(Cl_2/Cl^-) + \frac{RT}{2F}\ln(\frac{a(Ox)}{(a(Red))^2}) = +1.36 \text{ V} + \frac{59.2 \text{ mV}}{2}\log(\frac{p(Cl_2)/p_0}{(c(Cl^-)/c_0)^2})$$

We obtain $p(\text{Cl}_2) / p_0 = 1$, because 1 bar is the standard pressure, and with the standard concentration $c_0 = 1$ M we obtain $c(\text{Cl}^-) / c_0 = 0.01$. The value of z = 2 and the stoichiometric factor of Cl⁻ of 2 in the log() expression cancel, and we obtain for the potential $E(\text{Cl}_2/\text{Cl}^-) = +1.36 \text{ V} + 59.2 \text{ mV} \cdot \log(1/0.01) = +1.36 \text{ V} + 59.2 \text{ mV} \cdot 2 = +1.42 \text{ V}$. The activity of the reduced species, Cl⁻, is below 1, whereas the activity of the oxidized species, Cl₂, is equal to 1, therefore in this example the potential is shifted to more oxidizing, that is, more positive values.



Figure 2-5. Representation of the Nernst factor for a model reaction $Ox + z e^- \rightarrow Red$ at 25°C. (a) Plot as a function of the molar fraction of Ox. (b) Plot as a function of the concentration ratio of Ox and Red. Ideal conditions are assumed, such that activities can be replaced by concentrations.

Note the plus sign in Eq. 2-23 for the term +RT/zF..., whereas in the Nernst equation of the overall cell reaction, Eq. 2-10, there is a minus sign: -RT/zF... Values of the Nernst term are given in **Figure 2-5** at 25°C for *z* equal to 1 and 2. The logarithmic representation shows that the potential of the electrode changes with the now well-known value of 59.2 mV per decade of the concentration (activity) ratio of the oxidized and the reduced species for z = 1, and by half of that for z = 2. Theoretically, the potential diverges for $c(Ox) \rightarrow 0$ and $c(Red) \rightarrow 0$. In reality, the 'next best' available reaction in the system would become potential determining. Take, for example, the

reaction $Fe^{3+} + e^{-} \leftrightarrows Fe^{2+}$ in aqueous solution with $E^{\circ} = +0.77$ V. If we were to drive the reaction to the left, i.e. towards Fe^{3+} , the electrode potential would increase and at some point it would reach the potential for water decomposition and oxygen evolution to set in, $E^{\circ} = +1.23$ V at pH 0 (**Table 2-3**).

In some scientific domains the use of *formal potential* $E^{\circ'}$ is common (pronounced 'ee-noughtprime' or 'ee-zero-prime'). The formal potential is the reduction potential that applies to a half-cell reaction under a specified set of conditions, such as pH, ionic strength, concentration of complexing agents, etc. One example is the use of formal potentials for biological electrochemical reactions at pH 7, which is much closer to the physiological pH than the standard state of pH 0. The formal potential of a half-cell reaction in a given experimental environment is defined as the potential when the concentration ratio of Ox and Red equals 1, i.e. when the ln(...) term in the Nernst equation using concentrations vanishes. For an illustration we again look at the Fe³⁺/Fe²⁺ redox couple. The Nernst equation is

$$E(Fe^{3+}/Fe^{2+}) = E^{\circ}(Fe^{3+}/Fe^{2+}) + \frac{RT}{F}\ln(\frac{a(Fe^{3+})}{a(Fe^{2+})})$$
(2-24)

As the activity is given by $a = \gamma c$ the activity coefficient γ for Fe³⁺ and Fe²⁺ can be clustered with the standard half-cell potential E° , yielding the formal potential $E^{\circ'}$:

$$E(Fe^{3+}/Fe^{2+}) = E^{\circ}(Fe^{3+}/Fe^{2+}) + \frac{RT}{F}\ln(\frac{\gamma(Fe^{3+})}{\gamma(Fe^{2+})}) + \frac{RT}{F}\ln(\frac{c(Fe^{3+})}{c(Fe^{2+})})$$
(2-25)

Formal potentials are often used when electrochemical reactions are studied in a supporting electrolyte of relatively high concentration in the mol/L range. Actually, this is a quite common setting for electrochemical experiments (cf. Chapters V and VIII). In this case, the activity coefficients of Fe³⁺ and Fe²⁺ are approximately constant, given by the ionic strength of the supporting electrolyte, and the concentration of the iron-ions can be conveniently used instead of activities. The standard half-cell potential E° of Fe³⁺/Fe²⁺ is +0.77 V (cf. **Table 2-3**), yet the formal potential $E^{\circ'}$ of the couple is +0.73 V in 0.1 M HClO₄ and +0.70 V in 1 M HCl. In the latter case, there is also chloro-complex formation, which further affects the value of $E^{\circ'}$. Formal potentials are therefore useful empirical quantities in practical electrochemistry.

3 Thermodynamic Stability Diagrams

Half-cell reactions and their corresponding equilibrium potentials define stability regions of the involved species. For example, for the reaction $Fe^{2+} + 2 e^{-} \Rightarrow Fe$ the potential $E^{\circ}(Fe^{2+}/Fe) = -0.44 \text{ V}$ defines the stability region for Fe at $\leq -0.44 \text{ V}$ and for $Fe^{2+}(aq)$ at $\geq -0.44 \text{ V}$ (for the idealized case of $a(Fe^{2+}) = 1$, remember: a(Fe(s)) = 1). At -0.44 V the two species coexist, hence the equilibrium potential can be regarded as a 'phase boundary'. Its value / position changes with the concentration (activity) of Fe^{2+} . Another 'boundary' is at $E^{\circ}(Fe^{3+}/Fe^{2+}) = +0.77 \text{ V}$ for the reaction $Fe^{3+} + e^{-} \Rightarrow Fe^{2+}$, which marks the border between the stability regions of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$. Therefore, the representation $Fe / -0.44 \text{ V} / Fe^{2+} / +0.77 \text{ V} / Fe^{3+}$ can be regarded as a 1D stability diagram, much like a phase diagram (**Figure 2-6a**). There are different ways to represent thermodynamic stability data of elements and compounds involving the electrode potential, detailed in the following.

3.1 Pourbaix diagram

Half-cell reactions often involve species other than the main element or compound of the reaction. Of particular importance are the reactions of H₂ ($E^{\circ} = 0$ V) and O₂ ($E^{\circ} = +1.23$ V) where protons appear in the half-cell reactions equation (**Table 2-3**). This means that the equilibrium potential changes with the activity protons, i.e. the pH. The Nernst equations for the H₂ and O₂ reactions are as follows:

$$E_{\rm H} = E_{\rm H}^{\circ} + \frac{RT}{2F} \ln(\frac{a({\rm H}^+)^2}{a({\rm H}_2)}) = E_{\rm H}^{\circ} - \frac{RT}{2F} \ln(\frac{p({\rm H}_2)}{p_0}) - \ln(10)\frac{RT}{F} \rm{pH}$$
(2-26)

$$E_{\rm o} = E_{\rm o}^{\circ} + \frac{RT}{4F} \ln(\frac{a({\rm O}_2) \cdot a({\rm H}^+)^4}{a({\rm H}_2{\rm O})^2}) = E_{\rm o}^{\circ} + \frac{RT}{4F} \ln(\frac{p({\rm O}_2)}{p_0}) - \ln(10)\frac{RT}{F} \rm{pH}$$
(2-27)

We can see that in addition to the influence of the partial pressure of the gases, the potential of the two reactions depends on the pH, with the same dependence for both reactions. Effectively, the potential drops by the factor $\ln(10) \cdot RT/F$ (59.2 mV at 25°C) for every pH unit increase. We can therefore draw a stability diagram defined by these reactions with the potential on the vertical axis and the pH on the horizontal axis (**Figure 2-6b**). This potential-pH plot is called a *predominance area diagram* or *Pourbaix diagram*, after its inventor. In general, a Pourbaix diagram depicts the possible thermodynamically stable phases of an aqueous electrochemical system. It is important to remember that it does not provide any information on the kinetics of the described conversion reactions. **Figure 2-6b** shows the stability regions of water, hydrogen and oxygen, which is an important aspect, for example, in corrosion. With the pH dependence, the potential of the hydrogen

(Eq. 2-26) and oxygen reaction (Eq. 2-27) decreases from 0.00 V and +1.23 V at pH 0 to -0.83 V and +0.40 V at pH 14 for $E_{\rm H}$ and $E_{\rm O}$, respectively, at pH 14, 25°C and gas pressures of 1 bar. At pH 14, the reactions have to be rewritten with OH⁻ as balancing ion, 2 H₂O + 2 e⁻ \Rightarrow H₂ + 2 OH⁻ for the hydrogen reaction, and O₂ + 2 H₂O + 4 e⁻ \Rightarrow 4 OH⁻ for the oxygen reaction (cf. also Chapter I). We furthermore see that the reversible cell voltage of the overall reaction H₂ + $\frac{1}{2}$ O₂ \Rightarrow H₂O is constant at 1.23 V (at 25°C and gas pressures of 1 bar), because the protons or hydroxide ions cancel when forming the overall reaction from the half-cell reactions. Pourbaix diagrams are widely used to depict stability regions of metals in order to understand their tendency to corrode or develop passivating layers (cf. Chapter IX). For example, although aluminium is thermodynamically unstable in the presence of oxygen (as mentioned above), it develops a stable oxide layer at intermediate pH, which minimizes corrosion of the underlying metal.



Figure 2-6. (a) 1D stability diagram of iron at 25° C (actually, the situation pertains to low pH values, because iron forms hydroxides and oxides at intermediate and high pH values). (b) Potential-pH (Pourbaix) stability diagram of water at 25° C and gas pressures of 1 bar. The lines are described by Eqs. 2-26 and 2-27.

3.2 Latimer diagram

Many elements form compounds where the element has 3 or more different oxidation states. We encountered iron and oxygen already. Other examples are nitrogen, chlorine, and, of course, most transition metals. The electrochemical reactions between the different compounds an element forms can be represented in a table of reduction potentials, but in more comprehensive manner in a so-called *Latimer diagram*, which presents the compounds on a horizontal line with arrows in between characterizing electrochemical reactions with the corresponding (standard) reduction potential (even though the arrow might indicate an oxidation reaction). Examples for iron and oxygen are shown in **Figure 2-7**. Not only reactions between neighboring compounds are shown, but also those further apart. We remind ourselves that the half-cell potentials are not simply additive in sequential processes, but should be calculated based on the free energy values (Eqs. 2-18 to 2-20). Note that the Latimer diagram of oxygen indicates that oxygen reduction can go via a 2 electron step to

hydrogen peroxide and then, via another 2 electron step, to water, or directly via a 4 electron step from oxygen to water. This is important in the context of the cathodic reaction in fuel cells, which will be discussed in Chapter VII. Note furthermore that H_2O_2 does not appear in the Pourbaix diagram of water (**Figure 2-6b**), because, as we will see in the next section, it is thermodynamically not very stable and tends to disproportionate to oxygen and water.



Figure 2-7. Latimer diagrams of (a) iron with dissolved species Fe^{2+} and Fe^{3+} in water, and (b) oxygen. The indicated potentials are E° values (standard conditions) at 25°C.

3.3 Frost diagram

A similar representation, consisting of free energy vs. oxidation state, contains all the information of a Latimer diagram, but in a form which provides additional qualitative information. In such a plot, called *Frost diagram*, the value of $N \cdot E^{\circ}$, a measure for the free energy relative to that of the element (oxidation state zero), is plotted as a function of oxidation number *N*. The quantity $N \cdot E^{\circ}$ is proportional to the free energy of a compound $\Delta_r G^{\circ}$ in oxidation state *N* relative to its elemental form.

The procedure to draw a Frost diagram is as follows, using the reactions of iron as an example (Figure 2-8):

- 1. Place the element, here Fe(0), with N = 0 at the origin, the value of $N \cdot E^{\circ}$ is therefore also zero.
- 2. Choose the compound with the nearest oxidation number, here Fe²⁺ with N = 2, and plot N on the horizontal axis and the value N·E° on the vertical axis. Here, E° is the reduction potential for the reaction between the compound in question and the element. For our example: Fe²⁺ + 2 e⁻ ≒ Fe with E°(Fe²⁺/Fe) = -0.44 V. The value of N·E° is therefore -0.88 V.

For the next steps, we have two options:

3a. For the compound with the next higher (or lower) oxidation number, here Fe^{3+} with N = 3, use the formalism explained in (2): take the reaction that converts the element to the compound with the oxidation number in question and calculate $N \cdot E^{\circ}$, here $Fe^{3+} + 3e^{-} \Rightarrow Fe$

with $E^{\circ}(\text{Fe}^{3+}/\text{Fe}) = -0.037 \text{ V}$, hence $N \cdot E^{\circ} = -0.11 \text{ V}$. Again, plot the point at N (x-axis) and $N \cdot E^{\circ}$ (y-axis).

3b. Alternatively, one can use the reaction between the compound and the one next to it, take the corresponding E° value and calculate $\Delta N \cdot E^{\circ}$, where ΔN is the difference in oxidation state of the involved compounds. Then add this value to the previous one to obtain the yaxis value of that point. In our example, to determine the point pertaining to Fe³⁺, we take the reaction between Fe³⁺ and Fe²⁺, Fe³⁺ + e⁻ \leftrightarrows Fe²⁺, with $E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}$. With $\Delta N = 3 - 2 = 1$, we add the value of 0.77 V to the value for N = 2, -0.88 V, and obtain -0.11 V for N = 3.

The formalism also works for compounds with negative oxidation numbers, for example oxygen. The reader may easily verify that the values given in the Latimer diagram of oxygen (**Figure 2-7b**) translate to the Frost diagram of oxygen shown in **Figure 2-8b**.



Figure 2-8. Frost diagram of (a) iron and (b) oxygen, obtained from their respective Latimer diagrams (Figure 2-7).

Frost diagrams are useful to characterize reactions between compounds and their respective stability in qualitative terms. We can interpret the features of a Frost diagram as follows:

- Strong oxidizing agents are at the top right, i.e., Fe³⁺ and O₂.
- The lower the value *N*·*E*°, the lower the free energy of that compound, i.e., the higher its thermodynamic stability. For iron and oxygen the most stable compound is Fe²⁺(aq) and water, respectively.
- The slope of the tie line connecting two points corresponds to E° of that redox couple, e.g. $E^{\circ}(Fe^{2+}/Fe) = -0.44 \text{ V}$ and $E^{\circ}(Fe^{3+}/Fe^{2+}) = +0.77 \text{ V}$.
- The slope indicates the sign of E° , see previous bullet point.
- A convex point indicates the tendency of that species to undergo disproportionation (e.g. H₂O₂)

The last point is an important one. For illustration, we compare Fe^{2+} and H_2O_2 regarding their tendency towards disproportionation. The disproportionation reaction of Fe^{2+} is: $3 Fe^{2+} \leftrightarrows Fe + 2 Fe^{3+}$. This chemical reaction can be obtained from the half-cell reactions (1) $Fe^{2+} + 2 e^- \rightarrow Fe(s)$ and (2) $Fe^{3+} + e^- \rightarrow Fe^{2+}$ through the linear combination (2) $- 2 \cdot (1)$. The free reaction energy is therefore $\Delta_r G^\circ = \Delta_r G_2^\circ - 2 \cdot \Delta_r G_1^\circ = -z_2 F E_2^\circ + 2 \cdot z_1 F E_1^\circ = 233$ kJ/mol at 25°C. For the chemical equilibrium we recall Eq. 2-3, $\Delta_r G^\circ = -RT \ln(K)$, and obtain $K = 1.18 \cdot 10^{-41}$. We therefore see that the equilibrium is strongly on the Fe^{2+} side, meaning that it has a very, very low tendency to disproportionate. This is in agreement with the notion that, being the lowest point in the Frost diagram, it has a very high thermodynamic stability. Conversely, if Fe and Fe^{3+} coexist, they have a very strong tendency to comproportionate to Fe^{2+} . This will be important in the context of corrosion (cf. Chapter IX).

In analogous manner, we can calculate the tendency of hydrogen peroxide to disproportionate according to $H_2O_2 \leftrightarrows H_2O + \frac{1}{2}O_2$. We obtain the reaction free energy from the combination of half-cell reactions and half-cell potentials given in the Latimer diagram of oxygen (**Figure 2-7b**) as $\Delta_r G^\circ = -106$ kJ/mol. This shows that the reaction is spontaneous and $K = 3.81 \cdot 10^{18}$. The equilibrium is on the far right, which indicates that H_2O_2 has a strong tendency to disproportionate to O_2 and H_2O . Note that we are talking about thermodynamic stability here. We can buy, say, a 3% solution of hydrogen peroxide in water, which can be kept in the lab for a long time. The disproportionation of H_2O_2 is kinetically limited and needs an activation energy, yet if a catalyst (such as MnO₂) is added to the solution (which effectively lowers the activation energy), it will readily decompose.

Appendix A: Equilibrium of a Chemical Reaction

Consider a chemical reaction proceeding from reactants to products. The free energy of the reaction mixture G (unit: J) thereby changes from the value of the reactants G_r to the value of the products G_p . Let the extent of the reaction be characterized by the variable ξ (unit: mol), hence $G = G(\xi)$, where ξ runs from 0 (only reactants) to ξ_{max} (only products).¹ $G(\xi)$ does not change linearly from G_r to G_p but follows the behavior indicated in **Figure 2-A1** because of the mixing entropy term.



Figure 2-A1. Gibbs free energy of a reaction system as a function of the extent of reaction ξ . The value changes from the free energy of the reactants G_r to the free energy of the products G_p , going through a minimum at $\xi = \xi_{eq}$. The free energy of reaction $\Delta_r G$ is the slope of the curve, hence $\Delta_r G = 0$ at the equilibrium.

The equilibrium of the chemical reaction is found at the minimum of $G(\xi)$ where the extent of reaction is ξ_{eq} . For $\xi \neq \xi_{eq}$ the reaction tends towards decreasing G. The reaction Gibbs energy $\Delta_r G$ (unit: J/mol) characterizes the driving force towards the equilibrium and is defined as the slope of $G(\xi)$:

$$\Delta_{\rm r}G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} \tag{2-A1}$$

The symbol ' Δ_r ' can be understood as an operator $\partial/\partial \xi$. As we can see from **Figure 2-A1**, for $\xi < \xi_{eq}$ the reaction is driven in forward direction, and for $\xi > \xi_{eq}$ in backward direction. The slope of $G(\xi)$ is zero at the equilibrium, which yields the following important expression characterizing a chemical reaction at equilibrium:

$$\Delta_{\rm r}G = 0 \tag{2-A2}$$

¹ Example: for the ammonia synthesis reaction N₂ + 3 H₂ \rightarrow 2 NH₃, $\xi_{max} = 1$ mol corresponds to the reaction of one formula unit, i.e. consumption of 1 mol N₂ and 3 mol H₂, and production of 2 mol NH₃.

Appendix B: Theoretical Electrical Work

[from: P.H. Rieger, Electrochemistry, 2nd edition, Springer, 1994, p5]

The First Law of thermodynamics states that the change in the internal energy of a system ΔU equals the heat absorbed by the system Q plus the work done on the system W:

$$\Delta U = Q + W \tag{2-B2}$$

In elementary textbooks on the subject, for a reversible process at constant pressure and temperature usually only mechanical work is considered, to be precise: expansion work $dW = -p \cdot dV$. Here we also include the electrical work W_e :

$$W = -p \cdot \Delta V + W_{\rm e} \tag{2-B2}$$

Since for a reversible process at constant temperature $Q = T \cdot \Delta S$, we obtain

$$\Delta U = T \cdot \Delta S - p \cdot \Delta V + W_{\rm e} \tag{2-B3}$$

As the enthalpy change ΔH at constant pressure is

$$\Delta H = \Delta U + p \cdot \Delta V \tag{2-B4}$$

and at constant temperature the Gibbs free energy change ΔG is

$$\Delta G = \Delta H - T \cdot \Delta S \tag{2-B5}$$

we combine Eqs. 2-B3 to 2-B5 to obtain:

$$\Delta G = W_{\rm e} \tag{2-B6}$$

Hence, the electrical work associated with an electrochemical reaction under reversible conditions is given by the free energy of the reaction.

Appendix C: Temperature Dependence of Thermodynamic Functions

In many cases, one is interested in the temperature dependence of the Gibbs energy of reaction $\Delta_r G$ and the reversible cell voltage U_{cell} , which are connected according to $\Delta_r G = -z \cdot F \cdot U_{cell}$ (Eq. 2-5). We have seen that $\Delta_r G$ describes the spontaneity of a reaction, which is determined by the reaction enthalpy $\Delta_r H$ and reaction entropy $\Delta_r S$ via $\Delta_r G = \Delta_r H - T \cdot \Delta_r S$ (Eq. 2-7). This equation then describes the main temperature dependence of $\Delta_r G$. Based on thermodynamic tables, which typically list the formation enthalpy and entropy of compounds in their standard state at 25°C, we can calculate the standard reaction enthalpy $\Delta_r H^\circ$ and the standard reaction entropy $\Delta_r S^\circ$ at 25°C. Assuming those values to be independent of temperature in first approximation, we can then estimate $\Delta_r G^\circ$ according to Eq. 2-7. As an example, we take the reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O(g)$, for which we wish to determine $\Delta_r G^\circ$ and U_{rev}° at a temperature of 1'000°C. From **Table 2-1**, we get $\Delta_r H^\circ = -241.8$ kJ/mol and $\Delta_r S^\circ = -44.5$ J/(mol·K). Inserting T = 1'273 K into Eq. 2-7 yields $\Delta_r G^\circ(1'273 \text{ K}) = -228.5$ kJ/mol, and with Eq. 2-5 we get $U_{rev}^\circ(1'273 \text{ K}) = 0.960$ V.

However, both $\Delta_r H$ and $\Delta_r S$ are actually functions of temperature. In the following, we will review the definition of these thermodynamic functions and elaborate the description of their temperature dependence. This will allow us to calculate their values and, consequently, that of the Gibbs free energy $\Delta_r G$ and the reversible cell voltage U_{rev} at any given temperature with higher accuracy.

Enthalpy

The enthalpy measures the total energy content of a system and is defined as

$$H = U + pV \tag{2-C1}$$

It describes the energy to create the system (U) from its building blocks and 'make room for it' (*pV*). U is the *internal energy*, which is the sum of the kinetic and potential energies of the particles that form the system. For example, a highly energetic bond will release energy when broken. The term *pV* describes the volumetric work associated with expansion, for example during an explosion. For chemical reactions, the reaction enthalpy $\Delta_r H$ is obtained from the formation enthalpies $\Delta_f H$ according to $\Delta_r H = \sum_k (\nu_k \cdot \Delta_f H_k)$ (Eq. 2-8), where ν_k is the stoichiometric factor of compound *k*.

Now, we would like to work out the temperature dependence of the enthalpy of a compound and then that of the reaction enthalpy. At constant pressure where the substance is allowed to freely expand, the change of the enthalpy H of a compound with temperature T is the *heat capacity* at constant pressure c_p :

$$c_{\rm p} = \left(\frac{\partial H}{\partial T}\right)_p \tag{2-C2}$$

For an ideal monoatomic gas $c_p = 5/2 \cdot R = 20.8 \text{ J/(mol·K)}$, for an ideal diatomic gas $c_p = 7/2 \cdot R = 29.1 \text{ J/(mol·K)}$, and for an ideal polyatomic gas $c_p = 4 \cdot R = 33.3 \text{ J/(mol·K)}$. We can now write the differential change of the enthalpy as

$$dH = c_p dT = dU + p dV \tag{2-C3}$$

for constant pressure p. The c_p values at 25°C for the compounds of our example are listed in **Table 2-C1**.

Table 2-C1. Heat capacity c_p at constant pressure at 25°C.

Compound	<i>C</i> p	
	(J·mol ⁻¹ ·K ⁻¹)	
H ₂	28.8	
O_2	29.4	
$H_2O(g)$	33.6	

Under the assumption of constant heat capacity c_p we can now calculate the reaction enthalpy at temperature *T* as follows:

$$\Delta_{\rm r} H(T) = \Delta_{\rm r} H(T_0) + \Delta c_{\rm p} (T - T_0)$$
(2-C4)

where T_0 is 298 K. The reaction heat capacity is $\Delta c_p = \sum_k (v_k \cdot c_{p,k})$. For our example the value is -9.92 J/(mol·K). Eq. 2-C4 yields a reaction enthalpy at 1'000°C of $\Delta_r H^o(1'273 \text{ K}) =$ -251.5 kJ/mol. We see that it differs by about 10 kJ/mol from its value at 25°C.

In general, however, the heat capacity is not constant in *T*, hence $c_p = c_p(T)$. The enthalpy change of a substance between the standard temperature T_0 (298 K) and temperature *T* at constant pressure is calculated as follows:

$$H(T) - H(T_0) = \int_{T_0 = 298K}^{T} c_p(T) dT$$
(2-C5)

Eq. 2-Co. (Source	e. NIST Chemistry	Webbook, webb	JOOK.IIISt.gov)
Compound	a	<i>b</i> · 10 ³	c · 106
-	(J·mol ⁻¹ ·K ⁻¹)	(J·mol ⁻¹ ·K ⁻²)	(J·mol ⁻¹ ·K ⁻³)
H ₂	29.066	-0.837	2.012
O_2	25.723	12.979	-3.862
$H_2O(g)$	30.359	9.615	1.184

Table 2-C2. Parameters a - c for the calculation of the temperature dependent heat capacity at constant pressure c_p , Eq. 2-C6. (Source: NIST Chemistry WebBook, webbook.nist.gov)

Often the temperature dependence of c_p is given in the form of a polynomial:

$$c_{\rm p}(T) = a + bT + cT^2 \tag{2-C6}$$

The parameters a - c can be found in thermodynamic tables, and the values for our example are given in **Table 2-C2**. We might now be tempted to calculate the formation enthalpy of a compound at an arbitrary temperature *T* using Eqs. 2-C5 and 2-C6. Unfortunately, however, in thermodynamics the formation enthalpy of elements is *defined* to be zero at all temperatures. We therefore apply the formalism directly to the reaction enthalpy. In going in temperature from T_0 to *T* the value of $\Delta_r H(T)$ is obtained from the change in enthalpy of the involved compounds:

$$\Delta_{\rm r} H(T) = \Delta_{\rm r} H(T_0) + \int_{T_0 = 298\rm K}^{T} \Delta c_{\rm p}(T) dT$$
(2-C7)

The heat capacity $c_p(T)$ between 0 and 1'000°C for H₂, O₂ and H₂O(g) and $\Delta c_p(T)$ for the reaction is displayed in **Figure 2-C1a**. At 25°C, $\Delta c_p(298 \text{ K}) = -10.29 \text{ J/(mol·K)}$, and at 1'000°C, $\Delta c_p(1'273 \text{ K}) = -4.74 \text{ J/(mol·K)}$. The enthalpy change between $T_0 = 298 \text{ K}$ and temperature T can be calculated by inserting Eq. 2-C6 into Eq. 2-C5:

$$H(T) - H(T_0) = \int_{T_0 = 298K}^{T} c_p(T) dT = a(T - T_0) + \frac{b}{2}(T^2 - T_0^2) + \frac{c}{3}(T^3 - T_0^3)$$
(2-C8)

With this we can now calculate the reaction enthalpy at temperature T by inserting into Eq. 2-C7:

$$\Delta_{\rm r} H(T) = \Delta_{\rm r} H(T_0) + (\Delta a(T - T_0) + \frac{\Delta b}{2}(T^2 - T_0^2) + \frac{\Delta c}{3}(T^3 - T_0^3))$$
(2-C9)

where $\Delta a = \sum_k (v_k \cdot a_k)$, etc. The standard reaction enthalpy at 25°C is $\Delta_r H^\circ = -241.8$ kJ/mol. With Eq. 2-C9 and the values from **Table 2-C2**, we obtain a standard reaction enthalpy at 1'000°C of $\Delta_r H^o(1'273 \text{ K}) = -249.3 \text{ kJ/mol}$. The difference in reaction enthalpy is therefore rather small, considering the large temperature range. In **Figure 2-C1b** the enthalpy change for the individual compounds and the reaction system is plotted as a function of temperature. The difference to the value calculated assuming constant heat capacities according to Eq. 2-C4, -251.5 kJ/mol, is rather small.



Figure 2-C1. (a) Heat capacities at constant pressure c_p for hydrogen, oxygen and water vapor, and the reaction heat capacity Δc_p . The ideal values for a diatomic gas, 7/2 *R*, and a multiatomic gas, 4 *R*, are indicated. (b) Change of enthalpy of compounds $H(T) - H(T_0 = 298 \text{ K})$ and reaction enthalpy $\Delta_r H^\circ$.

Calorimetric entropy

According to the famous equation by Boltzmann $S = k \cdot \ln \Omega$, the entropy S of a system is related to the number of microstates Ω , which is the number of ways the particles of a thermodynamic system can be arranged for a given set of conditions (e.g., temperature). k (sometimes k_B) is the Boltzmann constant ($k = 1.381 \cdot 10^{-23}$ J/K). For a substance the number of energy states that its constituent particles can occupy increases with temperature, because thermal activation allows the access of higher energy states. The change in entropy dS is defined as the (reversible) heat $dq_{rev} = c_p \cdot dT$ that the system is exchanging with its environment divided by the temperature:

$$dS = \frac{c_{\rm p}}{T} dT \tag{2-C10}$$

As indicated above, we are considering a constant pressure process. Since the particles follow the Boltzmann energy statistics, at T = 0 only the ground state is populated. Therefore, the entropy of a substance in the form of a perfect crystal at T = 0 is zero. This is the 3^{rd} law of thermodynamics.

Therefore, entropy is the only thermodynamic potential for which we can calculate an absolute value.

As a first approximation, we can again assume that the heat capacities c_p are independent of temperature, hence constant. The reaction entropy at temperature *T* is then:

$$\Delta_{\rm r} S(T) = \Delta_{\rm r} S(T_0) + \Delta c_{\rm p} \ln(\frac{T}{T_0})$$
(2-C11)

With the values given in **Table 2-1** and **Table 2-C1** we obtain at 1'000°C a value of $\Delta_r S^{\circ}(1'273 \text{ K}) = -58.9 \text{ J/(mol·K)}$, which differs by about 15 J/(mol·K) from its value at 25°C.

For a more accurate calculation, we take the temperature dependence of the heat capacities into account. Integration of Eq. 2-C10 yields

$$S(T) = \int_{0}^{T} \frac{c_{\rm p}(T)}{T} dT$$
(2-C12)

The entropy of a compound as a function of temperature is displayed schematically in **Figure 2-C2a**. Step changes occur at the melting and boiling point.



Figure 2-C2. (a) Schematic entropy *S* of a compound as a function of temperature with melting point T_m and boiling point T_b . The entropy of fusion is $\Delta_{fus}S = \Delta_{fus}H / T_f$, the entropy of vaporization $\Delta_{vap}S = \Delta_{vap}H / T_b$, where $\Delta_{fus}H$ and $\Delta_{vap}H$ are the enthalpies of fusion and vaporization, respectively. (Source: P.W. Atkins, Physikalische Chemie (1990), Fig. 5-7, p. 120) (b) Absolute entropies *S*° for hydrogen, oxygen and water vapor, and reaction entropy $\Delta_r S^\circ$.

We see that qualitatively the temperature dependence does largely follow a logarithmic behavior as suggested by Eq. 2-C11, except at low temperature. In thermodynamic tables, the standard entropy S° for pure substances at 1 bar and 298 K is listed, cf. **Table 2-C3** for our example.

 Table 2-C3. Standard entropies S° at 25°C for compounds used in the example.

Compound	S°	
	$(J \cdot mol^{-1} \cdot K^{-1})$	
H ₂	130.7	
O_2	205.1	
$H_2O(g)$	188.8	

Note that entropy values are positive for all temperatures T > 0 due to the pinning of the value to S = 0 at T = 0 by the 3rd law of thermodynamics. In particular, the values are not zero for the elements at 25°C like in the case of the formation enthalpy. For the determination of entropy changes in a practical temperature range, we calculate, in analogy to the enthalpy, the difference to the tabulated values at 25°C:

$$S^{\circ}(T) = S^{\circ}(T_0) + \int_{T_0 = 298\text{K}}^{T} \frac{c_p(T)}{T} dT = S^{\circ} + \left(a\ln(\frac{T}{T_0}) + b(T - T_0) + \frac{c}{2}(T^2 - T_0^2)\right) \quad (2-\text{C13})$$

This yields more accurate results than the integration from T = 0. The entropies of hydrogen, oxygen and water vapor thus calculated are plotted in **Figure 2-C2b**. We can now calculate the reaction entropy at a given temperature according to $\Delta_r S = \sum_k (\nu_k \cdot S_k)$ (Eq. 2-9). For our example we obtain a value at 1'000°C of $\Delta_r S^\circ(1'273K) = -56.5$ J/(mol·K). The difference to the value calculated assuming constant heat capacities, -58.9 J/(mol·K), is small.

Assembly of the reaction Gibbs free energy and reversible voltage

With the refinements elaborated for the temperature dependence of the reaction enthalpy and entropy, we can now calculate the Gibbs free energy of reaction $\Delta_r G(T)$ (Eq. 2-7) and the reversible cell voltage $U_{rev}(T)$ (Eq. 2-5) with higher accuracy. First, we assume constant heat capacities c_p (**Table 2-C1**). Inserting Eqs. 2-C4 and 2-C11 into Eq. 2-7 leads to the following expression:

$$\Delta_{\rm r} G(T) = \Delta_{\rm r} H(T_0) - T \Delta_{\rm r} S(T_0) + \Delta c_{\rm p} ((T - T_0) - T \ln(\frac{T}{T_0}))$$
(2-C14)

For our sample reaction at 1'000°C this yields $\Delta_r G^{\circ}(1'273 \text{ K}) = -176.6 \text{ kJ/mol}$ and $U^{\circ}_{rev}(1'273 \text{ K}) = 0.915 \text{ V}$. With the further refinement, taking into consideration the temperature dependence of the heat capacities, we insert directly the values calculated for $\Delta_r H^{\circ}$ and $\Delta_r S^{\circ}$ at 1'000°C (see above) into Eqs. 2-7 and 2-5 to obtain $\Delta_r G^{\circ}(1'273 \text{ K}) = -177.3 \text{ kJ/mol}$ and $U^{\circ}_{rev}(1'273 \text{ K}) = 0.919 \text{ V}$.

The variation of the reversible cell voltage for our example over the temperature range from 0 to 1'000°C is displayed in **Figure 2-C3**. Below 100°C the thermodynamic quantities for liquid water have been used. The different levels of refinement indicate that the consideration of the temperature dependence of $\Delta_r H$ and $\Delta_r S$ yields the more pronounced difference than the further refinement by taking into account the temperature dependence of the heat capacity c_p .



Figure 2-C3. Temperature dependence of the standard reversible cell voltage U_{rev}° for the reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$. Below 100°C product water is liquid, assuming constant heat capacities. Above 100°C the product is steam and the values using the different approaches of refinement are plotted.

Appendix D: Oxidation Potential Formalism

If oxidation potentials were used for half-cell reactions, the reaction of interest would be written as an oxidation, and the hydrogen reaction as reduction:

$$\text{Red} \rightarrow \text{Ox} + \text{e}^-$$
 (2-D1)

$$\mathrm{H}^{+} + \mathrm{e}^{-} \rightarrow \frac{1}{2} \mathrm{H}_{2} \tag{2-D2}$$

This leads to the overall reaction Red + $H^+ \rightarrow Ox + \frac{1}{2} H_2$. We have chosen z = 1 for practical reasons. The corresponding Nernst expression is:

$$U_{rev} = U_{rev}^{\circ} - \frac{RT}{F} \ln(\frac{a(Ox)\sqrt{p(H_2)/p_0}}{a(Red)a(H^+)}))$$

= $(E_{ox}^{\circ} + \frac{RT}{F} \ln(\frac{a(Red)}{a(Ox)})) - (E_{red}^{\circ} + \frac{RT}{F} \ln(\frac{\sqrt{p(H_2)/p_0}}{a(H^+)}))$
= $E_{ox} - E_{red}$ (2-D3)

The Nernst expression for the half-cell reaction is therefore:

$$E_{\rm ox} = E_{\rm ox}^{\circ} + \frac{RT}{F} \ln(\frac{a({\rm Red})}{a({\rm Ox})})$$
(2-D4)

We see that, in contrast to the expression for reduction potentials (Eq. 2-23), a(Red) is in the numerator of the ln(...) expression and a(Ox) in the denominator.

As an example, we take the reaction $\text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{ e}^-$, which has an oxidation potential of $E_{\text{ox}}(\text{Fe/Fe}^{2+}) = +0.44 \text{ V}$. To obtain oxidation potentials, we just have to invert the sign of the reduction potentials from **Table 2-3**. Combining the oxidation reaction of iron with the proton reduction / hydrogen evolution reaction yields the overall reaction $\text{Fe} + 2 \text{ H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$ with the reversible cell voltage $U_{\text{rev}}^{\circ} = E_{\text{ox}}^{\circ} - E_{\text{red}}^{\circ} = +0.44 \text{ V} - 0 \text{ V} = 0.44 \text{ V}$. The positive value of U_{rev} indicates it is a spontaneous reaction, which is also what we obtain when we use the formalism with reduction potentials. Therefore, the thermodynamic consistency is maintained, we just have to make sure that we do not mix the two concepts.

Chapter III

Electrodes & Interfaces

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The electrodes in an electrochemical cell constitute the phase that supplies electrons for the cathodic reaction on one side and accepts electrons from the anodic reaction on the other side. Therefore, they need to be electronically conducting. Moreover, the electrodes are in contact with the electrolyte, and it is at this electrode-electrolyte interface that the electrochemical reaction takes place. It is important to understand the characteristics of this interface and how it can be described. If a half-cell reaction at an electrode is allowed to reach equilibrium, the energy of the electron in the electrode will assume a specific value, which defines the driving force or 'potential' of the electron energy¹. The topics of this chapter are mostly of generic nature, and although we commonly use examples of electrochemical components, for example high-temperature solid oxide devices (cf. Chapters IV and VII). In the last section, a very practical view will be placed on reference electrodes and their working principle.

1 The Electrified Interface

To begin with, we study the equilibrium of a half-cell reaction at an electrode and seek to describe the equilibrium using the concept of free energy *G* comprised of the contribution of the different species in the system under study. As a practical example, we take a copper electrode immersed in a solution of copper sulfate (**Figure 3-1a**). The corresponding half-cell reaction is: $Cu^{2+}(aq) + 2e^{-}$ \Rightarrow Cu(s). In general, upon immersion of the Cu rod in the solution, the reaction will not be at equilibrium. Hence it will proceed in forward or backward direction until the equilibrium is established. If Cu is oxidized, Cu²⁺ goes into solution, leaving behind a negative charge in the metal.



Figure 3-1. Schematic of the interfacial potential difference $\Delta \varphi$ between the electrode (m) and the electrolyte (s), leading to the accumulation of excess charges at the interface. (a) Metal electrode in a solution containing said metal ion. (b) Inert electrode ('redox electrode') with redox couple in solution.

¹ Of course, we require the two electrodes to be ionically connected via the electrolyte to provide the possibility of sustaining a continuous reaction.

Conversely, it will bring positive charge to the metal when plated by taking up two electrons. This charge flow between the electrode and the electrolyte phase¹ leads to the accumulation of net charge in the two phases and, hence, to the formation of a potential difference between metal and solution, which will oppose further reaction. For the description of the equilibrium we therefore also have to consider the difference in electrostatic potential between the phases. We do this by introducing the *electrochemical potential* $\tilde{\mu}_k^A$ of species *k* in phase A, which comprises of the chemical potential μ_k^A and the term $z_k F \varphi^A$ describing the electrical energy:

$$\tilde{\mu}_{k}^{A} = \left(\frac{\partial G^{A}}{\partial n_{k}}\right)_{p,T,n_{lsk}} = \mu_{k}^{A} + z_{k}F\varphi^{A} = \mu_{k}^{A\circ} + RT\ln(a_{k}) + z_{k}F\varphi^{A}$$
(3-1)

where z_k is the charge of species k, and φ^A is the electrostatic potential in phase A (= Galvani potential, see below). Therefore, the potential φ^A only contributes to the energy of the particle if it is charged, i.e., if it is an ion (or electron). The chemical potential depends on the activity of the species a_k in the well-known way via the term $RT \ln(a_k)$ (cf. Introduction). The electrochemical potential can be regarded as the change in the free energy G^A of phase A upon change in the content of species k. It has the unit J/mol².

The equilibrium between the Cu metal (m) and the Cu-ions in solution (s) is attained if the free energy in the two phases are equal: $G^{(m)} = G^{(s)}$. In terms of our half-cell reaction, this means that the free energy change $\Delta_r G$ described by the reaction equation must be zero. From Eq. 3-1 we deduce that $\Delta_r G$ is composed of the contributions of the 'partial molar free energies' $\tilde{\mu}_k$. Hence:

$$\Delta_{\mathbf{r}}G = \sum_{k} \nu_{k}\tilde{\mu}_{k} = 0 \tag{3-2}$$

For our sample reaction, we now introduce the electrochemical potentials for the Cu²⁺ ions and the electrons, the chemical potential of Cu(s) into Eq. 3-2 and solve for the potential difference $\Delta \varphi$ between the electrode and the electrolyte:

¹ The amount of charge that flows between electrode and electrolyte to reach equilibrium depends on the capacitance of the electrode, but is generally much smaller than the number of electrons in the metal and redox species in solution. Consequently, the change in activity a and, thus, the chemical potential μ of all the species is negligible.

² The term '(electro)chemical potential' is admittedly somewhat confusing, because the quantity does not have the unit of an electric potential (Volt). A more appropriate name might be 'partial molar (electrochemical) free energy'. In any case, 'potential' is used here in the same sense as 'thermodynamic potential' for G, H and S, meaning 'state function', which characterizes a function whose change does not depend on the path chosen but only on the starting and end point.

$$\Delta \varphi = \varphi^{(m)} - \varphi^{(s)} = \frac{1}{2F} (\mu_{Cu^{2+}}^{\circ} + 2\mu_{e}^{\circ} - \mu_{Cu}^{\circ}) + \frac{RT}{2F} \ln(a_{Cu^{2+}}) = \Delta \varphi^{\circ} + \frac{RT}{2F} \ln(a_{Cu^{2+}}) \quad (3-3)$$

The value $\Delta \varphi^{\circ}$ is the standard potential difference at $a(\operatorname{Cu}^{2^+}) = 1$. See the footnote¹ for an elaboration. The equation describes the change of the interfacial potential difference as a function of the activity of copper-ions and is a form of the Nernst equation (cf. Chapter II). In fact, as we will see later, the Galvani potentials $\varphi^{(m)}$ and $\varphi^{(s)}$ and the Galvani potential difference $\Delta \varphi$ cannot be determined experimentally, so we cannot actually establish the sign and magnitude of the interfacial potential difference. However, if we measure the potential of the electrode in question against a reference electrode (with or without liquid junction, cf. Chapter IV), the change in electrode potential *E* with variation of the concentration of Cu²⁺ can be measured with arbitrary precision.

The relationship of Eq. 3-3 holds for any half-cell potential at equilibrium. As another example, **Figure 3-1b** illustrates the reaction of a redox couple in solution, $Fe^{3+} + e^{-} \leftrightarrows Fe^{2+}$, with an inert electrode that catalyzes the reaction. For a generic reaction $Ox + ze^{-} \oiint$ Red we obtain the following expression, in analogy to the Nernst equation in Chapter II.

$$\Delta \varphi = \Delta \varphi^{\circ} + \frac{RT}{zF} \ln(\frac{a_{\text{Ox}}}{a_{\text{Red}}})$$
(3-4)

The potential drop between the electrode and the electrolyte is not infinitely sharp as implied in **Figure 3-1**. At the interface, a space charge layer develops with thickness in the nanometer range, over which the potential drops from $\varphi^{(m)}$ to $\varphi^{(s)}$ (cf. Section 3, 'The Electrochemical Double Layer'). Since the Galvani potential of a phase cannot be determined experimentally, it is essentially a conceptual tool to describe the electrical contribution to a change in the potential energy of a charged particle. Below we will see which quantities are actually experimentally accessible. The magnitude and sign of $\Delta \varphi$ in **Figure 3-1** are chosen arbitrarily here, as it is a quantity that is not experimentally measurable (except in very specific constellations). The change of $\Delta \varphi$ with the concentration of the redox-active species according to Eq. 3-4, however, is measurable in an electrochemical experiment.

¹ Insert $\tilde{\mu}_k$ with stoichiometric factors ν_k of the half-cell reaction $\operatorname{Cu}^{2+} + 2e^- \leftrightarrows \operatorname{Cu}$ into Eq. 3-2: $\tilde{\mu}_{\operatorname{Cu}}^{(m)} - (\tilde{\mu}_{\operatorname{Cu}}^{(s)} + 2\tilde{\mu}_{\operatorname{e}}^{(m)}) = 0$ with $\tilde{\mu}_{\operatorname{Cu}}^{(m)} = \mu_{\operatorname{Cu}} = \mu_{\operatorname{Cu}}^\circ$, $\tilde{\mu}_{\operatorname{Cu}^{2+}}^{(s)} = \mu_{\operatorname{Cu}^{2+}} + 2F\varphi^{(s)} = \mu_{\operatorname{Cu}^{2+}}^\circ + RTln(a_{\operatorname{Cu}^{2+}}) + 2F\varphi^{(s)}$, and $\tilde{\mu}_{\operatorname{e}}^{(m)} = \mu_{\operatorname{e}} - F\varphi^{(m)} = \mu_{\operatorname{e}}^\circ - F\varphi^{(m)}$.
2 Potentials in Electrochemistry and Surface Science

The phase potential φ was introduced above to describe the influence of the electrostatic potential on the energy of a particle. In particular, the concept is also applied to the electron. From the definition of the electrochemical potential of the electron $\tilde{\mu}_e = \tilde{\mu}_e^\circ - F\varphi$ we recognize that we can influence the energy of the electron by modifying the potential φ of the electrode, for example by connecting a potentiostat to it and changing its potential with respect to a reference electrode immersed in the same electrolyte. The chemical and electrical environment of the electron in the electrode characterized by $\tilde{\mu}_e^\circ$ and φ , respectively, requires us to look a bit deeper into the meaning of these terms.

2.1 Phase potentials

For the elaborations to follow in this section, we abandon the concept of an electrode in contact with electrolyte for the moment and only consider the electrode phase in the form of a (clean) piece of metal placed in vacuum. The electric potential φ of the phase is defined through the energy $q\varphi$ it takes to move a small positive test charge q from infinity to a point within the phase. φ is therefore called the *inner potential* or *Galvani potential*. 'Infinity' is the reference point far away from the electrode where we define $\varphi = 0^1$. In the absence of current, the inner potential of a conducting phase is uniform, i.e. it is the same everywhere. If this were not the case, charge (electrons in case of a metal) would flow (since they are mobile) until potential uniformity is established.



Figure 3-2. (a) Distribution of electric potential from within a metal phase into vacuum, showing the different potentials: inner (Galvani) potential φ , surface potential χ , and outer (Volta) potential ψ . (b) Origin of the surface potential for a metal ('jellium' model), and (c) water.

¹ Another reference point could be a piece of metal that is grounded and sufficiently far away from our test electrode. In textbooks, the 'point at infinity' is mostly used as reference.

In a gedankenexperiment (thought experiment), we are first moving the test charge from infinity through vacuum to a point 'just outside' of the electrode (Figure 3-2a). The associated work is solely related to the electrostatic charge of the metal and given by $q\psi$, where ψ is the *outer potential* or Volta potential of the electrode. Therefore, if the electrode is uncharged, $\psi = 0$. The point 'just outside' is at a distance of around 0.1 to 10 µm from the electrode, where image forces are not yet significant¹. When the test charge is moved through the metal surface into its interior, the difference in electric potential it experiences is the surface potential χ . The surface potential results from the surface dipole layer of a metallic phase. The positively charged metal ions form a sharp edge at the surface, yet electron density does not end sharply at the edge. Finite electron density can also be found beyond the surface, which is a consequence of the shape of the electron wave function ('jellium' model²): electrons 'spill over' the edge, which creates a positive charge density just below the surface and a negative charge density just beyond the surface (Figure 3-2b). A charge moving across the boundary of the phase must overcome the surface potential χ created by this dipole. In metals, the surface potential is on the order of volts. A surface dipole layer is also found in water or aqueous electrolytes, as the water molecules near the surface are oriented on average such that the hydrogen atoms are pointing away from the surface (Figure 3-2c). The surface potential of water is ~ 0.13 V. Therefore we can write down the following relationship between the potentials introduced in this sub-section:

$$\varphi = \chi + \psi \tag{3-5}$$

2.2 Fermi level and work function

Now we consider that the test charge is an electron, and the electrode sufficiently large, such that the transfer of one electron does not lead to a change in the charge of the metal and the potential distribution. For the movement of an electron from a reference point outside the metal into its interior, we have taken into account the electrical energy related to the change in electric potential. However, upon entering a phase, the electron will also experience a change in its chemical

The position 'just outside' the surface is somewhat ill-defined. An alternative, more palpable conceptual approach for introducing the Volta potential is the cavity model, where it is assumed that the electrode in question contains a cavity (see sketch, the horizontal lines in the vacuum outside the metal surface denote equipotential lines) with a small opening, into which we bring the test charge. Since the interior of this cavity is largely devoid of an electric field, there is a constant potential: the Volta potential ψ .



² The term 'jellium' alludes to the 'positive jelly' background of the metal ions, over which the free electrons distribute.

¹ Cavity potential:

environment. The splitting of the energy of a particle into a chemical and an electrical term, as described by the electrochemical potential $\tilde{\mu}$, is of a conceptual nature, and in reality the chemical and electrical terms cannot be disentangled. In an electron conducting solid, the electronic levels form bands of allowed energies. At T=0 the bands are filled from the ground state, following Fermi-Dirac statistics, up to a certain energy, the *Fermi level* $E_{\rm F}$. In metals, the Fermi level lies within an energy band. Upon thermal activation, i.e., at T > 0, electrons can be excited to energies slightly above E_F, leaving behind 'electron holes'. Exited electrons and corresponding holes provide electronic conductivity. The energy distribution of electrons and holes is restricted to a region in the range of a few kT around $E_{\rm F}$, quantitatively given by the Fermi-Dirac distribution¹. At room temperature, $kT \cong 25$ meV, whereas the value of $E_{\rm F}$ is in the eV range (see below). The concept of Fermi level and Fermi-Dirac distribution can also be applied to semiconductors². The electrochemistry of semiconductors is, however, beyond the scope of this text. The Fermi level is a notion from solid-state physics, hence it is measured in energy per particle (unit: eV). It signifies the highest energy possessed by an electron in a metal. In physical chemistry, this electron energy is termed the *electrochemical potential of the electron* $\tilde{\mu}_{e}$. In chemistry, energies are normally given per mole of substance (unit: kJ/mol), therefore those two quantities are equivalent (within the boundaries explained in footnote 1 below) and we can write: $E_{\rm F} = \tilde{\mu}_{\rm e}/N_{\rm A}$.

Before we look in a bit more detail at the meaning of $E_{\rm F}$ and its relation to the electric potentials discussed above, another important quantity is introduced and explained: the electron work function or simply *work function* Φ (or $\Phi_{\rm e}$). The work function is the minimum energy required to remove an electron from a metal to a point in the vacuum 'just outside' of the surface. It has therefore the unit of energy, and values are typically given 'per particle', hence in eV. In order to better understand the relation between the different potentials introduced in this section, the Fermi level and the work function, a schematic electron energy diagram for a metal in vacuum is presented in **Figure 3-3**. We see that the work function Φ comprises the energy related to the surface potential χ and also the chemical energy contribution given by the chemical potential $\mu_{\rm e}$. From the balance of arrows we find: $\Phi = -\mu_{\rm e}/N_{\rm A} + e\chi$. Hence, the work function depends on the chemical

¹ The Fermi-Dirac distribution function is $f(E) = 1 / (1 + \exp((E - \tilde{\mu}'_e))/kT))$, where $\tilde{\mu}'_e = \tilde{\mu}_e/N_A$. The distribution describes the probability $(0 \le f(E) \le 1)$ of an electron having an energy *E*, where $\tilde{\mu}'_e$ is the electrochemical potential of the electron, which is identical to the Fermi level E_F at T = 0. At finite temperature, $\tilde{\mu}'_e$ is the electron energy *E* for which the distribution function is 0.5, hence $f(\tilde{\mu}'_e) = 0.5$. $\tilde{\mu}'_e$ decreases with temperature, but the difference to E_F is on the order of $(kT)^2$ and therefore very small. For practical purposes in electrochemical applications, we can take $\tilde{\mu}'_e \approx E_F$.

² In semiconductors, the Fermi level lies in the band gap between the valence band and the conducting band. At finite temperature, electrons are excited from the valence to the conduction band, which enables electronic conductivity. In doped semiconductors, electrons are excited from the donor level to the conduction band for n-type semiconductors, and holes are excited from the valence band to the acceptor level for p-type semiconductors.

environment of the e^- in the material and the surface dipole. Its value for elemental metals is in the range of eV. For example, $\Phi(Cs) = 1.95 \text{ eV}$, $\Phi(Os) = 5.93 \text{ eV}$. In fact, the work function depends on the configuration of atoms at the surface of the material, which influences the surface dipole and, thus, the surface potential χ . For example, whereas on polycrystalline Ag the work function is 4.26 eV, on Ag single crystals it depends on the crystal face: 4.64 eV for (100), 4.52 eV for (110), and 4.74 eV for (111)¹. Some trends for the different metals can be observed. For example, alkali metals have a relatively low work function. We can imagine the electrons here to be somewhat loosely bound, whereas the work function of noble metals tends to be high. The work function of a metal M shows some degree of correlation with the standard potential of the corresponding half-cell reaction $M^{z+} + ze^- \rightarrow M$. The work function can be experimentally measured, for example by a Kelvin probe (cf. below, Section 2.4) or through the photoelectric effect². Another important property of the work function can be inferred from Figure 3-3: it does not change if the metal is electrically charged, i.e. if there is a finite Volta potential.



Figure 3-3. Relationship between the quantities introduced in this chapter related to the electron energy for an electronically conducting solid in vacuum. The vertical axis indicates electron energy, which increases with decreasing electrode potential. Arrows pointing upwards represent positive energy values, arrows pointing downwards negative ones. The Fermi level E_F (concept of solid-state physics, unit: eV) is equivalent to the electrochemical potential $\tilde{\mu}_e$ of electrons (concept of physical chemistry, unit: kJ/mol) divided by N_A and characterizes the maximum energy possessed by the electrons in a metal, referenced to the vacuum level. It comprises of a chemical energy term μ_e (chemical potential) and an electrostatic term with the Galvani (inner) potential φ , which itself is composed of the surface potential χ and the Volta (outer) potential ψ . The energy is shown 'per electron' here. The work function Φ is the energy required to extract an electron from the metal to a point 'just outside' its surface. The horizontal lines below E_F indicate occupied electron energy levels, representing an energy band with quasi-continuous energy levels. The situation here is shown for a metal with positive excess charge, hence $\psi > 0$.

¹ Source: Wikipedia, https://en.wikipedia.org/wiki/Work_function

² Einstein was awarded the 1921 Nobel Prize in Physics for 'his discovery of the law of the photoelectric effect'.

We go back to discussing the Fermi level E_F , which is closely related to the work function Φ . As we can see from **Figure 3-3**, E_F includes the contribution of the work function Φ plus that of the Volta potential ψ , and we write, also remembering the equivalence of the Fermi level and the electrochemical potential of the electron:

$$-\tilde{\mu}_{e} / N_{A} = -E_{F} = \Phi + e\psi \tag{3-6}$$

For an uncharged metal ($\psi = 0$), E_F is identical in absolute value to Φ : $-E_F = \Phi$. The relationship shows that with the work function being a positive number, E_F and $\tilde{\mu}_e$ are negative, indicating that the electron being bound in the solid is an energetically favorable situation¹.



Figure 3-4. Electron energy diagram for two initially uncharged metals A and B in vacuum, (a) before and (b) after making contact. Equilibrium requires the Fermi levels in the two metals to align. Hence, owing to the different work functions, the two phases will assume a different excess charge, which will yield a Volta potential ψ , which can be measured.

The work function of metals being different has important implications. Let us consider two different, uncharged metals A and B with dissimilar work functions Φ^A and Φ^B . Their Volta potentials are zero. Their Fermi levels are therefore $E_F^A = -\Phi^A$ and $E_F^B = -\Phi^B$ (Figure 3-4a). When the two metals are brought into contact, their Fermi levels must become equal at equilibrium, i.e., the electrochemical potentials of the electrons must be the same in A and B. The equilibrium is established by electrons flowing from the metal with the higher Fermi level, here A, to the one with the lower one, B, until a common Fermi level is established. Metal A thus becomes positively charged and B negatively charged, with a dipole layer forming at the contact (Figure 3-4b). Since the metals are now charged, they exhibit different Volta potentials. With the help of Eq. 3-6, we can calculate the difference in the Volta potentials of A and B, which is the *contact potential difference*:

¹ Even if we apply a high negative potential to the metal ($\psi \ll 0$), the electrons still need to overcome the barrier of the work function to leave the solid. Once outside the metal phase, they are accelerated by the electric field created by the negative charge of the metal. When the metal is heated, more electrons can pass this barrier per time. This thermionic emission of electrons is the working principle of electron guns, for example used in old type TVs with a cathode-ray tube. Also, electrons can tunnel through the barrier from the negatively charged metal to the vacuum, a phenomenon called 'field emission'.

$$\Delta \psi = \psi^{\mathrm{A}} - \psi^{\mathrm{B}} = -\frac{\Phi^{\mathrm{A}} - \Phi^{\mathrm{B}}}{e}$$
(3-7)

Next, we go back to the situation of an electrode in contact with an electrolyte and seek to describe the equilibrium of an electrochemical half-cell reaction at the interface using the concept of electron energy, i.e., the Fermi level E_F (solid-state physics terminology) or the electrochemical potential of the electron $\tilde{\mu}_e$ (physical chemistry terminology). For simplicity, we consider a redox reaction with single electron transfer $Ox + e^- \leftrightarrows Red$, and the electrode being of a material not taking part in the reaction, such as Pt, yet able to exchange electrons with the redox couple Ox/Red (redox electrode). The electron energy in the solution $\tilde{\mu}_e^{(s)}$ is given by the electron energy associated with the redox couple $\tilde{\mu}_e$ (redox). At equilibrium, it aligns with the energy level of electrons $\tilde{\mu}_e^{(m)}$ in the electrode (**Figure 3-5a**), hence $\tilde{\mu}_e^{(m)} = \tilde{\mu}_e$ (redox) or E_F (metal) = E_F (redox). For details on the derivation, see **Appendix A**. Therefore, the notion of a Fermi level is also a useful concept for a redox couple in the electrolyte. This, however, does not imply that there are free electrons in the solution ! There are two distributions of energy levels associated with E_F (redox), owing to the different charges of Ox and Red, which results in the energy of Red being slightly lower than that of Ox (Gerischer model).



Figure 3-5. (a) Electron energy diagram for a metal electrode in equilibrium with an electrochemical reaction $Ox + e^- \leftrightarrows Red$ in solution, which leads to alignment of the Fermi levels E_F / electrochemical potentials of the electron $\tilde{\mu}_e$. The energy of the oxidized and reduced species are represented by two distributions (called 'shoelace' curves, shown here for an equimolar concentration of Ox and Red). Overlap between the two curves indicates the location of the electrochemical potential of the electron associated with the redox couple $\tilde{\mu}_e^{(s)}$ (redox) (Gerischer model). (b) Definition of the absolute electrochemical potential of a half-cell reaction, here the H⁺/H₂ redox couple, based on the work function of the bare metal Φ_M and the Volta potential difference $\Delta \psi$ between the electrode and the electrolyte, which yields the work function of the redox couple in the electrolyte Φ_s . The work to move the electron from the metal to the electrolyte at equilibrium is zero, because the Fermi levels of electrode and electrolyte are equal.

2.3 The absolute electrode potential

The reference point of the electrochemical series (cf. Chapter II) is the standard hydrogen electrode (SHE). The tendency of a redox couple to undergo oxidation or reduction is therefore measured relative to the H^+/H_2 couple, for which the standard electrode potential is defined as 0.00 V. This is a completely arbitrary choice, which is not even very practical, because the handling of a hydrogen reference electrode is cumbersome and, in fact, an activity of $a(H^+) = 1$ is not even possible to attain experimentally under ideal conditions. Instead of an arbitrary choice of reference potential, (some) scientists developed the idea of finding a more 'fundamental' anchor point for the electrochemical series. Here, the conceptual framework of solid-state physics, where phases are often studied in vacuum, came in handy. The minimum binding energy of an electron in a metal (or semiconductor) is the work function, and since electrochemical reactions involve the transfer of electrons from / to the Fermi level of electrodes, it appears to make sense to somehow use this quantity to describe the absolute potential of an electrode.

We picture a half-cell reaction in equilibrium at an inert electrode, e.g. Pt, as described in the previous section. It is important to realize that this equilibrium involves the electron energy in the electrode as well as the electrolyte containing the redox couple. At equilibrium, a Galvani potential difference (cf. Section 1) $\Delta \varphi = \varphi_{\rm M} - \varphi_{\rm S}$ forms between metal and solution. Therefore, there is also an equilibrium outer potential difference $\Delta \psi = \psi_M - \psi_S$ between the two phases, connected via Eq. 3-5. Since outer (Volta) potentials can be measured, this gives us the opportunity to identify an experimental quantity for an electrode potential without the need of a second (reference) electrode. For the definition of the absolute electrode potential E_{abs} of a half-cell reaction, we consider the situation depicted in Figure 3-5b. The absolute electrode potential is associated with the work to bring an electron from the electrode through the electrode-electrolyte interface to the electrolyte and across its surface to a point in vacuum in front of the electrolyte. Since the Fermi levels in the electrode and electrolyte are aligned, the work of bringing the electron across the electrodeelectrolyte interface is zero. The work to move the electron from the electrolyte, more specifically: from the redox couple in the electrolyte (all other constituents of the electrolyte are considered electrochemically inactive), to the point in vacuum in front of it is the work function of the electrolyte $\Phi_{\rm s}$. The same work is obtained via another path, where the electron is first extracted from the electrode to a point in vacuum just in front of it, for which the work function of the bare metal $\Phi_{\rm M}$ has to be invested. Then, the electron is moved in the vacuum from the point outside of the electrode to a point outside of the electrolyte, which is associated with the work $e \Delta \psi$. The total work, Φ_s , is specific to the redox couple in question and uniquely related to its chemistry in the given electrolyte. For more details, cf. Appendix A. If another inert metal were used as electrode material, for example Pd instead of Pt, its dissimilar work function would be compensated by a dissimilar Volta potential difference to yield the same value of Φ_s . Therefore, this quantity suggests itself as an absolute measure of electrode potential. The absolute electrode potential E_{abs} of the half-cell reaction between Ox and Red at equilibrium is thus defined as:

$$E_{\rm abs}(\rm redox) = \frac{\Phi_{\rm s}}{e} = \frac{\Phi_{\rm M}}{e} + (\psi_{\rm M} - \psi_{\rm s}) = \frac{\Phi_{\rm M}}{e} + \Delta\psi$$
(3-8)

Work functions and Volta potentials can be measured, hence values of E_{abs} are experimentally accessible. However, the measurements are associated with considerable uncertainty. Since the 1960s the absolute potential of the SHE has been sought to be determined. The accepted value is¹

$$E_{\rm abs}({\rm SHE}) = 4.44 \pm 0.02 \text{ V}$$
 (3-9)

This means that an energy of ~4.5 eV is required to remove an electron from the redox couple H^+/H_2 at pH 0 to the vacuum in front of the electrolyte². Therefore, the SHE and the absolute potential scale are connected via: $E_{abs} = E_{SHE} + 4.44$ V. For example, the couple Fe^{3+}/Fe^{2+} with $E(Fe^{3+}/Fe^{2+}) = +0.77$ V vs. SHE has an absolute electrode potential of $E_{abs}(Fe^{3+}/Fe^{2+}) = +5.21$ V. In some branches of science, such as semiconductor physics or photoelectrochemistry, potentials are often given in terms of the absolute potential scale.

2.4 What are we measuring ?

An electrochemical cell is connected electrically 'to the outside world' via the electrodes. If we connect them to a voltmeter, this device is built to give us a reading of a potential difference, i.e., a voltage, between the two electrodes. Thinking about the different potentials and energy quantities introduced in this chapter, what are we actually measuring with the voltmeter? We may argue we are measuring the difference in Galvani potential of the electrodes. This is not strictly true. What we are measuring is the difference in the energy of the electrons in the two electrodes, and as we know by now, this energy is composed of a chemical and an electrical term. Thus, what we are measuring is the difference in the Fermi level $E_{\rm F}$ or the electrochemical potential of the electron $\tilde{\mu}_{\rm e}$. We can think of the electron energy as the 'electron pressure' in the hydraulic analogy (cf. Introduction). For illustration, we consider a sample cell consisting of a Cu electrode dipping into a

¹ S. Trasatti, Pure Appl. Chem. 58(7), 1986, 955

² The electrolyte would obviously boil in vacuum, hence this process is merely conceptual. The experiments to determine $E_{abs}(SHE)$ are not straightforward and involve indirect measurements of a number of different quantities.

CuSO₄(aq) solution on the right and a hydrogen reference electrode on the left (Figure 3-6). The representation of this cell in shorthand notation is: Cu' | Pt | H₂ | H⁺(aq) | Cu²⁺(aq) | Cu. We have introduced a copper phase on the left in contact with the Pt electrode, because we are using copper wires to measure the cell potential. We will see why this seemingly irrelevant detail is important. We are assuming an ideal liquid junction between the electrolyte S' of the H₂ reference electrode compartment and the Cu²⁺ containing electrolyte S, which will give us no liquid junction potential (cf. Chapter IV). The two half-cell reactions $2 \text{ H}^+ + 2 \text{ e}^- \leftrightarrows \text{H}_2$ and $\text{Cu}^{2+} + 2\text{ e}^- \leftrightarrows \text{Cu}$ are in equilibrium, so the respective $\tilde{\mu}_e$ values in electrode and electrolyte match. For a detailed elaboration, see **Appendix B**. Also, the electron energy levels of the Pt electrode and the Cu' cable are aligned. The electron energy in the Cu electrode on the right is $\tilde{\mu}_e$ and the one in the Pt electrode and Cu' lead on the left is $\tilde{\mu}'_e$, and the difference is what we measure as a cell voltage E_{cell} (Figure 3-6):

$$\Delta \tilde{\mu}_{\rm e} = \tilde{\mu}_{\rm e} - \tilde{\mu}_{\rm e}' = \frac{\Delta_{\rm r} G}{z} = -F E_{\rm cell}$$
(3-10)

As we know, the (reversible) cell potential E_{cell} (the same as the reversible cell voltage U_{rev}) is connected to the Gibbs free energy of reaction $\Delta_r G$ (cf. Chapter II)¹.

The electrochemical potential of the electron $\tilde{\mu}_{e}$ is composed of its chemical potential μ_{e} and the electrical contribution given by the Galvani potential φ : $\tilde{\mu}_{e} = \mu_{e} - F\varphi$. The chemical potential of electrons μ_{e} is not the same in different metals, such as Pt and Cu, $\mu_{e}(Pt) \neq \mu_{e}(Cu)$, hence when the two metals are in contact, $\tilde{\mu}_{e}(Pt) = \tilde{\mu}_{e}(Cu)$, the Galvani potential will be different: $\varphi_{Pt} \neq \varphi_{Cu}$. This means that when a Cu cable is connected to a Pt electrode, there is a jump in the Galvani potential at the interface between the two metals. In our sample cell, the cell potential E_{cell} we are measuring is therefore *not* the difference in the Galvani potentials of the Cu and Pt electrode (as implied in some textbooks), but the difference in the Galvani potentials of the cables made of the same material, here Cu, connected to the voltmeter: $E_{cell} = \varphi_{Cu} - \varphi_{Cu}$.²

¹ Half-cell reactions at equilibrium: Hydrogen electrode: μ(H₂) - 2μ̃(H⁺) - 2μ̃_e = 0, hence μ̃_e = 0.5μ(H₂) - μ̃(H⁺). Copper electrode: μ°(Cu) - μ̃(Cu²⁺) - 2μ̃_e = 0, hence μ̃_e = 0.5μ°(Cu) - 0.5μ̃(Cu²⁺). Thus Δμ̃_e = μ̃_e - μ̃_e' = 0.5μ°(Cu) - 0.5μ̃(Cu²⁺) - 0.5μ(H₂) + μ̃(H⁺) Considering the overall reaction Cu²⁺ + H₂ ⇔ Cu + 2 H⁺ the Gibbs free energy of reaction is Δ_rG = Σν_kμ̃_k = μ°(Cu) + 2μ̃(H⁺) - μ̃(Cu²⁺) - μ(H₂) = 2Δμ̃_e. With μ̃_e(Cu) = μ̃_e and μ̃_e(Cu') = μ̃_e' we obtain Δμ̃_e = μ̃_e(Cu) - μ̃_e(Cu') = μ̃_e - μ̃_e' = Δ_rG/z = -FE_{cell} (here: z = 2).
² We can build the cell potential E_{cell} from the different Galvani potential differences in the cell:

We can build the cell potential E_{cell} from the different Galvani potential differences in the cell: $E_{cell} = \Delta \varphi (Cu^{2+}/Cu) - \Delta \varphi (H^+/H_2) + \Delta \varphi (Cu/Pt)$ $= (\varphi_{Cu} - \varphi_S) - (\varphi_{Pt} - \varphi_S) + (\varphi_{Pt} - \varphi_{Cu'}) = \varphi_{Cu} - \varphi_{Cu'}$ (Remember that we assumed that $\varphi_{S'} = \varphi_{S}$.)



Figure 3-6. Sample cell Cu' | Pt | H₂ | H⁺(aq) | Cu²⁺(aq) | Cu, showing the distribution of the electrochemical potential of electrons $\tilde{\mu}_e$ and the Galvani potential φ across the cell and relation to the measured cell potential E_{cell} . The junction between electrolyte solutions S' and S is assumed to be ideal, i.e. $\varphi_{S'} = \varphi_{S}$.

In conclusion of this section, it is helpful to categorize the measurability of the different potentials and energy quantities introduced. It is perhaps most straightforward to start by looking at which quantities are not experimentally accessible. The Galvani potential φ , although an important ingredient of the electrochemical potential, cannot be experimentally determined, because the chemical and electrical energy contributions of a particle cannot be disentangled. Also the surface potential χ cannot be measured experimentally, it can be, at best, estimated. The Volta potential ψ , being an outer potential, is experimentally accessible, for example using a Kelvin probe. Also the work function Φ is a measurable quantity, as mentioned already, and therefore also the Fermi level $E_{\rm F}$. The most straightforward quantity to measure is the cell potential $E_{\rm cell}$ / cell voltage U of an electrochemical cell, also the potential of an electrode E against a certain reference¹, often with a precision of 1 mV or better. Therefore, also a change in cell voltage or electrode potential can be measured with such precision. The absolute potential E_{abs} , on the other hand, cannot be measured directly, only inferred from the estimated E_{abs} of the SHE.

¹ beware of liquid junction potentials, though (cf. Chapter IV) !

3 The Electrochemical Double Layer

In general, as we have seen, the Galvani potential φ is different in phases that are in contact with each other. This is particularly true for an electrode-electrolyte interface. In this section, we will assume that we have an inert metal electrode in contact with an electrolyte without 'active' species, comprised only of solvent plus inert ions, such as Na⁺ and F⁻. Therefore, we do not have electrochemically active species for which we can / need to define a half-cell equilibrium. This electrode-electrolyte interface is *ideal polarizable* (cf. also Chapter V), meaning that we can change the electrode potential (using a potentiostat and a suitable reference electrode) in a wide range (~2 V in aqueous solution) without triggering charge transfer reactions. This will change the charge on the electrode and result in a redistribution of the ions in solution close to the electrode surface.



Figure 3-7. Models of the electrochemical double layer (EDL). The electrolyte solution contains cations, anions and solvent molecules (not shown). The blue line shows change of the (Galvani) potential φ from the electrode to the electrolyte. In the Helmholtz model (1853) a rigid layer of counter-charges is assumed at a distance *d* from the electrode. The Gouy-Chapman model (1910) considers the thermal motion of ions in solution counteracting the shielding of the charge on the electrode. The Stern model (1924) is essentially a combination of the Helmholtz and the Gouy-Chapman model with a rigid and a diffuse part of the double layer.

The Galvani potential φ changes from its value in the metal electrode φ_M to its value in the solution φ_S over a distance on the order of nanometers. The excess charge on the metal attracts ions of opposite charge in the solution through Coulomb interactions, which electrically screen the electrode charge against the bulk of the electrolyte. Since the ions are of finite size, the potential change occurs over a certain distance in the electrolyte. The charge in the electrode, on the other hand, is located very close to metal surface (<0.1 Å) owing to the high charge density of electrons¹.

¹ In semiconductors the carrier density (electrons and/or holes) is much lower, hence in this case the change of potential is also gradual in the electrode.

The structure at the electrode-electrolyte interface consisting of two layers or regions of opposite charge is called the *electrochemical double layer* (EDL). Considering the presence of cations and anions in the solution, the existence of the EDL is manifested by a space charge region in the electrolyte, where an excess charge of ions of opposite charge to the charge on the electrode can be found. The structure and properties of the EDL can be described by various models of increasing complexity (**Figure 3-7**), which have been put forward and refined since the mid-19th century¹. A unique property of the EDL, which also happens to be of technical relevance, is its capacitance. This means that it can be 'charged', and it can store the charge as an excess or deficiency of electrons in the electrochemical double layer capacitors (EDLC), also called supercapacitors or ultracapacitors, which employ electrodes containing high surface area carbon particles, which yields a very high interfacial area to the electrolyte (usually of the non-aqueous type).

The combination of metal electrode and (aqueous) electrolyte solution generally studied in this chapter reflects the importance of this type of electrified interface. Many reactions of practical importance are based on such a configuration. Also, it is the most straightforward setup for studying electrochemical fundamentals in the laboratory. However, the phenomenon of an electrified interface can also be found in other environments, some of which are also application relevant. A solid electrode may also be in contact with a molten salt electrolyte at high temperature (>600°C), such as in an Al electrolysis cell (cf. Chapter VII). In addition, there may be two immiscible electrolytes (an aqueous one and a non-aqueous one) in contact with each other. Furthermore, an electrified interface is formed when a membrane with 'fixed charges', a so-called ion exchange membrane, is in contact with a liquid electrolyte solution (cf. Chapter IV). Last but not least, we should not forget semiconductor electrodes and their unique electronic structure. Semiconductor electrochemistry and related subjects (e.g. photoelectrochemistry) are important scientific topics, but beyond the scope of this course.

3.1 Helmholtz model

The Helmholtz model describes a simple layer of counter-ions in the solution, located at a distance d from the surface of the electrode. This is referred to as rigid or compact double layer. It can be

¹ As we know from Section 2.1 each phase has a surface potential χ . If we bring together two phases, such as the electrode and electrolyte here, the change in Galvani potential φ across the interface is given by the difference in surface potentials $\Delta \chi = \chi_M - \chi_S$. This contribution is omitted in **Figure 3-7**. It would essentially lead to an offset of φ by $\Delta \chi$ very close to the interface. The double layer models discussed here were established before the concept of surface potential was introduced and studied in the 2nd half of the 20th century. In any case, we are primarily concerned about the distribution of the phase potential φ in the electrolyte solution.

thought of as an arrangement of charges like in a plate capacitor. The potential drops linearly from the value in the metal φ_M to the value in the electrolyte φ_S . Therefore, there is a constant electric field between the two layers of opposite charge. As the potential difference $\Delta \varphi = \varphi_M - \varphi_S$ increases, the number of charges in the double layer increases, which can be characterized by the charge density σ (unit: As/cm²]. The capacitance of the Helmholtz double layer C_H is given in analogy to the capacitance of a parallel plate capacitor:

$$C_{\rm H} = \frac{\sigma}{\Delta \varphi} = \frac{\varepsilon \varepsilon_0}{d} \tag{3-11}$$

where ε is the dielectric constant of the medium between the charged layers and ε_0 is the vacuum permittivity ($\varepsilon_0 = 8.854 \cdot 10^{-12}$ F/m). The distance d is the separation of the 'plates' of the capacitor. In our case, it is given by the distance of the center of counter-ions from the electrode surface. This is the radius of the ion plus the thickness of the solvent layer ('solvation shell', cf. Chapter IV) around the ion that remains intact when the ion approaches the electrode. As we will see below, in many cases the solvation shell can also be disrupted, when the ion has a strong chemical interaction with the electrode (Section 0, 'Specific adsorption'). The value of d is therefore on the order of a few Å. The plane on which the counter-ions are located in the solution is also called the *Helmholtz layer.* We can now estimate the Helmholtz capacity $C_{\rm H}$ by inserting a value of d of, say, 5 Å and for ε we take the dielectric constant of water at room temperature (78.3) and obtain $C_{\rm H} = 139 \,\mu \text{F/cm}^2$. Experimental values are in the range of 10 to 40 μ F/cm². The difference to the calculated value is explained as follows. The potential difference $\Delta \phi$ is in the range of 1 V, with the separation d of 5 Å an electric field strength $\Delta \phi/d$ of around 10⁹ V/m is obtained. Due to this extremely high electric field, the movement and rotation of the water molecules is restricted, which effectively reduces the dielectric constant of water. To obtain the experimental capacitance values mentioned, the dielectric constant is in the range from 6 to 20. This shows us that the environment of the water molecules is very different in the double layer and we cannot use properties of bulk water to describe its behavior.

3.2 Gouy-Chapman model

A more sophisticated model of the electrochemical double layer was developed at the beginning of the 20th century, at a time when statistical thermodynamics had been established. In the Gouy-Chapman model the thermal motion of ions in the electrolyte is taken into consideration. Therefore, we have two counteracting phenomena: the electrostatic force between the charge on the electrode and the ions in solution, and the entropy driven dispersal of ions. Therefore, the double layer extends further into the solution and is called *diffuse double layer* (Figure 3-7). As before, the metal is

assumed to be a perfect conductor. The local (Galvani) potential in the solution $\varphi(x)$ varies as a function of the distance x from the electrode surface. Far away from the electrode, the potential is assumed to be constant φ_8 in the bulk of the electrolyte. The concentration c_k of ion k at position x, averaged over a sufficiently large period of time ('statistical mechanics'), follows *Boltzmann statistics*, with the energy of the ion given by $z_k F \varphi(x)$:

$$c_k(x) = c_k^0 \exp(-\frac{z_k F}{RT}(\varphi(x) - \varphi_{\rm S}^\infty))$$
(3-12)

where we choose the concentration in the bulk c_k^0 and the corresponding potential φ_S^∞ there as reference. We introduce the deviation of the potential from the value in the bulk as $\Delta \varphi(x) = \varphi(x) - \varphi_S^\infty$. Since ions carry a charge, the local charge density $\rho(x)$ (unit: C/cm³) and the potential $\Delta \varphi(x)$ are related through *Poisson's equation*:

$$\frac{d^2 \Delta \varphi(x)}{dx} = -\frac{\rho(x)}{\varepsilon \varepsilon_0}$$
(3-13)

In analogy to the Helmholtz model, we assume that the solvent provides a continuum with dielectric constant ε , in which the ions can move freely. The charge density ρ is composed of the contribution of each ion *k* with $\rho_k = z_k F c_k$. With this and Eq. 3-12 by inserting into Eq. 3-13 we obtain the *Poisson-Boltzmann equation*:

$$\frac{d^2 \Delta \varphi(x)}{dx} = -\frac{F}{\varepsilon \varepsilon_0} \sum_k z_k c_k^0 \exp(-\frac{z_k F}{RT} \Delta \varphi(x))$$
(3-14)

To obtain an analytical solution we simplify our system and assume a z-z electrolyte. The result for the distribution of the potential $\Delta \varphi(x)$ in the double layer is then obtained after some tedious algebra (cf. for example Bard and Faulkner¹ or Schmickler² for details):

$$\frac{\tanh(zF\Delta\varphi(x)/4RT)}{\tanh(zF\Delta\varphi_0/4RT)} = \exp(-\kappa x)$$
(3-15)

¹ A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd Edition, Wiley, 2001

² W. Schmickler, E. Santos, Interfacial Electrochemistry, 2nd Edition, Springer, 2010

where $\Delta \varphi_0$ is the value of $\Delta \varphi$ at x = 0, i.e. at the electrode surface. The parameter κ is an important parameter with the dimension length⁻¹. Thus, its inverse has the unit of length and is called the *Debye length L*_D:

$$\kappa = \sqrt{\frac{2(zF)^2 c^0}{\varepsilon \varepsilon_0 RT}} = \frac{1}{L_{\rm D}}$$
(3-16)

The Debye length characterizes the screening length of the electrode charge in the solution. Or, in other words, it describes the distance over which the potential $\Delta \varphi$ drops to zero. We can see from Eq. 3-16 that its value depends on the dielectric constant, the temperature and, in particular, the concentration of the electrolyte. The higher the concentration c^0 , the smaller the Debye length L_D , hence the double layer is compressed. In aqueous solutions L_D is typically on the scale of a few nanometers. We can insert the constants into Eq. 3-16 and obtain at room temperature $\kappa = (3.29 \cdot 10^7) \cdot z \cdot (c^0)^{V_2}$ where c^0 is given in mol/L and κ in cm⁻¹. For z = 1 and a concentration of $c^0 = 0.01$ M we get $L_D = \sim 3$ nm. In **Figure 3-8a** sample profiles of $\Delta \varphi$ given by Eq. 3-15 are plotted for different values of $\Delta \varphi_0$. For small electrode charges $zF\Delta \varphi_0 \ll 4RT$, hence $\Delta \varphi \lesssim 80$ mV at room temperature for a 1:1 electrolyte, we obtain¹ the *Debye-Hückel* approximation:

$$\Delta \varphi(x) = \Delta \varphi_0 \exp(-\kappa x) \tag{3-17}$$

This solution, a simple exponential decay, is shown in Figure 3-8a as a dashed line.



Figure 3-8. (a) Potential profiles through the diffuse layer in the Gouy-Champan model for an aqueous 1:1 electrolyte at 25°C. The Debye length L_D of 30.4 Å corresponds to a concentration of 0.01 M. (adapted from A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd Edition, Wiley, 2001, p548) (b) Gouy-Chapman capacitance for an aqueous 1:1 electrolyte with different concentrations at 25°C. The horizontal red line indicates a typical experimental value of 20 μ C·cm⁻².

¹ for $x \ll 1$: tanh(x) $\approx x$

We are now interested in the charge density on the electrode σ_M (C/cm²), which is equal in magnitude but opposite in sign to the charge density in the solution σ_S . Again after some algebra (cf. for example Bard, Faulkner or Schmickler) we arrive at the following expression relating the surface charge σ to the potential drop $\Delta \varphi_0$ in the double layer:

$$\sigma_{\rm M} = -\sigma_{\rm S} = \sqrt{8RT\varepsilon\varepsilon_0 c^0} \sinh(\frac{zF}{2RT}\Delta\varphi_0) = \frac{2RT}{zF}\varepsilon\varepsilon_0\kappa\sinh(\frac{zF}{2RT}\Delta\varphi_0)$$
(3-18)

Again it is interesting to look at the limiting case of low $\Delta \varphi_0$, for which we obtain¹ from Eq. 3-18: $\Delta \varphi_0 = \sigma_M / \varepsilon \varepsilon_0 \kappa$. From the Poisson equation (Eq. 3-13) and the potential distribution (Eq. 3-17) we calculate the charge density in solution: $\rho(x) = -\varepsilon \varepsilon_0 \kappa^2 \Delta \varphi_0 \exp(-\kappa x) = -\sigma_M \kappa \exp(-\kappa x)$. We are interested in the (differential) capacitance of the double layer in the Gouy-Chapman model, which we obtain from Eq. 3-18:

$$C_{\rm GC} = \frac{d\sigma_{\rm M}}{d\Delta\varphi_0} = \varepsilon\varepsilon_0\kappa\cosh(\frac{zF}{2RT}\Delta\varphi_0)$$
(3-19)

Sample values of C_{GC} are calculated and plotted in **Figure 3-8b** for different electrolyte concentrations. We see that the capacitance shows a minimum at $\Delta \varphi_0 = 0$. This describes the situation where the potential in the electrolyte is uniform and the electrode surface is uncharged $(\sigma_M = 0)$. The potential of the electrode, at which it is uncharged, measured against some reference electrode, is called the *potential of zero charge* (PZC), E_{PZC} . For example, for Hg in NaF at r.t. it is -0.193 V vs. SHE². The minimum of GC is obtained from Eq. 3-19 at $\Delta \varphi_0 = 0$ as $C_{GC,min} = \varepsilon \varepsilon_0 \kappa$. This describes a plate capacitor with a separation distance of the 'electrodes' given by the Debye length $L_D = 1/\kappa$. The capacitance increases once the electrode potential difference or the Galvani potential difference of the metal to the value corresponding to the PZC, $E - E_{PZC} = \varphi_M - \varphi_{PZC}$.³

¹ for $x \ll 1$: $\sinh(x) \approx x$

² N. Eliaz, E. Gileadi, Physical Electrochemistry, 2nd Edition, Wiley-VCH, 2009, Table 3-12.1, p150

³ The Gouy-Chapman capacitance (Eq. 3-19) is given by the potential $\Delta \varphi_0 = \varphi(x=0) - \varphi_S^{\infty}$ in the electrolyte, whereas with a potentiostat we are adjusting the electrode potential $E - E_{PZC}$. In the first approximation, we can assume $E - E_{PZC} \approx \Delta \varphi_0$, i.e. the change in potential of the electrode translates to an identical change of the Galvani potential of the electrolyte at the interface. This corresponds to a constant surface potential difference $\Delta \chi$ between metal and solution. This is, however, not strictly true. The metal-solvent interaction modifies the surface potentials. An in-depth discussion is, however, beyond the scope of this text (for details, cf. for example Schmickler).

According to Eq. 3-19 and as shown in **Figure 3-8b**, the calculated values of the Gouy-Chapman capacitance are proportional to κ and, hence, inversely proportional to the Debye length L_D . At a concentration of $c^0 = 0.1$ M, L_D is ~3 Å for an aqueous 1:1 electrolyte at 25°C. This is the size range of hydrated ions. The Gouy-Chapman model does not take the finite size of ions into account but treats them at point charges. This means that the model only holds for rather dilute electrolytes with concentration $c^0 \leq 10^{-2}$ M. Therefore, for higher salt concentrations, the model is inaccurate and further refinement of the double layer model is called for.

3.3 Stern model

The Stern model is a combination of the Helmholtz and the Gouy-Chapman models. The Gouy-Chapman model overestimates the capacitance at large charge densities and electrolyte concentrations. This is a result of the assumption of point charges. This neglect of the finite size of ions is obviously unrealistic. Essentially, a solvated ion can approach the electrode surface only to a distance equal to its solvated radius *d* (**Figure 3-7**). Hence, the combination of the features of the Helmholtz and Gouy-Chapman models suggests itself, which was done by Stern. In the Stern model, there is a region of high electric field next to the electrode with firmly held counter-ions (Stern layer¹). Here, the dielectric constant of the solvent is significantly lower than its bulk value due to the restricted mobility. Beyond that is a diffuse layer according to the Gouy-Chapman description. The dielectric constant increases rapidly with distance in this region. The Galvani potential $\rho_{\rm S}$ varies linearly with distance within the Stern layer and then decreases approximately in exponential manner within the diffuse layer. The capacitance of the double layer in the Stern model $C_{\rm Stern}$ is therefore a series combination of a Helmholtz capacitance $C_{\rm H}$ and a Gouy-Chapman capacitance $C_{\rm GC}$:

$$\frac{1}{C_{\rm Stern}} = \frac{1}{C_{\rm H}} + \frac{1}{C_{\rm GC}}$$
(3-20)

The smaller of the two capacitances will govern the overall capacitance. The diffuse layer capacitance dominates when the solution concentration is low. The description by the Stern model, although still relatively simple, agrees fairly well with experimental data from a qualitative point of view (**Figure 3-9**). At low electrolyte concentration, the dip in capacitance around the PZC is clearly observed. In the Stern model, the capacitance is dominated by the diffuse layer in this region. At high electrolyte concentration ('high' meaning ≥ 0.01 M) or charge density, the capacitance is

¹ Actually, this is the same as the Helmholtz layer, except that in the Stern model not all of the excess charges in the solution are located in that layer.

dominated by the Helmholtz layer. Effectively, the size of solvated ions influences the thickness of the Helmholtz layer and thus the capacitance value.



Figure 3-9. (a) Differential capacitance *C* of the double layer in the Stern model, calculated from the combination of the diffuse layer capacitance C_{GC} in **Figure 3-8b** and a Helmholtz capacitance C_H of 20 μ F·cm⁻² according to Eq. 3-20. (b) Experimental capacitance for a non-specifically adsorbing electrolyte (adapted from A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd Edition, Wiley, 2001, p545 with original data from D.C. Grahame, Chem. Rev. 41(3), 1947, 441).

3.4 Specific adsorption

So far, we have treated the ions as solvated charged particles that can approach the electrode surface to a minimum distance given by the ionic radius and the dimensions of the solvation shell. In reality, many ions display a chemical interaction with metal surfaces, which leads to the phenomenon of *specific adsorption*. In this case, the concentration of a species at the interface is greater than can be accounted for by electrostatic interactions. The phenomenon is characterized in that the ion strips off part of its solvation shell and adsorbs directly on the electrode surface (**Figure 3-10a**). This is of particular importance for many anions, which have a weak hydration shell, hence the energy of solvation is overcome relatively easily by the energy of adsorption of the ion on the electrode. If, for example, we look at the different halide ions in aqueous solution, only fluoride, being relatively small and "hard" with a pronounced hydration shell¹, does not show the tendency towards specific adsorption. The trend to specific adsorption then increases from chloride to bromide and iodide with increasing ion size and decreasing charge density.

¹ although it is not as pronounced as for most metal cations.

The region next to the electrode in the resulting double layer is described by the *inner Helmholtz plane* (IHP), which is defined by the centers of the specifically adsorbed ions, and the *outer Helmholtz plane* (OHP) at greater distance, where the solvated ions are located. In this case, there are also solvent molecules adsorbed on the electrode surface. The presence of specifically adsorbed anions can lead to an overcompensation of the surface charge, which can result in a minimum of the potential at the distance of the IHP (**Figure 3-10b**).

Specific adsorption has important consequences on the electrochemical characteristics of the interface. On the one hand, adsorbed species may allow certain electrochemical reactions to happen. For example, the electrochemical oxidation of chloride to chlorine, $2 \text{ Cl}^- \rightarrow \text{Cl}_2 + 2 \text{ e}^-$, requires Cl^- to be adsorbed on the electrode surface before charge transfer occurs (cf. Chapter V). On the other hand, adsorbed species may block reaction sites at the electrode surface and hamper electrochemical reactions involving other species. For example, the adsorption of (bi)sulfate ions of sulfuric acid on the Pt electrocatalyst surface inhibits the electrochemical reduction of oxygen to water in the cathodic reaction of a fuel cell (cf. Chapter VII).



Figure 3-10. Electrochemical double layer model including specific adsorption according to Grahame (1947). (a) Double layer schematic showing specifically adsorbed ions at the inner Helmholtz plane (IHP) and solvated ions located at the outer Helmholtz plane (OHP). (b) Distribution of potential φ in the double layer upon change of the electrode potential in the case of specific adsorption. At the potential of zero charge E_{PZC} of the electrode, some anions are adsorbed, at $E > E_{PZC}$ the positive charge of the electrode is overcompensated by further anion adsorption at the IHP.

4 Electrode Types

We return to the situation where there are electrochemically active species present in our electrodeelectrolyte system. In general, there is a wide variety of different half-cell reaction types that are of interest and technical relevance. In addition to the $M \mid MX(aq)$ electrode and redox electrode, which we discussed in Section 1, there are a number of common classes of electrode processes, such as gas evolving or consuming electrodes (cf. chlor-alkali electrolysis in Chapter VI, and fuel cell reactions in Chapter VII), reactions leading to the formation of a new solid phase in or on the electrode (e.g., lead acid battery electrode reactions, Chapter VII) or insertion / intercalation reactions (as in the lithium-ion battery, Chapter VII). A common basic classification of reactions is according to electrodes of the first, second and third kind (Figure 3-11). In electrodes of the first kind a metal electrode is immersed in an electrolyte containing ions of the same metal, for example $Zn \mid Zn^{2+}(aq)$. In electrodes of the second kind, there is additionally a sparingly soluble salt comprising the metal cation deposited on the metal, as in Ag | AgCl(s) | Ag⁺(aq), Cl⁻(aq). The solubility product of AgCl is 1.96 · 10⁻¹⁰ M² at 25°C. Common reference electrodes are of this electrode type (cf. below). Electrodes of the third kind are redox electrodes, where there electrode is inert and does not participate in the electrochemical reaction between species in solution, e.g. Pt | $Fe^{2+}(aq)$, $Fe^{3+}(aq)$. Important types of electrodes and corresponding reactions will not be discussed here, except reference electrodes, but in connection with a corresponding application in the chapters to follow. Furthermore, there are non-aqueous, solid-state, molten salt or still other types of electrochemical systems, which are not treated explicitly here, but conceptually the topics discussed here can also be translated to those type of configurations.



Figure 3-11. Classification of electrodes with sample reactions given. (a) Electrodes of the first kind are electrodes of a metal M in contact with a solution containing ions of same metal M^{2+} . (b) Electrodes of the second kind are metal electrodes with a deposit of a sparingly soluble salt containing the metal cation. (c) Electrodes of the third kind (redox electrodes) are non-consumable electrodes with a redox couple in solution. This is but one classification, in practice there are many more types.

4.1 Reference electrodes

The difficulty of determining the electron energy ('potential') of an electrode in an electrochemical system has been discussed in Section 2.4. Although we may, in principle, find ways to determine the absolute potential of an electrode 'hosting' a half-cell reaction, it would certainly not be practical. Therefore, it electrochemistry electrode potentials are normally measured against a reference electrode. A reference electrode has a known and stable potential, which serves as a reference point, against which the potential of the working electrode, i.e., the electrode of interest, is measured. Therefore we establish the potential of an electrode by measuring the potential difference to the reference electrode. In Chapter II, we have introduced the hydrogen reference electrode. The standard hydrogen electrode (SHE) defines the origin of the electrochemical potential scale. A hydrogen reference electrode is, however, somewhat impractical, since it requires the use of hydrogen (a flammable, even explosive gas). Other half-cell reactions that yield a stable potential are preferred. In addition to having a defined potential, it should be stable, that is, it should not change when a small measurement current is passed through it. This type of electrode is called an ideal non-polarizable electrode (cf. also Chapter V). Moreover, its electrolyte should be compatible with the electrolyte under study. As we will see, some reference electrodes contain chloride ions, which may affect the reaction at the working electrode. Furthermore, the reference electrode potential should show a small or, ideally, no temperature dependence, and the compounds involved should not be toxic. The most widely used reference electrode, the calomel electrode (see below) is based on mercury, so certainly it fails this last requirement. In the following, we will introduce a selection of commonly used reference electrode types.



Figure 3-12. The silver-silver chloride (a) and calomel (b) electrode are widely used types of reference electrodes. (c) The schematic shows the functional principle of a reference electrode: through a defined half-cell reaction at equilibrium with a stable and robust electrode potential, the difference of the inner potential of the reference electrode (RE) and the solution (S) is effectively 'pinned' to a constant (yet *a priori* unknown) value.

An easy to use and widely employed reference electrode is the silver-silver chloride (Ag/AgCl) electrode. It is an electrode of the second kind, as it is based on Ag that is coated with a layer solid

AgCl in a chloride solution (Figure 3-12a). Its half-cell diagram is Ag(s) | AgCl(s) | Cl(aq). The element that is undergoing the redox reaction is silver:

$$Ag^{+}(aq) + e^{-} \leftrightarrows Ag(s)$$
 (3-21)

In addition, the solid AgCl is in chemical equilibrium with Ag⁺ and Cl⁻ ions in solution:

$$AgCl(s) \leftrightarrows Ag^{+}(aq) + Cl^{-}(aq)$$
(3-22)

The equilibrium constant is the solubility product $K_{sp}^{AgCl} = a(Ag^+) \cdot a(Cl^-)^1$. We can combine these two reactions to the following Ag/AgCl electrode reaction:

$$AgCl(s) + e^{-} \leftrightarrows Ag(s) + Cl^{-}(aq)$$
 (3-23)

The potential of the electrode is described by the equilibrium between Ag and Ag⁺ described by the Nernst equation (remember that a(Ag) = 1):

$$E_{Ag^{+}|Ag} = E_{Ag^{+}|Ag}^{\circ} + \frac{RT}{F} \ln(a_{Ag^{+}}) = \underbrace{E_{Ag^{+}|Ag}^{\circ} + \frac{RT}{F} \ln(K_{sp}^{AgCl}) - \frac{RT}{F} \ln(a_{Cl^{-}})}_{= \text{ const.}}$$
(3-24)

We can replace the activity of the silver-ions $a(Ag^+)$ by $K_{sp}^{AgCl} / a(Cl^-)$, and combine the constants to the standard electrode potential of the Ag/AgCl electrode $E_{Ag|AgCl|Cl^-}^{\circ}$. Its value is obtained from the Ag⁺/Ag standard electrode potential $E^{\circ}(Ag^+/Ag) = +0.7996$ V and the solubility product given above to give $E_{Ag|AgCl|Cl^-}^{\circ} = +0.2224$ V. This corresponds to a (hypothetical) chloride activity of 1. The resulting Nernst expression is:

$$E_{\text{Ag}|\text{AgCI}|\text{CI}^-} = E_{\text{Ag}|\text{AgCI}|\text{CI}^-} - \frac{RT}{F} \ln(a_{\text{CI}^-})$$
(3-25)

In practice, KCl supporting electrolyte is added to the solution. KCl(aq) has the advantage that the mobility of K⁺ and Cl⁻ ions is almost the same, which minimizes the diffusion potential if a liquid junction, such as a porous glass frit, is used to separate the electrolyte compartment of the Ag/AgCl electrolyte from the working electrolyte (cf. Chapter IV). Moreover, with the added KCl, the activity

¹ AgCl is a solid, hence a(AgCl) = 1

3-27

of the Cl⁻ ions is effectively adjusted, which determines the potential of the electrode according to Eq. 3-25. A commonly used KCl concentration in Ag/AgCl electrodes is 3.5 M. Often, a saturated KCl solution is used, with excess KCl crystals to maintain saturation. The potential of this saturated Ag/AgCl electrode is +0.1976 V at 25°C (**Table 3-1**).

Table 3-1. Selected reference electrodes and properties. The potential *E* is given vs. the standard hydrogen electrode (SHE) at 25°C. (Sources: https://www.edaq.com/wiki/Reference_Electrode_Potentials, accessed 02-Jul-2021; P. Spitzer, S. Wunderli, in: Handbook of Reference Electrodes, G. Inzelt, A. Lewenstam, F. Scholz (Eds.), Chapter 5, Springer, 2013; H. Kahlert, in: Electroanalytical Methods, F. Scholz et al. (Eds.), Chapter III.2, Springer, 2010)

Туре	Electrode reaction	Conditions	E vs. SHE	$\partial E / \partial T$		
			(V)	(mV/K)		
Hydrogen	$2 \text{ H}^+ + 2 \text{ e}^- \leftrightarrows \text{H}_2$	$a(H^{*}) = 1$	0^{a1}	0^{a2}		
		var. <i>a</i> (H⁺)	−0.059·pH ^{a3}			
Silver Chloride	$AgCl + e^{-} \leftrightarrows Ag + Cl^{-}$	$a(Cl^{-}) = 1$	+0.2224	-0.6		
		3.5 M KCl	+0.2046	-0.73		
		sat. KCl ^b	+0.1976	-1.01		
Calomel	$Hg_2Cl_2 + 2 e^- \leftrightarrows 2 Hg + 2 Cl^-$	$a(Cl^{-}) = 1$	+0.268			
		0.1 M KCl	+0.3337	-0.06		
		1.0 M KCl	+0.2801	-0.24		
		sat. KCl ^{b,c}	+0.2412	-0.65		
Mercurous sulfate ^d	$Hg_2SO_4 + 2 e^- \leftrightarrows 2 Hg + SO_4^{2-}$	sat. K ₂ SO ₄	+0.6513	-0.81		
Mercuric oxide	$HgO + H_2O + 2 e^- \leftrightarrows Hg + 2 OH^-$	1 M NaOH	+0.1077	-0.25		
Copper sulfate	$Cu^{2+} + 2 e^{-} \leftrightarrows Cu$	sat. CuSO ₄	+0.316			
al standard hydrogen electrode (SHE), $\mathbf{p} = 1$ ($\mathbf{p} = 1$ her						

a standard hydrogen electrode (SHE), pH 0 and $p(H_2) = 1$ bar_a

^{a2} the potential of the SHE is defined as 0 V at all temperatures

^{a3} reversible hydrogen electrode (RHE) (cf. Chapter II for details)

^b~4.2 M at 25°C

^c saturated calomel electrode (SCE)

^d mercurous sulfate electrode (MSE)

Another commonly used type of reference electrode of similar chemistry is the *calomel electrode* (**Figure 3-12b**). Calomel is Hg₂Cl₂, a paste-like solid that is an ingredient of this electrode type, along with metallic mercury and KCl solution. The schematic of the calomel electrode is: Pt | Hg(l) | Hg₂Cl₂(s) | Cl⁻(aq). In analogy to the Ag/AgCl electrode, the electrode reaction equation is:

$$Hg_2Cl_2(s) + 2e^- \implies 2Hg(s) + 2Cl^-(aq)$$
 (3-26)

Again, the potential of the calomel electrode is determined by the activity of the chloride ions:

$$E_{\rm Hg|Hg_2Cl_2|Cl^-} = E_{\rm Hg|Hg_2Cl_2|Cl^-} - \frac{RT}{F} \ln(a_{\rm Cl^-})$$
(3-27)

with $E^{\circ}_{\text{Hg}|\text{Hg}_2\text{Cl}_2|\text{Cl}^-} = +0.268 \text{ V}$ vs. SHE. Also in this case different concentrations are used in practice, the most common one being the saturated calomel electrode (SCE) with a potential of +0.2412 V at 25°C (**Table 3-1**). Owing to the high chloride concentration and low solubility

product, the concentration of Hg_2^{2+} in the solution is very small¹. The toxic nature of Hg is a shortcoming of the calomel electrode compared to the Ag/AgCl electrode.

A number of other commonly used reference electrodes are listed in **Table 3-1**. For temperatures other than 25°C, the coefficient $\partial E/\partial T$ can be used to calculate the potential. For a wide temperature window or more accurate values, corresponding tables can be consulted. It is important to note that the potential of the SHE is *defined* as zero at all temperatures. The reader is referred to Chapter II for an elaboration of the difference between the standard hydrogen electrode (SHE) and the reversible hydrogen electrode (RHE).

The unique characteristics of reference electrodes consisting of electrodes of the second kind allows the combination of two such electrodes with a common supporting electrolyte. One such cell, comprising a cadmium amalgam electrode and a mercurous sulfate electrode is the *Weston element* (For details, see **Appendix C**). It has a cell potential of 1.01864 V at 20°C. It used to be the basis of the definition of the unit Volt.

The stable potential of a reference electrode implies that there is a constant Galvani potential difference $\Delta \varphi$ between the electrode and the solution (**Figure 3-12c**). This is not only true for aqueous electrolytes but also for organic ones. Here, an example of a redox couple often used as a reference is the ferrocenium/ferrocene (Fc⁺/Fc) couple, say in acetonitrile. Its absolute potential on the vacuum scale has been calculated as +4.988 V². The value is obviously different in other non-aqueous solvents.

Other electrolyte classes call for different reference electrodes, which are compatible, stable and practical in the respective chemical environment. For example, in lithium-ion batteries (cf. Chapter VII), metallic lithium is often used as reference electrode, and potentials are given 'vs. Li^+/Li' . In solid-oxide electrolytes, the oxygen electrode is a straightforward and practical reference electrode, the potential being determined by the oxygen partial pressure that the oxygen electrode is exposed to (cf. Chapters IV, VII and VIII).

4.2 3-Electrode configuration

With a reference electrode, we can determine, monitor and control the electrode potential of a working electrode accurately, taking into consideration the precision of the reference electrode

¹ which is evidently a good thing, since it is poisonous, and we do not really want it in the solution.

² source: J. Chem. Theory Comput. 6, 2010, 2721

potential (determined, for example, by the temperature) and other phenomena related to the experimental setup, such as liquid junctions (cf. Chapter IV). We discuss in the following the typical experimental configuration for electrochemical measurements using solid electrodes in a liquid electrolyte (Figure 3-13). The electrode of interest is the *working electrode* (WE), its potential is measured against a reference electrode (RE). In order to study electrochemical reactions taking place at the WE, a *counter electrode* (CE) is needed to balance the electrons supplied to or taken from the WE with a corresponding reaction at the CE. The faradaic current flowing between the WE and the CE is measured as cell current, whereas the potential between the WE and the RE is only determined using a small measurement current, which is in the μA or nA range. This is the commonly used 3-electrode configuration for an electrochemical laboratory cell (Figure 3-13a). In order to probe the potential of the WE as accurately as possible, often a Luggin capillary is used, which is mostly a glass capillary filled with electrolyte, whose tip is placed around 1 mm from the surface of the WE. Because there is only negligible current flowing in the reference circuit, this placement avoids that the potential measured with the RE contains significant contributions of an ohmic drop in the electrolyte. Laboratory cells often also contain ports for bubbling the electrolyte with a gas (Figure 3-13b). In addition, the glassware may be double-walled to allow the circulation of heating fluid to control the temperature of the cell. The experimental setup typically used in the laboratory will be revisited in Chapter VIII.



Figure 3-13. (a) Schematic of a typical 3-electrode configuration used in the laboratory comprising working electrode (WE), reference electrode (RE), and counter electrode (CE). The potential of the WE is often probed with a Luggin capillary placed close to it. (source: P.W. Atkins, J. de Paula, Physical Chemistry, 8th Edition, W.H. Freeman & Co., 2006, Fig. 25.40, p939) (b) Example of a laboratory electrochemical cell (source: achema.sg).

Appendix A: Fermi Level and Half-Cell Reaction at Equilibrium

We have seen that when contact is established between two metals, at equilibrium their Fermi levels match (Figure 3-4). We can use the same concept to describe a half-cell reaction at equilibrium at an electrode-electrolyte interface. We consider the generic reaction $Ox + e^- \Rightarrow$ Red. Although we do not have free electrons in the solution obeying Fermi statistics, we can describe the equilibrium between the species Ox and Red in terms of the electrochemical potential of the electron $\tilde{\mu}_e$ (redox) associated with the redox couple, which is equivalent to the Fermi level $E_{\rm F}({\rm redox})$ in solution (differing in value by the factor N_A) (Gerischer model). We consider a redox electrode, for example Pt, to catalyze the electrochemical reaction, which we immerse into the electrolyte solution containing the redox couple Ox/Red. Initially both phases will carry no excess charge ($\psi = 0$). In this case, the Fermi level of the electrode of metal M, $E_{\rm F}^{\rm M}$, is given by its work function $\Phi_{\rm M}$: $E_{\rm F}^{\rm M}$ = $-\Phi_{\rm M}$. We also assign a work function $\Phi_{\rm redox}$ to the redox couple. Upon immersion of the electrode in the electrolyte containing Ox and Red, electrons will flow from the phase with higher $E_{\rm F}$ to the one with lower $E_{\rm F}$. In our example in Figure 3-A1a, electrons flow from the solution to the metal, i.e., Red is oxidized to Ox, until the Fermi levels align. The flow of electrons across the electrodeelectrolyte interface leads to the accumulation of net charge on the two phases, hence the metal and solution will develop a Volta potential ψ_{M} and ψ_{S} , respectively (Figure 3-A1b)¹.



Figure 3-A1. Electron energy diagram of an electrochemical half-cell reaction at the electrode-electrolyte interface, (a) before and (b) after establishment of the equilibrium, requiring that the Fermi levels in electrode and electrolyte align.

¹ Remember that the work function is unchanged upon charging of the phase, because it depends on the chemical potential of the electron μ_e in the respective phase and the surface potential χ of same phase. Both these quantities are not affected by the charge of the phase.

Once the Fermi levels align, we have: $E_F^M = E_F(\text{redox})$. We use the relation $-E_F = \Phi + e\psi$ to describe the equilibrium condition between metal M and solution S:

$$\Phi_{\rm M} + e\psi_{\rm M} = \Phi_{\rm S} + e\psi_{\rm S} \tag{3-A1}$$

We take Φ_S to mean Φ_{redox} , because the redox system Ox/Red involves an electron that can be thought to have a work function in the solution¹. We rearrange Eq. 3-A1 and obtain

$$\Phi_{\rm redox} = \Phi_{\rm M} + e(\psi_{\rm M} - \psi_{\rm S}) \tag{3-A2}$$

The work function of the electron associated with the redox couple Φ_{redox} is specific to its chemistry. The absolute electrode potential $E_{\text{abs}}(\text{redox})$ of a redox reaction at equilibrium is therefore defined based on this work function as $E_{\text{abs}}(\text{redox}) = \Phi_{\text{redox}} / e$ (Eq. 3-8 in the main text).

The electron work function of a redox couple in the electrolyte is a somewhat difficult notion to grasp. For the purpose of illustration, we consider the reaction $Fe^{3+} + e^{-} \leftrightarrows Fe^{2+}$ in a solution in contact with a metal, and suppose that the reaction is at equilibrium. We now transfer an electron from the solution via the vacuum to the metal in the following way (from W. Schmickler, E. Santos, Interfacial Electrochemistry, 2nd Edition, Springer, 2010, p32):

- 1. Take an Fe²⁺ ion from the solution into the vacuum above the solution; the work required is the negative of $\Delta_{sol}G(Fe^{2+})$, the Gibbs free energy of solvation of the Fe²⁺ ion.
- 2. Remove an electron from the Fe^{2+} ion, turning it into an Fe^{3+} ion; the work required is the third ionization energy I_3 of iron.
- 3. Put the Fe³⁺ ion back into the solution, and gain $\Delta_{sol}G(Fe^{3+})$.
- 4. Take the electron from just outside the solution across to a position just outside the metal; the work required is $-e(\psi_M - \psi_S)$
- 5. Take the electron to the Fermi level of the metal, and gain $-\Phi_M$ in energy.

The work function Φ_{redox} of the Fe³⁺/Fe²⁺ couple is then obtained by considering the energy steps 1-5 and inserting into Eq. 3-A2: $\Phi_{\text{redox}}(\text{Fe}^{3+}/\text{Fe}^{2+}) = (\Delta_{\text{sol}}G(\text{Fe}^{3+}) - \Delta_{\text{sol}}G(\text{Fe}^{2+}) + I_3) / N_A$, where we have taken $\Delta_{\text{sol}}G$ and I_3 to be expressed on a molar basis and Φ on a per particle basis.

¹ We assume the solution to contain no other electrochemically active species.

Appendix B: Representation of Full Cell with Fermi Levels at Equilibrium

Taking the arguments of Appendix A further, we look here at a description of the electron energy levels in the two electrodes of a full cell using the concept of Fermi level. We consider the left electrode to be a standard hydrogen electrode (SHE) and the right electrode to host an arbitrary redox reaction $Ox + e^- \Rightarrow$ Red (**Figure 3-B1**). At both electrodes, the half-cell reactions are at equilibrium, hence the Fermi levels in the metal and the solution are aligned. The Fermi level is equivalent to the electrochemical potential of the electron and thus expressed as $E_{\rm F} \cdot N_{\rm A} = \tilde{\mu}_{\rm e} = \mu_{\rm e} - F\varphi$. The Fermi level in the solution contains the contributions of the chemical potential of the electron associated with the respective half-cell reaction, $\mu_{\rm e,SHE}$ and $\mu_{\rm e,redox}$, and the Galvani potential in the solution $\varphi_{\rm S}$. Since we assume the same electrolyte phase S throughout the cell (we are neglecting liquid junction effects), $\varphi_{\rm S}$ is uniform in the electron $\mu_{\rm e,M}$ and $\mu_{\rm e,M'}$ and the Galvani potentials $\varphi_{\rm M}$ and $\varphi_{\rm M'}$, respectively. The cell voltage $E_{\rm cell}$ that can be measured between the two electrodes is:

$$-e E_{cell} = E_{F}(redox) - E_{F}(SHE) = E_{F}^{M'} - E_{F}^{M} = \frac{\mu_{c,M'}}{N_{A}} - e \varphi_{M'} - \frac{\mu_{c,M}}{N_{A}} + e \varphi_{M}$$
(3-B1)

or

$$E_{\text{cell}} = -\frac{1}{F} (\mu_{\text{e,M}'} - \mu_{\text{e,M}}) + (\varphi_{\text{M}'} - \varphi_{\text{M}})$$
(3-B2)



Figure 3-B1. Representation of the electron energy at equilibrium in an electrochemical full cell with two electrodes. The left electrode is a standard hydrogen electrode (SHE), and an electrochemical reaction $Ox + e^{-1} \Rightarrow Red$ is at equilibrium at the right electrode. The cell voltage E_{cell} that can be measured is given by the difference of the Fermi level of the two electrodes.

Only if the two electrodes are of the same metal, hence $\mu_{e,M'} = \mu_{e,M}$, is the cell voltage the difference of the Galvani potential of the electrodes:

$$E_{\rm cell} = \varphi_{\rm M} - \varphi_{\rm M} \tag{3-B3}$$

From Figure 3-B1 we can furthermore find that the equilibrium cell voltage E_{cell} is given by the difference of the chemical potential of the electron associated with the two redox couples:

$$E_{\text{cell}} = -\frac{1}{F} (\mu_{\text{e,redox}} - \mu_{\text{e,SHE}})$$
(3-B4)

Appendix C: Weston Element

The Weston element is an electrochemical cell made from two electrodes of the second kind immersed in a common electrolyte (**Figure 3-C1**). Therefore, it has a very stable potential, which was used as a voltage standard for most of the 20th century.



Figure 3-C1. Weston element in an H-type glass cell.

The negative electrode is a cadmium amalgam electrode in a saturated solution of CdSO4:

$$\operatorname{Cd}^{2+}(\operatorname{aq}) + 2 e^{-} \leftrightarrows \operatorname{Cd}(\operatorname{Hg})$$
 (3-C1)

The electrode is in contact with solid CdSO₄, which is actually not a sparingly soluble salt¹. Still, the potential of the electrode is determined by the solubility product and the activity of sulfate, since the electrolyte is a saturated solution of CdSO₄ in contact with solid CdSO₄ crystals at the electrode:

$$E_{\text{Cd}^{2+}/\text{Cd}} = E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} + \frac{RT}{2F} \ln(a_{\text{Cd}^{2+}}) = E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} + \frac{RT}{2F} \ln(K_{\text{sp}}^{\text{CdSO}_{4}}) - \frac{RT}{2F} \ln(a_{\text{SO}_{4}^{2-}}) \qquad (3-C2)$$

$$E_{\text{Cd}|\text{CdSO}_4|\text{SO}_4^{2^-}} = E_{\text{Cd}|\text{CdSO}_4|\text{SO}_4^{2^-}}^{\circ} - \frac{KI}{2F} \ln(a_{\text{SO}_4^{2^-}})$$
(3-C3)

The positive electrode is a mercurous sulfate reference electrode:

$$Hg_2SO_4(s) + 2e^{-} \quad \leftrightarrows \quad 2Hg(l) + SO_4^{2-}(aq) \tag{3-C4}$$

¹ solubility of CdSO₄ at 25°C: 76.4 g / 100 mL (en.wikipedia.org/wiki/Cadmium_sulfate)

Mercurous sulfate, Hg₂SO₄, is a salt with relatively low solubility¹. The potential of the electrode is given by:

$$E_{\text{Hg}_{2}^{2+}/\text{Hg}} = E_{\text{Hg}_{2}^{2+}/\text{Hg}}^{\circ} + \frac{RT}{2F} \ln(a_{\text{Hg}_{2}^{2+}}) = \underbrace{E_{\text{Hg}_{2}^{2+}/\text{Hg}}^{\circ} + \frac{RT}{2F} \ln(K_{\text{sp}}^{\text{Hg}_{2}\text{SO}_{4}}) - \frac{RT}{2F} \ln(a_{\text{SO}_{4}^{2-}}) \quad (3-C5)$$

$$E_{\text{Hg}|\text{Hg}_{2}\text{SO}_{4}|\text{SO}_{4}^{2-}} = E_{\text{Hg}|\text{Hg}_{2}\text{SO}_{4}|\text{SO}_{4}^{2-}}^{\circ} - \frac{RT}{2F} \ln(a_{\text{SO}_{4}^{2-}}) \quad (3-C6)$$

If we combine the two electrodes to form a cell, the Weston element, and calculate its potential, we see that the terms with the activity of sulfate, which are the same for both electrodes, cancel and the potential E_{Weston} is then only determined by the standard potentials of the two electrodes:

$$E_{\text{Weston}} = E_{\text{Hg}|\text{Hg}_2\text{SO}_4|\text{SO}_4^{2^-}}^{\circ} - E_{\text{Cd}|\text{CdSO}_4|\text{SO}_4^{2^-}}^{\circ}$$
(3-C7)

The cell potential is very stable and has a value of 1.018638 V at 20°C with a temperature coefficient of 40.6 μ V/K.² Using the cell notation, the Weston element is written as follows:

$$Cd(Hg, \omega=12.5) | CdSO_4(s) | CdSO_4(sat) | Hg_2SO_4(s) | Hg(1)$$
(3-C8)

¹ solubility of Hg₂SO₄ at 25°C: 51 mg / 100 mL (https://en.wikipedia.org/wiki/Mercury(I)_sulfate)

² source: en.wikipedia.org/wiki/Weston_cell

Chapter IV

Electrolytes

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Also in this chapter, we look at the functions of a main constituent of an electrochemical cell. In Chapter III we studied the general characteristics of electrodes, how the energy of the electrons contained within can be described, and how this leads to a difference in potential between the two electrodes. A continuous electrochemical reaction can, however, only take place with a suitable electrolyte forming an ionic bridge between the two electrodes.

The main role of the electrolyte in an electrochemical cell is to mediate the transport of ionic charges between the electrodes to allow the cell reaction to proceed in continuous manner. Therefore, for reasons of charge conservation, the ionic current in the electrolyte must be equal to the electronic current in the circuit¹ (**Figure 4-1a**). Whereas the electrodes constitute the electron conducting phase, the electrolyte is an ion conducting material. In many cases, reactants are transported to the electrodes via the electrolyte, or products are taken up. For example, in an aluminium smelter, Al₂O₃ is dissolved in a molten salt electrolyte and metallic Al is produced at the cathode (cf. Chapger VI). The electrolyte contains mobile charge carriers (= *ions*) that move under the influence of the electric field (cf. Chapter V). *Anions* are negatively charged ions and move towards the anode, *cations* are positively charged ions and move towards the cathode. Metal ions in solution, Me^{z+}, are common cations in many applications. We have to be aware, though, that metal ions can form complexes that have a different charge than the bare metal cation. For example ferric ions, Fe³⁺, form the complex [Fe(CN)₆]³⁻ (ferricyanide).



Figure 4-1. (a) Schematic of an electrochemical cell indicating the role of the electrolyte as ion conductor. During steady-state cell operation, the ionic current I_i is equal to the electronic current I_c . (b) The resistance of the electrolyte is dependent on its geometry, characterized by the spacing of the electrodes L and their surface area A.

¹ Note on terminology: 'electric current' encompasses both ionic and electronic current.

The transport of charge carriers in the electrolyte is associated with friction losses, which we measure as a resistance (unit: Ohm = Ω). In analogy to an electronic circuit, the voltage ΔU or potential drop across a resistor is proportional to the current *I*:

$$\Delta U_{\Omega} = I \cdot R \tag{4-1}$$

This is *Ohm's law*. To minimize this 'ohmic drop' in the electrolyte, the ionic transport should proceed 'easily', i.e. with low resistance. The resistance of the electrolyte against the flow of charge leads to waste heat production in the cell¹. The heat Q produced in the resistor per time (unit: J/s = W) is given by

$$\frac{dQ}{dt} = P_{\Omega} = \Delta U_{\Omega} \cdot I = R \cdot I^2$$
(4-2)

This is *Joule's law*. The material property that describes the 'ease' with which ions can move through the electrolyte is the resistivity ρ , which is the inverse of the conductivity σ . These quantities are defined as follows:

$$\frac{1}{\rho} = \sigma = F \cdot \sum_{k} |z_{k}| \cdot c_{k} \cdot u_{k}$$
(4-3)

Each ion type *k* contributes with its charge z_k , concentration c_k (unit: mol/L), and mobility u_k (unit: $m^2 \cdot V^{-1} \cdot s^{-1}$) to the overall conductivity of the electrolyte. As we will see below, the mobility is not a constant but decreases with concentration, because the moving ions increasingly impair each other's movement. The unit of resistivity is Ω ·cm, that of the conductivity $\Omega^{-1} \cdot cm^{-1} = S \cdot cm^{-1}$, where *S* is the unit 'Siemens' (inverse Ohm).

How do we get from the resistivity / conductivity to the resistance? The resistance R of the electrolyte depends on its geometry (**Figure 4-1b**). The resistance of a block or prismatic shape is proportional to its length L in the direction of current flow and inversely proportional to the cross-sectional area A:

¹ In some cases the heat generation in the electrolyte is used to maintain a high cell temperature, such in the Al-electrolysis cell (Hall-Héroult process), cf. Chapter VI.

4-4

$$R = \rho \cdot \frac{L}{A} = \frac{1}{\sigma} \cdot \frac{L}{A} \tag{4-4}$$

In a measurement cell to determine the conductivity / resistivity, L/R is called the 'cell constant', because it is determined by its geometry. If we consider the current density i = I/A, we express the ohmic drop by $\Delta U_{\Omega} = i \cdot R_a$, where $R_a = R \cdot A$ is the *area specific resistance* or *area resistance* (unit: $\Omega \cdot cm^2$). In the characterization of some electrochemical cells, e.g., fuel cells, it is common to specify the area resistance of the electrolyte, because multiplying it by the current density yields directly the ohmic voltage drop. Note that the unit is not Ω/cm^2 but $\Omega \cdot cm^2$, because the resistance *R* is inversely proportional to the area *A* (Eq. 4-4).¹ The relation to the conductivity and resistivity is then

$$R_{\rm a} = \rho \cdot L = \frac{L}{\sigma} \tag{4-5}$$

We wish to furthermore develop a 'differential' expression of Ohm's law connecting the current density *i* to the conductivity σ , which will be useful in later chapters. For this, we insert Eq. 4-4 into Eq. 4-1, introduce the current density i = I/A and divide both sides by *L*. The ohmic drop ΔU_{Ω} divided by *L* is the electric field *E* (unit: V/m), the driving force for charge flow². Therefore, we obtain for the current density:

$$i = \sigma \cdot E = -\sigma \cdot \nabla \varphi \tag{4-6}$$

The electric field *E* at a given location is the negative gradient of the electric potential φ at that point: $E = -\nabla \varphi$. This means that cations (+ charge) are moving from high to low potential, i.e., down the potential gradient, and vice-versa for anions (- charge). Eq. 4-6 holds for any point in a phase, even if the conductivity is a function of position³.

The resistance of the electrolyte is in most cases dominating the ohmic resistance of an electrochemical cell, because its ionic conductivity is much smaller than the electronic conductivity of the electrode phase. Nevertheless, in some cases, cell components other than the electrolyte or

¹ The area resistance relates to the resistance like the current density relates to the current, in the sense that the values are normalized to the area.

² Explicitly: $\Delta U_{\Omega} = IR = \frac{1}{\sigma} \cdot \frac{L}{A} \cdot I$. With i = I/A and dividing by L yields $\frac{\Delta U_{\Omega}}{L} = E = \frac{i}{\sigma}$.

³ Actually, we should write the electric field as a vector **E**, as well as the current density **i**. Furthermore, for an anisotropic conductor, for example a solid electrolyte with layer structure, we have to introduce the conductivity tensor σ .

contact resistances can contribute significantly to the ohmic resistance of the cell. In polymer electrolyte fuel cells, for example, there is a contact resistance between the gas diffusion layer and the flow field plate (cf. Chapter VII) of about 25 m Ω ·cm².¹

category	sub-category	example	electrolyte	charge carrier(s)
	aqueous	lead-acid battery	H ₂ SO ₄ (aq.)	$\mathrm{H}^{+},\mathrm{HSO}_{4}^{-}$
liquid	non-aqueous	Li-ion battery	non-aq. solvent + salt	Li ⁺ , anion
•	molten-salt	Al-electrolysis	fused salt (cryolite)	Al ³⁺ , O ²⁻ ,
	IX ^a membrane	chlor-alkali electrolysis	cation exchange mem.	Na^+
polymer	salt-in polymer	LiPo battery	PEO+Li-salt(+solvent)	Li ⁺ , anion
solid	oxide	solid oxide fuel cell	oxide ceramic	O ²⁻
	other	solid state Li-batt.	sulfide	Li ⁺

Table 4-1. Classification of electrolytes

^a ion-exchange membrane

There is a wide range of different electrolytes, which can be categorized into different classes (**Table 4-1**). Here, we will study following types in some detail to develop an understanding of key features, characteristics and requirements: aqueous electrolytes, polymer electrolytes and solid state ion conductors. Although technically important, non-aqueous electrolytes (used for example in lithiumion batteries) and molten salts (used in Al-electrolysis) will not be covered. The charge transport in the various electrolytes, dissolved salts place via different *ionic charge carriers*. In aqueous or organic electrolytes, dissolved salts yield mobile hydrated / solvated ions. In crystalline solids, charge transport is related to the mobility of defects in the crystal lattice. In molten salts, all the constituent ions are mobile and carry charge. In many technical applications, the transport of certain ions is desired, whereas the movement of other ions is sought to be minimized. For example, in Liion batteries using a liquid electrolyte, we want the lithium-ion, Li^+ , to move between the electrodes, because it takes part in the electrochemical reaction. In reality, however, the counter ion (e.g., PF_6^-) moves as well, which can lead to undesired polarization effects.

Example:

A water-swollen proton exchange membrane (cf. Section 2.3) used in a water electrolyzer has a conductivity of $\sigma = 100 \text{ mS/cm}$ and a thickness of $L = 150 \text{ }\mu\text{m}$. To obtain the area resistance, we insert into Eq. 4-5 and obtain $R_a = L / \sigma = 0.15 \Omega \cdot \text{cm}^2$. Assuming that the electrolyzer operates at a current density of 2 A/cm², this will yield an ohmic drop of $\Delta U_{\Omega} = 0.3 \text{ V}$.

H.A. Gasteiger et al., in: Handbook of Fuel Cells - Fundamentals, Technology and Applications, Vol. 3,
 W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.), John Wiley & Sons, Chichester, 2003, 593-610
1 Aqueous Electrolytes

Water based electrolytes are by far the most common. Many batteries employ an aqueous electrolyte, such as the common primary (non-rechargeable) alkaline battery or the secondary (rechargeable) lead-acid battery (cf. Chapter VII). Furthermore, important industrial electrochemical conversion processes are based on aqueous electrolytes. For example, alkaline water electrolyzers use a ~30% KOH solution. Its conductivity is in the range of 0.5 S/cm at room temperature. For comparison, the conductivity of sea water with a salt content of ~3.5 m-% is ~50 mS/cm, and that of tap water 50 μ S/cm. For comparison, copper has a conductivity (electronic) of $6 \cdot 10^5$ S/cm. Even the conductivity of 316L stainless steel, which has a relatively poor conductivity for a metal, of 10^4 S/cm is still several orders of magnitude above the value for the best-known aqueous electrolytes. Deionized water has a conductivity of $<1 \mu$ S/cm, high purity water for the analytics laboratory $<0.1 \mu$ S/cm. If one were to remove all ions from water, one would be left only with protons, H⁺, and hydroxide ions, OH⁻, with a concentration of 10^{-7} M at room temperature, formed through the autoprotolysis of water. These cause the intrinsic conductivity of water of 0.055 μ S/cm at 25°C (see below). This corresponds to a specific resistivity of 18.2 MΩcm.

1.1 Strong electrolytes

The mechanism of ionic conduction in aqueous electrolytes is based on the presence of dissolved ions in the water, which is the solvent. The ions move under the influence of an electric field (cf.



Figure 4-1. (a) Conductivity of selected electrolyte solutions at room temperature as a function of concentration. HAc = CH_3COOH (acetic acid) is a weak electrolyte, all other compounds are strong electrolytes. (b) Schematic representation of the inner hydration shell around an anion and a cation. The partial charges in the water molecule are indicated, forming a dipole.

above), yielding an ionic current. The ions originate from compounds that, when dissolved in water, yield mobile ions of opposite charge: anions (negatively charged ions) and cations (positively charged ions). In strong electrolytes¹, the dissolved compound dissociates or ionizes completely into anions and cations. Soluble salts are strong electrolytes, such as NaCl or CuSO₄, as well as strong acids, e.g. HCl, and bases, e.g., NaOH. The concentration of solute in a solution is given by its molarity (unit: mol/L = M, L = volume of solution), molality (unit: mol/kg, kg = mass of solvent), or mass fraction (unit: mass-%). The conductivity of an electrolyte generally increases with the concentration of the solute up to a point where the solubility limit is reached or the conductivity goes through a maximum and starts to drop with further increase of the concentration (Figure 4-**3a**). In the low concentration region, the conductivity of strong electrolytes appears to follow a linear increase with concentration. This can be understood with the help of Eq. 4-3. If the ion mobility uis constant, the conductivity σ is proportional to the concentration c of the dissolved ionic species. However, the ion mobility is not a constant, as we can see qualitatively. At elevated concentration, it decreases strongly. To understand this, we have to look at the hydration sphere² of ions in solution (Figure 4-3b). The water molecules around the dissolved ions are oriented according to their dipole. The oxygen is pointing away from anions and toward cations. The first layer of water molecules forms the relatively rigid inner hydration sphere (or 'shell'). The mobility of H₂O is strongly restricted here. Beyond is the outer hydration sphere, which is more loosely bound, and the orientation of the water molecules is more disordered. Figure 4-3b also indicates that cations tend to have more water molecules in their inner hydration shell than anions. This is a result of their generally smaller ionic radius and, therefore, higher charge density.³ At low concentration of an electrolyte, the ions are sufficiently far apart for their hydration spheres not influence each other. Therefore, the ion mobility is nearly constant. With increasing concentration, however, the hydration spheres start to influence each other and overlap, which impairs the mobility of the ions. This effect can become so strong that the conductivity goes through a maximum and then decreases again (if a further increase in concentration is not limited by the solubility). At very high electrolyte concentration, ions may not be regarded as separate entities anymore due to the lack of water separating them (ion association, see below). Also, for example in the case of sulfuric acid, high concentrations of H₂SO₄ and low concentration of H₂O disfavor the ionization of the acid. In pure H₂SO₄ less than 0.1% of molecules are dissociated.

¹ The term 'electrolyte' is somewhat ambiguous, since it can mean the compound that is dissolved, e.g. NaCl, as well as the solution that is formed, or, in the broader sense, any ionically conducting phase.

² The term 'hydration' refers to water as solvent. In general and for non-aqueous solvents the term 'solvation' is used.

³ Solutions of metal aquo complexes are acidic owing to the ionization of the water ligands. The deprotonation reduces the charge of the complex, such as in the following example for Cr(III): [Cr(H₂O)₆]³⁺ ≒ [Cr(H₂O)₅(OH)]²⁺ + H⁺ The chromium(III) aquo complex has a pK_a of 4.3.



Figure 4-3. (a) Molar conductivity of different electrolyte solutions at 25°C divided by the equivalence number $v_{\pm} |z_{\pm}|$ (termed 'equivalent conductivity'). All compounds except acetic acid are strong electrolytes. The linear dependence on the square root of concentration is Kohlrausch's law (Source: C.H. Hamann, A. Hamnett, W. Vielstich, Electrochemistry, 2nd Edition, Wiley-VCH, 2007, Fig. 2.10, p25). (b) Schematic representation of the two transport mechanisms of protons in water.

As we can see from **Figure 4-3a**, in a dilute solution the conductivity σ is approximately proportional to the concentration *c*. We can therefore define a new quantity, the *molar conductivity* Λ_m :

$$\sigma = \Lambda_{\rm m} \cdot c \tag{4-7}$$

A detailed experimental analysis, however, shows that even at low concentration the molar conductivity is not independent of concentration. If it is plotted as a function of \sqrt{c} a linear relationship is found (**Figure 4-3a**). This relationship is universal for strong electrolytes and was first described by Kohlrausch in 1900. Therefore we can write:

$$\Lambda_{\rm m} = \Lambda_{\rm m}^0 - A\sqrt{c} \tag{4-8}$$

where Λ_m^0 is termed the *limiting molar conductivity*, i.e., the molar conductivity at infinite dilution. The decrease of the molar conductivity with concentration has to do with the growing electrostatic interaction between ions. We see from the data that the value of the slope *A* in Eq. 4-8 is larger for electrolytes that dissociate into more highly charged ions. Intuitively, this makes sense since interionic interactions will be stronger in this case.

The values of the (limiting) molar conductivities of strong electrolytes comprise contributions from both the anions and the cations. It is also Kohlrausch who put forward the law of independent migration of ions: in dilute solutions where interionic interactions are small, the individual ions migrate essentially independently of each other. Therefore, we can write the limiting molar conductivity Λ_m^0 as a sum of the contributions from the anions and the cations:

$$\Lambda_{\rm m}^0 = \nu_+ \cdot \lambda_+ + \nu_- \cdot \lambda_- \tag{4-9}$$

where v_+ and v_- are the stoichiometric factors, and λ_+ and λ_- the *limiting molar conductivities of the single ions*. A collection of molar conductivities for some common cations and anions is given in **Table 4-2**.

Table 4-2. Molar conductivities λ (Source: CRC Handbook of Chemistry & Physics. 88th ed., CRC Press, 2007) of ions at infinite dilution at 25°C. The mobility and diffusivity are calculated using Eqs. 4-10 and 4-21, respectively. Ac⁻ = acetate.

cations	λ+	и+	D +	anions	λ-	u-	D-
	(S·cm ² ·mol ⁻¹)	(cm ² ·V ⁻¹ ·s ⁻¹)	(cm ² ·s ⁻¹)		(S·cm ² ·mol ⁻¹)	(cm ² ·V ⁻¹ ·s ⁻¹)	(cm ² ·s ⁻¹)
H^{+}	350	$3.63 \cdot 10^{-3}$	9.31·10 ⁻⁵	OH-	198	$2.05 \cdot 10^{-3}$	$5.27 \cdot 10^{-5}$
Li ⁺	38.7	$4.01 \cdot 10^{-4}$	$1.03 \cdot 10^{-5}$	F-	55.4	$5.74 \cdot 10^{-4}$	$1.47 \cdot 10^{-5}$
Na^+	50.1	$5.19 \cdot 10^{-4}$	$1.33 \cdot 10^{-5}$	Cl-	76.3	$7.91 \cdot 10^{-4}$	$2.03 \cdot 10^{-5}$
K^+	73.5	$7.62 \cdot 10^{-4}$	$1.96 \cdot 10^{-5}$	Br⁻	78.4	$8.13 \cdot 10^{-4}$	$2.09 \cdot 10^{-5}$
Mg^{2+}	106	$5.49 \cdot 10^{-4}$	$7.05 \cdot 10^{-6}$	NO ₃ -	71.4	$7.40 \cdot 10^{-4}$	$1.90 \cdot 10^{-5}$
Ca^{2+}	119	$6.17 \cdot 10^{-4}$	$7.92 \cdot 10^{-6}$	CO32-	166	$8.60 \cdot 10^{-4}$	$1.10 \cdot 10^{-5}$
Cu^{2+}	107	$5.54 \cdot 10^{-4}$	$7.12 \cdot 10^{-6}$	SO4 ²⁻	160	$8.29 \cdot 10^{-4}$	$1.06 \cdot 10^{-5}$
Al^{3+}	189	$6.53 \cdot 10^{-4}$	$5.59 \cdot 10^{-6}$	PO4 ³⁻	279	$9.60 \cdot 10^{-4}$	$8.22 \cdot 10^{-6}$
Fe ²⁺	108	$5.60 \cdot 10^{-4}$	$7.19 \cdot 10^{-6}$	ClO ₄ -	67.3	$6.98 \cdot 10^{-4}$	$1.79 \cdot 10^{-5}$
Fe ³⁺	204	$7.05 \cdot 10^{-4}$	$6.03 \cdot 10^{-6}$	Ac-	40.9	$4.24 \cdot 10^{-4}$	$1.09 \cdot 10^{-5}$

By comparing Eq. 4-7 with Eq. 4-3, we can relate the molar conductivity λ to the mobility *u*:

 $\lambda = |z| F u \tag{4-10}$

The molar conductivity describes the ease of ion transport of an ensemble of particles (hence the unit 'per mol'), whereas the mobility describes this property on a 'per particle' basis. The relationship to the diffusivity D will be derived in Section 1.4.

Example:

We calculate the limiting molar conductivity of dilute sulfuric acid. At low concentration, H₂SO₄(aq). dissociates into 2 H⁺ and 1 SO₄²⁻ ions. We can therefore calculate the limiting molar conductivity of sulfuric acid as $\Lambda^0 = (2\cdot350 + 1\cdot160)$ S·cm²·mol⁻¹ = 860 S·cm²·mol⁻¹, which agrees well with the data in **Figure 4-3a** if we divide the value by the equivalence number ($\nu_{\pm} \cdot z_{\pm} = 2$).

Based on the values of λ for the different ions in **Table 4-2** we can discuss several aspects. The extraordinary high mobility of protons is striking. Protons in water do not exist in 'naked' form, obviously, they are attached to one or several water molecules, to form *hydronium* ions, H₃O⁺, *Zundel* ions, H₅O₂⁺, or *Eigen* ions, H₉O₄⁺. The association of the proton with H₂O molecules is very dynamic, hence H⁺ can hop ('tunnel') rapidly from one H₂O molecule to the next. In a cascade of H⁺ jumps driven by a potential gradient combined with H₂O rotation, the protonic charge can therefore be transported much more rapidly than a single H⁺ can move. This charge transport via *structural diffusion* also referred to as *Grotthus mechanism* is based on the rearrangement of the hydrogen bond network, which leads to the net movement of the protonic charge. The diffusivity *D* of H⁺ in water of 9.31 · 10⁻⁵ cm²/s at room temperature is about 4 times higher than the diffusivity of H₂O (2.25 · 10⁻⁵ cm² s⁻¹). Proton transport in water is a combination of the two mechanisms (**Figure 4-3b**). A similar mechanism is at work in the transport of OH⁻. Differences between the mobilities of H⁺ and OH⁻ are traced to differences in the hydration structures and dynamics, and different jump barriers.

When comparing the mobility of the different alkali ions, we see that the value increases with the size of the ion from Li^+ to K^+ . This is somewhat counterintuitive, since we would expect smaller ions to move more easily (cf. Stokes' law in Section 1.4). The reason has to do with the hydration sphere, which decreases in size from Li^+ to K^+ due to the decreasing charge density on the ion. Consequently, the hydrodynamic radius of ion plus hydration shell decreases as well and, thus, the mobility increases. A similar effect is seen for the halide ions, but it is less pronounced, because anions generally have a smaller hydration shell due to their larger size compared to the cations in the same period.

Finally, we also notice the effect of ion charge. The higher the charge of an ion, the more current is associated to its movement, hence the larger the molar conductivity.

1.2 Weak electrolytes

Whereas strong electrolytes dissociate or ionize completely into anions and cations, weak electrolytes have a finite degree of dissociation, such as weak Brønsted acids and bases, e.g. acetic acid and ammonia. As an example, we look at an acid HA and its conjugate base A⁻:

$$HA \stackrel{\leftarrow}{\Rightarrow} H^+ + A^- \tag{4-11}$$

The activity of involved compounds is given by the law of mass action:

$$K_{a} = \frac{a(\mathrm{H}^{+}) \cdot a(\mathrm{A}^{-})}{a(\mathrm{HA})}$$
(4-12)

where K_a is the acid dissociation constant. The acid strength is typically tabulated as $pK_a = -\log(K_a)$. If for simplicity we use concentrations instead of activities and assume a total concentration of HA and A⁻ of c_{tot} , we can introduce the degree of dissociation α and write $c(H^+) = c(A^-) = \alpha \cdot c_{tot}$ and $c(HA) = (1-\alpha) \cdot c_{tot}$. Inserting into Eq. 4-11 we obtain

$$K_{\rm a} = \frac{\alpha^2}{1 - \alpha} \cdot \frac{c_{\rm tot}}{c_0} \tag{4-13}$$

with $c_0 = 1$ M. For increasing concentration c_{tot} , the degree of dissociation α decreases. We can now write for the conductivity

$$\sigma = \alpha c_{\text{tot}} (\lambda_{+} + \lambda_{-}) = \alpha c_{\text{tot}} \Lambda_{\text{m}}$$
(4-14)

In the case of acetic acid, we have a decrease in the molar conductivity with concentration that is much more pronounced compared to strong electrolytes (**Figure 4-3a**). This is a consequence of the low degree of dissociation of acetic acid owing to its weak acid characteristic ($pK_a = 4.76$).

Example:

We estimate the conductivity of acetic acid at a concentration of 0.01 M. To start with, considering its pK_a of 4.76 we assume that the degree of dissociation is small at this low concentration and assume 1- $\alpha \approx 1$. From Eq. 4-11 we obtain $\alpha \approx \sqrt{K_a / (c_{tot} / c_0)} = 4.17\%$. With this, we calculate a molar conductivity of $\Lambda_m = \alpha \cdot (\lambda_{H^+} + \lambda_{Ac^-}) = 16.3 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, which agrees well with the value in **Figure 4-3a**. This yields a conductivity of $\sigma = \Lambda_m \cdot c_{tot} = 0.16 \text{ mS/cm}$.

1.3 Ion aggregation

The effective separation of anions and cations in an electrolyte is a prerequisite for the development of ionic charge carrying entities. Water has a strong dipole moment and, hence, a high dielectric constant. Therefore, ions are typically well hydrated in water, except at high electrolyte concentration where the number of water molecules available to for the hydration shells becomes limiting. Most non-aqueous solvents are much less polar than water. Therefore, due to their low dielectric constant they do not have the 'power' to separate charges very effectively. The dielectric constants of a number of common solvents are listed in **Table 4-3**.

https://depts.washington.edu/eooptic/linkfiles/ dielectric_chart[1].pdf) solvent ε

Table 4-3. Dielectric constants ε of various solvents at 20°C. (Source:

solvent	3
ethylene carbonate	89.6
water	80.1
dimethylacetamide	37.8
acetonitrile	37.5
methanol	32.7
acetone	20.7
1,2-dimethoxyethane	7.2
1,4-dioxane	2.25

The *solvation* shell in low- ε solvents is therefore much weaker than in water. This can lead to the phenomenon of *ion association*. If ions are insufficiently separated, they can form various types of ion pairs and ion aggregates (**Figure 4-4**). This obviously impairs the ability of the electrolyte to transport ionic charges. Also, depending on the composition of the ion aggregate, an ion might actually move in the 'wrong' direction. Consider, for example, an ion aggregate formed by a cation M^+ and two anions X^- . The resulting ion aggregate $[AX_2]^-$ is negatively charged and under the influence of an electric field will move towards the anode. The cation M^+ , if properly solvated, will obviously move towards the cathode. This situation can for instance be found in the electrolyte of lithium-ion batteries. Electrolytes used in lithium-ion batteries typically consist of an organic solvent or solvent mixtures, such as ethylene carbonate (EC) and dimethoxyethane (DME), plus a lithium salt, for example LiPF₆. EC has a high dielectric constant and is able to solvate the ions well, yet its viscosity is rather high. On the other hand DME has a low ε , its ability to solvate ions is poor, but it has a low viscosity. With a mixture of EC and DME, a favorable combination between the properties of these two solvents is obtained.



Figure 4-4. Schematic illustration of various manners of ion association. IP = ion pair. Anions and cations are depicted as red or blue spheres, respectively, solvent molecules as green ellipses (Source: Batteries 4, 2018, 62).

1.4 Molar conductivity, mobility & diffusivity

In this section we will be looking at ways to describe the transport of ionic charges in an electrolyte using the concepts of molar conductivity, mobility and diffusivity, and form relationships between those quantities. To start with, we consider the forces acting on an ion with charge z > 0 with its solvation sphere moving with constant drift velocity v in a solution where there is an electric field *E* driving charge transport (**Figure 4-5**).



Figure 4-5. Force balance on an ion in solution moving with constant drift velocity v.

The force exerted on the particle¹ by the electric field is

$$F_e = zeE \tag{4-15}$$

with *e* the elementary charge. The movement of the ion creates a viscous drag force F_d , which we describe using Stokes' law, which has been established for macroscopic spherical particles.

$$F_{\rm d} = 6\pi\eta r v \tag{4-16}$$

The force is governed by the (dynamic) viscosity η of the solution and the radius *r* of the particles. Note that this is not the ionic radius but the effective hydrodynamic radius of the ion plus its hydration shell. For example, we recall from the discussions above that the hydrodynamic radius of the alkali ions decreases from Li⁺ to Na⁺ and K⁺. We now assume the ion depicted in **Figure 4-5** to move with constant drift velocity *v*. Therefore, the driving force for migration F_e is equal to the drag force F_d , and the drift velocity *v* is proportional to the electric field *E*. The proportionality constant is the mobility *u*, which is then defined by

$$u = \frac{v}{E} = \frac{ze}{6\pi\eta r} \tag{4-17}$$

¹ This picture of forces acting on a particle is evidently a macroscopic view, yet given a sufficiently large number of particles, we thus describe the average behavior of the *ensemble*.

The unit of the mobility is $m^2 \cdot s^{-1} \cdot V^{-1}$. We recall the relationship between molar conductivity λ and mobility *u* (Eq. 4-10). Obviously, the Stokes model of a hard sphere in a fluid continuum is of limited accuracyfor the description of an ion in a solvent whose molecules are of roughly equal size. Nevertheless, we can get an idea of the 'effective', i.e. hydrodynamic, radii of ions by taking measured conductivity values and using Eqs. 4-10 and 4-17 to calculate *r*.

Example:

From the mobility values in **Table 4-2**, we calculate the hydrodynamic radii r_h of Li⁺, Na⁺ and K⁺ and compare the obtained values to their ionic radii r_i of 60, 95 and 130 pm (source: R.G. Compton, H.W. Sanders, Electrode Potentials, Oxford Chemistry Primers, 1996, p49), respectively. The viscosity of water at 25°C is 0.89 mPas. From Eq. 4-17 we obtain the values for r_h of 240, 180 and 130 pm for Li⁺, Na⁺ and K⁺. We see that the hydration of alkali cations strongly decreases from Li⁺ to Na⁺ and K⁺.

Next, we aim to establish the relationship of u and λ to the diffusivity (or diffusion coefficient) D, which describes the rate of random motion of particles (not only ions, but also solvent molecules and other, uncharged solutes). For the general case, we consider the movement of a particle under the influence of a concentration / activity gradient. First, we recall the chemical potential of a particle $\mu = \mu^{\rho} + RT \cdot \ln(a)$ (cf. Introduction and Chapter III). The thermodynamic driving force for the movement of the particle is

$$F_{\rm thd} = -\frac{d\mu}{dx} = -RT \frac{d\ln(a)}{dx} \approx -\frac{RT}{c} \frac{dc}{dx}$$
(4-18)

For simplicity we have replaced the activity by the concentration and assume only a change along one spatial dimension, x. The particle is moving down the concentration gradient. At this point, we invoke Fick's first law of diffusion, J = -D(dc/dx), which states that the particle flux J (unit: mol·cm⁻²·s⁻¹) is proportional to the concentration gradient (dc/dx), with the proportionality constant being the diffusion coefficient D (cf. also Chapter V). The particle flux is also given by $J = v \cdot c$, with v the drift velocity. We can now rearrange Eq. 4-18 to solve for the concentration gradient dc/dxand also express it using Fick's first law:

$$\frac{dc}{dx} = -\frac{c}{RT}F_{\text{thd}} = -\frac{J}{D} = -\frac{vc}{D}$$
(4-19)

Multiplying by -D/c and solving for the drift velocity v yields

$$v = -\frac{D}{c}\frac{dc}{dx} = \frac{D}{RT}F_{\text{thd}}$$
(4-20)

Eq. 4-20 describes in general the dependence of the drift velocity of particles as a result of a thermodynamic driving force F_{thd} . This can be a concentration gradient, but it can also be an electric field. For the latter, we know the dependence of the drift velocity on the electric field (Eq. 4-17) and the thermodynamic driving force (Eq. 4-15), which we convert to a molar force $F_e = zeN_A E = zFE$. Inserting into Eq. 4-20 and solving for *D* yields

$$D = \frac{kT}{|z|e}u = \frac{RT}{|z|F}u \tag{4-21}$$

This is the *Einstein relation*. We take the absolute value of the ion charge |z|, because the relation holds for any ion and the values of D and u (and also λ) are always positive.

Based on these findings, we can develop further relations. Taking the description of the mobility using Stokes' law (Eq. 4-17) and entering it into the Einstein relation (Eq. 4-21) we obtain the *Stokes-Einstein equation*:

$$D = \frac{kT}{6\pi\eta r} \tag{4-22}$$

Combining Eqs. 4-10 and 4-21 gives us a correlation between the molar conductivity of an ion and its diffusivity:

$$\lambda = \frac{(zF)^2}{RT}D\tag{4-23}$$

This is the important *Nernst-Einstein equation*. One application of this equation is the determination of ionic diffusion coefficients from conductivity measurements, another is the prediction of conductivities using models of ionic diffusion. With the relationships presented so far, we still have not provided an explanation or theoretical background of the apparent linear decrease of the molar conductivity as a function of the square root of concentration in the low concentration range (**Figure 4-3a**), i.e. Kohlrausch's law. To do this, we first need to look at the description of the activity of ions in solution. The chemical potential of an ion in solution (cf. Introduction) is

$$\mu = \mu^{\circ} + RT \ln(a) = \mu^{\circ} + RT \ln(\frac{m}{m_0}) + RT \ln(\gamma_{\pm})$$
(4-24)

if we express the concentration as molality, where γ_{\pm} is the *mean activity coefficient* of the salt in solution. We could equally well use the molarity for the concentration and recall from the Introduction that the activity coefficient would then be different. We wish now to find a mathematical expression of γ_{\pm} . For this, we recall the *Debye-Hückel theory* (cf. Chapter III). The basic idea of the theory is that individual ions possess an atmosphere of ions of opposite charge (**Figure 4-6a**). Due to the opposite charges of anions z_{\pm} and cations z_{\pm} , anions are more likely to be found near cations, and vice versa. The higher likelihood of finding counter-ions in the ionic cloud of an ion leads to a decrease of the chemical potential of the central ion as a result of its electrostatic interaction with its *ionic atmosphere*. The difference in energy to the case of an ideal electrolyte solution without any interaction between ions is characterized by the term $RT \ln(\gamma_{\pm})$. The analysis¹ leads to a description of the mean activity coefficient γ_{\pm} of a salt in an electrolyte solution called *Debye-Hückel limiting law*:

$$\ln(\gamma_{\pm}) = -|z_{\pm}z_{-}| \frac{F^{2}}{8\pi\varepsilon\varepsilon_{0}N_{A}RT} \frac{1}{L_{D}}$$
(4-25)

 $L_{\rm D}$ is the *Debye length*, which describes the screening length of ionic charge (cf. also Chapter III)²:

$$L_{\rm D} = \sqrt{\frac{\varepsilon \varepsilon_0 RT}{2\rho F^2 m_0 I}} \tag{4-26}$$

The properties of the solvent enter the equation through the dielectric constant ε . The screening length L_D is governed by the *ionic strength* $I = \frac{1}{2}\sum z_k^2 (m_k/m_0)$, which is dimensionless here³, ρ is the density of the solution. We see that $\ln(\gamma_{\pm})$ is negative, hence $\gamma_{\pm} < 1$, which indicates that the ion in solution is stabilized by its ionic cloud. The properties of the electrolyte enter the equation via the ionic strength *I*, which does not only comprise the contribution of the salt of interest, but of

¹ cf. for example Atkins & de Paula 'Physical Chemistry', 8th Edition (2006) for the derivation.

² The Debye length L_D is defined here based on the molality of the solution via the ionic strength *I*, in Chapter III it was defined using the molarity concentration scale (Eq. 4-3-16). Evidently, the two forms are equivalent.

³ Here, as for example in Atkins & De Paula's 'Physical Chemistry', the ionic strength is based on molalities rendered dimensionless by dividing by the standard molality $m_0 = 1$ mol/kg. In other textbooks, it is defined based on molarities c_k , $I = \frac{1}{2} \sum z_k^2 c_k$, or molalities m_k , $I = \frac{1}{2} \sum z_k^2 m_k$. IUPAC lists both the latter expressions (https://goldbook.iupac.org/terms/view/I03180).

all ions in the solution. Therefore, the activity coefficient γ_{\pm} of a salt changes, even if its concentration is constant, if we change the concentration of the supporting electrolyte. To reflect this dependence, the Debye-Hückel limiting law¹ is often expressed as



Figure 4-6. (a) Schematic representation of the ionic atmosphere. The circles indicate the size of the ionic cloud represented by the Debye length L_D , which describes representative distance from a central ion where counter-ions can be found on average (Source: C.H. Hamann, A. Hamnett, W. Vielstich, Electrochemistry, 2nd Edition, Wiley-VCH, 2007, Fig. 2.16, p39). (b) Illustration of the deformation of the ionic cloud as a result of an ion moving under the influence of an electric field. (Source: Stephen Lower, Simon Fraser University²)



Figure 4-7. (a) Mean activity coefficient γ_{\pm} of selected electrolytes at 25°C and theoretical values according to the Debye-Hückel limiting law (Source: C.H. Hamann, A. Hamnett, W. Vielstich, Electrochemistry, 2nd Edition, Wiley-VCH, 2007, Fig. 2.17, p51). (b) Experimental values of γ_{\pm} for some alkali salt electrolytes up to higher concentrations. *I* is the ionic strength (Source: R.G. Compton, H.W. Sanders, Electrode Potentials, Oxford Chemistry Primers, 1996, Fig. 2.8, p48).

For water at 25°C ($\varepsilon = 78.5$, $\rho = 998 \text{ kg/m}^3$) A = 1.172. If we wish to use the base-10 logarithm we have $\log(\gamma_{\pm}) = -A'|_{z+z-}|\sqrt{I}|$ with A' = 0.509. Essentially, Eq. 4-25 states that the smaller the screening length L_D , i.e., the larger the ionic strength I, the larger the deviation from an ideal solution. Eq. 4-

¹ The law fundamentally also applies to single ions k: $\ln(\gamma_k) = -A \cdot z_k^2 \cdot \sqrt{I}$.

² http://www.chem1.com/acad/webtext/solut/solut-8.html

25 is plotted in **Figure 4-7a** ($z_+ = 1$, $z_- = -1$) along with experimental data for selected electrolytes. We see that, indeed, the values of the activity coefficient for the two sample electrolytes follow the Debye-Hückel limiting law well up to a concentration of around 0.01 mol/kg (≈ 0.01 M). At higher concentrations, the values are underestimated. A more accurate description is obtained using the extended Debye-Hückel equation, which is not treated here. When the concentration is further increased, for some electrolytes (such as HCl, LiCl or NaCl) an upturn in the activity coefficient is observed, even to values >1 (**Figure 4-7b**). While the Debye-Hückel framework describes ion-ion interactions, the behavior at higher concentrations is due to ion-solvent effects. Values of $\gamma_{\pm} > 1$ mean that the ions are destabilized compared to their ideal, 'uncharged' behavior. This is a result of the reduced availability of water to fully solvate the ions.

These considerations on interactions between ions in an electrolyte get us closer to understanding the behavior of the molar conductivity with \sqrt{c} (Figure 4-3a). Based on the Debye-Hückel theory, *Onsager* developed a theoretical expression to account for the empirical relation found by Kohlrausch (Eq. 4-8):

$$\Lambda = \Lambda_0 - (B_1 \Lambda_0 + B_2) \sqrt{\frac{c}{c_0}}$$
(4-28)

This is the *Debye-Hückel-Onsager equation*¹. B_1 and B_2 again depend on the properties of the solvent (such as dielectric constant and viscosity) and temperature. For water at room temperature and a 1-1 electrolyte ($z_+ = |z_-| = 1$), $B_1 = 0.229$ and $B_2 = 60.27$ S·cm²·mol⁻¹. For an interpretation of these parameters, we look at the effect an ion in motion has on its solvent shell and ionic cloud (**Figure 4-6b**). The parameter B_1 is related to the so-called ion atmosphere relaxation effect. Due to the movement of the ion, its ionic cloud is distorted, its center being behind that of the ion. This creates an opposing electric field, which restrains the motion of the ion. The parameter B_2 describes the electrophoretic effect. When the ion moves forward through the solution, it tends to take its ion atmosphere with it, yet the oppositely charged ions in its cloud are driven to move in backward direction. This results in a viscous drag force opposing ion motion. Like the Debye-Hückel theory

1 Explicit expression: $\Lambda = \Lambda_0 - \left(\frac{|z_+z_-|F^2}{12\pi\varepsilon\varepsilon_0 N_A RT}\Lambda_0 \cdot \frac{q}{1+\sqrt{q}} - \frac{(z_+ + |z_-|)F^2}{6\pi\eta N_A}\right) \cdot \frac{1}{L_D}$ where L_D is the Debye length, as introduced in the text (Eq. 4-26). The definition of q is $q = \frac{|z_+z_-|}{(z_+ + |z_-|)(z_+t_- + |z_-|t_+)}$

where t_+ and t_- are the transference numbers of the cation and anion, respectively (see Section 1.5). Remember that $z_+ > 0$ and $z_- < 0$. For a symmetric (z-z) electrolyte, $q = \frac{1}{2}$.

Eq. 4-28 is a limiting law valid only at very low concentrations, usually less than 1 mM. The different slopes of the curves in **Figure 4-3a** are related to the stoichiometry of the salt and the charges of the ions.

1.5 Transference effects

We have seen that the ions in an electrolyte move with different drift velocities according to their mobilities. The total ionic current is carried partially by cations moving toward the cathode and partially by anions moving toward the anode. The fraction of the total current I_{tot} carried by an ion k is called the transference number t_k :

$$t_{k} = \frac{I_{k}}{I_{\text{tot}}} = \frac{\left|z_{k}\right| c_{k} u_{k}}{\sum_{j} \left|z_{j}\right| c_{j} u_{j}} = \frac{\lambda_{k} c_{k}}{\sum_{j} \lambda_{j} c_{j}} = \frac{\lambda_{k} v_{k}}{\sum_{j} \lambda_{j} v_{j}}$$
(4-29)

with v_k the stoichiometric factor of the ion. The transference numbers of all the ions in a solution add up to unity: $\Sigma t_k = 1$.

Example:

We calculate the transference numbers of the ions in K₂SO₄ electrolyte. The molar conductivities can be retrieved from **Table 4-2**: $\lambda(K^+) = 73.5 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, $\lambda(\text{SO}_4^{2-}) = 160 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. The stoichiometric factors are 2 for K⁺ and 1 for SO₄²⁻. We therefore obtain $t(K^+) = 0.48$ and $t(\text{SO}_4^{2-}) = 0.52$. Therefore, the charge transport is split about equally between cations and anions.

For a z-z electrolyte, we can simplify the expression a bit and write

$$t_{+} = \frac{\lambda_{+}}{\lambda_{+} + \lambda_{-}}$$
 and $t_{-} = \frac{\lambda_{-}}{\lambda_{+} + \lambda_{-}}$ (4-30)

Considering the extremely high mobility of protons, the charge in acid solutions is generally carried predominantly by H⁺. For example, in HCl(aq), $t_{+} = 0.82$, whereas in KCl(aq), $t_{+} = 0.50$. These values correspond to the case of a dilute solution, in concentrated solutions the values may change somewhat.



Figure 4-8. Schematic representation of a Hittorf cell with 3 compartments filled with electrolyte, which are separated by a porous frit. Upon passage of a charge Q, the transference numbers t_{+} and t_{-} can be calculated from the change in the electrolyte concentration in the anode and cathode compartments.

There are two traditional experimental methods to determine transference numbers: The *Hittorf* method and the moving boundary method. We will be looking at the Hittorf method (1853) in the following. Consider a 3-compartment electrochemical cell, consisting of an anode, a cathode and a center compartment, filled with an electrolyte containing A^{z+} and B^{z-} ions (**Figure 4-8**). When current is flowing, in the electrolyte the two ions A and B carry the charge according to their transference numbers t_+ and t_- . At the cathode, upon passing a charge Q the amount of cations that have reacted (for example, through metal plating) is Q/z_+F (Faraday's law), but only $t_+(Q/z_+F)$ cations have entered the cathode compartment from the center compartment, whereas $t_-(Q/|z_-|F)$ anions have moved out. The charge Q passed through the center compartment is carried in part by cations, $t_+(Q/z_+F)$, and in part by anions, $t_-(Q/|z_-|F)$. At the anode, $Q/|z_-|F$ anions are converted (for example through gas evolution), and $t_-(Q/|z_-|F)$ anions are transported into the anode compartment, while $t_+(Q/z_+F)$ cations have moved out. We can now calculate the change in the content of ions (in mol) in the cathode and anode compartment, Δn_{ca} and Δn_{an} , respectively, from a balance of influx, outflux and conversion. Charge balance needs to be maintained everywhere in the cell.

$$\Delta n_{\rm ca} = (t_+ - 1)\frac{Q}{z_+F} = -t_-\frac{Q}{z_+F}$$
(4-31)

$$\Delta n_{\rm an} = (t_{-} - 1) \frac{Q}{|z_{-}|F} = -t_{+} \frac{Q}{|z_{-}|F}$$
(4-32)

Hence, we can obtain the transference numbers t_+ and t_- from the change in the salt concentration in the two compartments, which we can determine experimentally:

$$\frac{t_{-}}{t_{+}} = \frac{\Delta n_{\rm ca} z_{+}}{\Delta n_{\rm an} \left| z_{-} \right|} \tag{4-33}$$

In some texts, transference numbers are called 'transport numbers'. In yet some other texts, a distinction is made between transport numbers and transference numbers, in particular in the context of non-aqueous electrolytes (cf. for example F.M. Gray, Polymer Electrolytes, 1997). In electrolytes with ion association, such as organic electrolytes, there are different types of ionic (and neutral) species. For example, if we have a salt MX in an organic solvent, in addition to the solvated ions M^+ and X^- , there may be ionic and neutral ion pairs $[M_2X]^+$, $[MX_2]^-$, [MX], etc. The charged entities will migrate under the influence of an electric field, while uncharged species, e.g., $[MX]_0$, will only diffuse. The transport number of the different species is characterized by *T*. For our example, the effective transport of M^+ ions characterized by the transference number t_+ is therefore related to the transport number *T* of the different species according to $t_{M^+} = T_{M^+} + 2T_{[M_2X]^+} - T_{[MX_2]^-}$. And likewise for the ion X^- : $t_{X^-} = T_{X^-} + 2T_{[MX_2]^-} - T_{[M_2X]^+}$. This is for example of relevance in lithium-ion battery electrolytes, where ion aggregation readily occurs, and the main interest is in the transport of Li⁺ ions. The accompanied transport of counter-ions can lead to the formation of concentration gradients in the electrolyte.

1.6 Liquid junction

A potential difference develops at any interface, or junction, where there is a separation of charge. At an electrode-electrolyte interface, this potential difference is described by the Nernst equation (cf. Chapter III). A potential can also develop when electrolyte solutions of differing composition are separated by a boundary, such as a porous frit, which prevents convective mixing of the electrolytes, yet allows diffusive and migrative transport across it.



Figure 4-9. Generally, when a porous frit or membrane (not selective towards any ion) separates 2 electrolytes of different composition and / or different concentration, a liquid junction is formed as a result of the dissimilar mobility u of the ions. Here, the effect is illustrated using hydrochloric acid solutions of different concentration. $u(H^+) > u(Cl^-)$ leads to a constant excess (+) charge on the left and (-) charge on the right side of the junction in the steady-state.

Let us look at an example of two solutions of hydrochloric acid with different concentration, separated by a glass frit (**Figure 4-9**). Due to the 10-fold higher concentration of HCl in compartment β , diffusion across the boundary is dominated by the ions in phase β . Since the diffusivity / mobility of H⁺ is much higher than that of Cl⁻ (cf. **Table 4-2**), a positive charge will build up in compartment α and leave behind a negative charge in compartment β . We hereby assume that the two compartments are large and ideally mixed, such that the concentrations are uniform and remain unchanged. The potential difference that forms across the boundary and the associated

electric field leads to a migrative transport term, which causes H^+ ions to slow down and Cl^- ions to speed up in the region of the junction. Eventually, a steady-state is reached where both ions are moving at the same rate. The corresponding potential difference is called the *liquid junction potential*. In case of an electrolyte with equal composition but different concentration on the two sides, the liquid junction potential E_{LJ} is given by:

$$E_{\rm LJ} = \Delta \varphi = \varphi_{\beta} - \varphi_{\alpha} = -\left(\frac{t_+}{z_+} - \frac{t_-}{|z_-|}\right) \frac{RT}{F} \ln\left(\frac{a_{\beta}}{a_{\alpha}}\right)$$
(4-34)

This is a *diffusion potential* and the effect is not a thermodynamic one, since we do not have an equilibrium: ions are constantly moving across the boundary and we are describing a quasi steady-state¹. Therefore, the liquid junction potential is a kinetic effect. This can be seen from the fact that the transference numbers appear in the equation, which are determined by the mobilities of the ions involved. For the example illustrated in **Figure 4-9**, with $t_+ = 0.821$ and $t_- = 0.179$, we obtain a liquid junction potential of $E_{LJ} = -36.0$ mV at 25°C (we have used activity coefficients of 0.9 and 0.8 for 0.01 M and 0.1 M HCl, respectively). Under ideal conditions or for estimates, the activities can be replaced by concentrations, obviously. The obtained negative value of E_{LJ} indicates that the potential is lower in β than in α , which is consistent with our argument of how the different mobilities of H⁺ and Cl⁻ lead to the indicated charge separation. Furthermore, Eq. 4-34 shows that if the transference numbers for a binary z-z-salt are close to $\frac{1}{2}$, the liquid junction potential becomes very small. Ideally, for $t_+ = t_- = 0.5$ it vanishes. This is important for the notion of a salt bridge (see below).

We now consider the more general case of a liquid junction between two electrolyte solutions of different composition and concentration. An analysis (cf. for example Rieger, pp. 136) of the species / charge transport and electric potential change across the liquid junction leads to the following general expression for the liquid junction potential:

$$E_{\rm LJ} = \varphi_{\beta} - \varphi_{\alpha} = -\frac{RT}{F} \sum_{k} \int_{\alpha}^{\beta} \frac{t_{k}}{z_{k}} d\ln a_{\rm k}$$
(4-35)

The integral sign means that we have to integrate the expression through the junction between the phases α and β for all ions. Furthermore, the transference numbers t_k may depend on the activity / concentration of the ions. For an expression that is easier to use we have to make some assumptions:

¹ by assuming that the electrolyte compartments are very large, such that the concentration of the solutions remains approximately constant, despite the constant flux of ions across the junction.

i) we assume ideal solutions, hence $\gamma_{\pm,k} = 1$; ii) the mobilities u_k and, hence, the transference numbers t_k are independent on concentration; iii) the concentration c_k varies linearly through the junction. Certainly, the first two assumptions only apply for dilute solutions. With these assumptions, we obtain the *Henderson equation*:

$$E_{\rm LJ} = -\frac{RT}{F} \cdot \frac{\sum_{k}^{k} \frac{|z_{k}| \cdot u_{k}}{z_{k}} \cdot (c_{k}^{\beta} - c_{k}^{\alpha})}{\sum_{k}^{k} |z_{k}| \cdot u_{k} \cdot (c_{k}^{\beta} - c_{k}^{\alpha})} \cdot \ln(\frac{\sum_{k}^{k} |z_{k}| \cdot u_{k} \cdot c_{k}^{\beta}}{\sum_{k}^{k} |z_{k}| \cdot u_{k} \cdot c_{k}^{\alpha}})$$
(4-36)

The reader will find that for the same electrolyte in α and β with different concentrations, Eq. 4-36 will simplify to Eq. 4-34.

Liquid junctions are a bit of a nuisance in electrochemical setups, since E_{IJ} is part of the overall voltage measured between two electrodes (Figure 4-10a): $E_{cell} = \Delta \varphi_{\beta} - \Delta \varphi_{\alpha} + E_{LJ}$. We can also write the expression using electrode potentials: $E_{cell} = E_{\beta} - E_{\alpha} + E_{LJ}$ (cf. also Chapter II). For example, if the working electrolyte is different from the electrolyte used in the reference electrode compartment, a liquid junction potential will form at the porous frit separating the two compartments. This will shift the measured potential of the working electrode by E_{LJ} . Therefore, the concept of a salt bridge was introduced around the turn of the 19th to the 20th century. The salt bridge, SB, is inserted between the two dissimilar electrolyte solutions S' and S, thus creating two liquid junctions, between S' and SB and between S and SB (Figure 4-10b). The salt bridge contains a concentrated electrolyte with ideally equal mobility of cations and anions, for example KCl¹. Owing to the high concentration², the mobility of the ions of the salt bridge will dominate the liquid junction potential, which, consequently, will be very small (in the range of mV). Therefore, the salt bridge will reduce the potential difference between S' and S to values that can in most cases be considered negligible. A salt bridge is also a useful tool to bridge electrolytes that contain ions which are not supposed to be mixed. For example, in a Cu-Zn (Daniell) cell Cu2+ ions should not be present in the compartment of the Zn electrode, as this would lead to the chemical reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ (cf. Chapter I). In electroanalytical chemistry, where only very small sensing currents are passed between working and reference electrode, the salt bridge is often gelified, for example with agar-agar³, to help prevent the convective intermixing of solutions.

¹ If the presence of Cl⁻ is not desired, for example if one of the electrolytes contains Ag⁺, KNO₃ can be used instead.

² The saturation concentration of KCl in water at 25° C is ~4.2 M.

³ Agar-agar is a jelly-like substance consisting of natural polysaccharides, containing agarose.



Figure 4-10. (a) Schematic of a cell with liquid junction and corresponding distribution of phase potential φ . (b) Situation with salt bridge (SB) inserted between solutions S' and S. | = phase boundary, | = liquid junction, || = salt bridge.

2 Polymer Electrolytes

Polymer electrolytes are ion conducting membranes and offer the advantage of physically separating the anode and cathode compartment of the electrochemical cell. The 'bulk transport' of liquid and gas through the membrane by convective transport is therefore avoided. This is helpful in cases where constituents on the two sides are not supposed to mix.

Example:

Traditional water electrolyzers employ liquid KOH solution as electrolyte with a diaphragm, a porous separator, to separate anode and cathode. The produced hydrogen and oxygen can easily pass through the diaphragm, which can lead to the formation of an explosive gas mixture. In a membrane electrolyzer, anode and cathode are separated by a polymer electrolyte, which prevents gas from passing from one side to the other. The membrane can furthermore be made very thin (~0.1 mm), which leads to a comparatively low ohmic resistance of the cell.

A membrane is a component that allows the transfer of certain compounds while preventing the passage of unwanted ones. It is therefore a selective barrier. Membranes are typically flat and thin, meaning that their in-plane dimension is much larger than their thickness. Key requirements for polymer electrolytes are:

- High **conductivity** will yield a low resistance and, thus, small ohmic loss.
- Selectivity: transport of desired ions is preferred, others species should not be able to pass to minimize unwanted side-reactions, cross-contamination or other adverse processes.

Also, water or solvent transport is often undesired to avoid concentration changes in the electrolyte, which could lead to precipitation effects. Ideally, the polymer is a single-ion conductor for the desired ion, which means that its transference number is unity (t = 1), which represents a transport selectivity of 100%. In reality, the transport selectivity of a polymer electrolyte is finite, and there is generally a trade-off between conductivity and selectivity. Furthermore, polymer electrolytes need to be mechanically robust, chemically stable, of low-cost, and easy to process, replace, recycle, etc. Last but not least, the material needs to be compatible with the electrodes if they are in direct contact ('zero-gap' configuration).

An ion conducting membrane is designed to transport ionic charge carriers within its polymer matrix. Essentially there are 2 methods to accomplish this. In a first approach, a polymer is mixed with a salt. The polymer itself is thereby uncharged. An example of this concept are polymer electrolytes for the lithium-ion battery. A typical representative is poly(ethylene oxide) (PEO) that

is doped with a lithium salt, e.g., LiClO₄, LiN(CF₃SO₂)₂, yielding a so-called 'salt-in-polymer' electrolyte. The ethylene oxide (EO) units complex Li⁺. A common mixture contains one Li-salt equivalent per 10 to 20 EO units. Pure PEO has a high crystallinity of about 85 % and a melting point T_m of 65°C, yet the addition of the Li-salt increases the fraction of the amorphous, conducting phase. Elevated temperatures above the crystalline melting temperature are required to obtain practical conductivities of 10^{-3} S/cm. The conduction mechanism in PEO-LiX complexes is based on the segmental motion of the polymer chains (**Figure 4-11a**) and the mobility of the ions is therefore related to the glass transition temperature, T_g , of the polymer (T_g of pure PEO: -64° C). The conductivity of PEO based polymer electrolytes can be improved and the conducting regime extended to room temperature by adding a suitable solvent and / or plasticizer to form a gel polymer electrolyte. In any case, the Li⁺ as well as the anion are mobile, i.e., the transference number of Li⁺ is less than 1, hence transference effects are observed as in a liquid electrolyte. In fact, the mobility of the anion is typically larger than the one of Li⁺, because the lithium-ion is more strongly interacting with the polymer.



Figure 4-11. (a) Illustration of the conduction mechanism in a PEO-LiX polymer electrolyte based on the segmental motion of the polymer chain. The anion is not shown for simplicity. (Source: J. Mater. Chem. A 3, 2015, 19218). (b) Sketch of the different types of ion-exchange membrane polymers with fixed ions and exchangeable counter-ions. (Source: Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, Elsevier, 2018, DOI: 10.1016/B978-0-12-409547-2.14285-4).

2.1 Ion-exchange membranes

In the second design principle for polymer electrolytes, ionic groups (fixed charges) are covalently bound to the polymer. The obtained material is an *ion-exchange membrane* (IEM). The material is also referred to as an *ionomer*, a copolymer in which up to 15 mol % of the repeat units contain ionic groups. The density of ionic groups is described by the *equivalent weight* (EW), the mass of

dry polymer per exchange site (unit: g/mol), or its reciprocal value, the *ion exchange capacity* (IEC). Typical values for the EW and IEC are 1'000 g/mol and 1.0 mmol/g, respectively. Polymers with a higher content of ionizable groups become water soluble and are called *polyelectrolytes*. In an IEM, the charge of the fixed ionic groups is balanced by *counter-ions*. Counter-ions are ions with charge opposite to the charge of the fixed ions. IEMs are categorized into *cation-exchange membranes* (CEMs), anion-exchange membranes (AEMs) and amphoteric ion-exchange membranes (AIEMs), the latter containing both fixed anion and fixed cation groups (Figure 4-11b). The fixed ions usually are strongly or weakly acidic and basic functional groups. Anionic head-groups for cation exchange membranes are acids, such as the strongly acidic sulfonic acid ($pK_a - 1$ or below) or the weakly acidic carboxylic acid (pK_a ~4.5). The dissociation of the acid yields mobile H^+ . Such membranes are also called proton exchange membranes (PEMs). Traditional cationic head-groups for anion exchange membranes are of the quaternary ammonium type, e.g., $-N^{+}(CH_{3})_{3}$. Tertiary amines are weak bases that are protonated at pH values below their pK_a and thus develop a positive fixed charge. Amphoteric ion-exchange membranes are technologically less relevant, yet useful in some separation technologies. Another type of technically relevant class of membranes are bipolar membranes, which consist of a layer of anion exchange polymer and a layer of cation exchange polymer. They are used in separation and purification processes in various applications.

2.2 Ion-exchange membranes in salt solutions

A general feature of an ion-exchange membrane, as the name implies, is its ability to exchange counter-ions when immersed in an electrolyte solution. For example, for a CEM, two types of counter-ions, say A^+ and B^{n+} with charge +1 and +*n*, respectively, will distribute ('partition') between the membrane 'm' and the solution 's' phase according to $A_m^+ + \frac{1}{n} \cdot B_s^{n+} \rightleftharpoons A_s^+ + \frac{1}{n} \cdot B_m^{n+}$. In general, the molar ratio of A to B in the membrane will be different from that in the solution. The selectivity of the ion-exchange material for counter-ions between the membrane and the adjacent electrolyte solution is described by the counter-ion exchange equilibrium, expressed by the *selectivity coefficient* K_B^A (also called 'partition coefficient'):

$$\frac{(X_{\rm B})^{1/n}}{X_{\rm A}} = \frac{(c_{\rm B}^{(\rm m)})^{1/n}}{c_{\rm A}^{(\rm m)}} = K_{\rm A}^{\rm B} \frac{(c_{\rm B}^{(\rm s)})^{1/n}}{c_{\rm A}^{(\rm s)}}$$
(4-37)

where X_A and X_B represent the molar fraction of counter-ions in the membrane with $X_A + n \cdot X_B = 1$, and *c* is the concentration (molarity). Note that the selectivity coefficient is not necessarily constant over the entire concentration range of A and B. Selectivity coefficients for ions that are not tabulated can be obtained by combining known selectivity coefficients. For example, if the partitioning coefficient between ions A and B is K_A^B , and that between ions A and C is K_A^C , then the partitioning coefficient between ions B and C is $K_B^C = K_A^C / K_A^B$.

Example:

The selectivity coefficient $K_{\rm H}^{\rm CS}$ for Cs⁺ over H⁺ in NafionTM (cf. below) at room temperature is 9.1. We calculate the molar ratio of Cs⁺ to H⁺ in the membrane when it is immersed in a solution with 0.08 M HCl and 0.02 M CsCl. Both cations are of charge +1, which simplifies the calculation according to Eq. 4-37. We obtain: $X_{\rm Cs} / X_{\rm H} = 9.1 \cdot 0.02 \text{ M} / 0.08 \text{ M} \cong 2.3$. Hence, 67% of cation exchange sites are occupied by Cs⁺ and 33% by H⁺. This means that cesium-ions show a much stronger interaction with the cation exchange sites than protons.

The presence of fixed ions on the ion-exchange polymer leads to the rejection of co-ions from the membrane phase. Co-ions are ions with a charge of the same sign as the charge of the fixed ions. This phenomenon is called *Donnan exclusion*. It is, however, not complete. A small concentration of co-ions and excess counter-ions is present in the membrane. This content of excess electrolyte increases with the ionic strength of the solution. If the concentration of ions in solution is comparable to the concentration of fixed ions in the membrane or exceeds it, Donnan exclusion breaks down and significant excess electrolyte is taken up by the membrane.

Device →	Fuel cell	Chlor-alkali electrolysis	Redox flow battery ^a	Li-polymer (LiPo) battery
membrane	CEM (PEM ^b)	CEM	CEM or AEM	PEO + Li-salt
liquid electrolyte	none (H ₂ O)	(-): NaOH(aq) (+): NaCl(aq)	$H_2SO_4(aq)$	none or added plasticizer
preferred ion	H^{+}	Na ⁺	H ⁺ , HSO ₄ -	Li ⁺
barrier for	H_2, O_2	OH-, Cl-	V(II,III,IV,V)	A- c

Table 4-4. Selected technically relevant electrochemical devices with polymer electrolyte with corresponding polymer and, where applicable, liquid electrolyte. Desired transport selectivity is indicated. CEM = cation exchange membrane, AEM = anion exchange membrane.

^a all-vanadium type

^b proton exchange membrane (PEM)

° anion of Li-salt, e.g. ClO₄⁻, PF₆⁻

From a species transport point of view in a practical application of an IEM, there is typically a preferred ion to transport charge in the polymer electrolyte, whereas the passage of some other ions or uncharged species is not desired for different reasons. In **Table 4-4**, the type of membrane used in a few technically relevant applications is listed, together with requirements of the transport selectivity of the material. The passage of unwanted species through the membrane can lead to a safety hazard, efficiency loss, product contamination, or other undesired side effects.

For the description of the equilibrium concentration / activity of co-ions and counter-ions in an ion exchange membrane immersed in an electrolyte solution containing the same said ions, we require

that the electrochemical potential of the ions $\tilde{\mu}_k = \mu_k^\circ + RT \ln a_k + z_k F \varphi$ is the same for each mobile ion k in the membrane (m) and in the solution (s): $\tilde{\mu}_k^{(m)} = \tilde{\mu}_k^{(s)}$. This is the *Donnan equilibrium*. Upon insertion of the expression for the electrochemical potential, we see that owing to the different activities of the ions in the two phases, a difference in the electric potential φ develops between the membrane and the solution, which is the *Donnan potential* E_D :

$$E_{\rm D} = \Delta \varphi = \varphi^{\rm (m)} - \varphi^{\rm (s)} = -\frac{RT}{z_k F} \ln \frac{a_k^{\rm (m)}}{a_k^{\rm (s)}}$$
(4-38)

where z_k is the charge of the ion (cations: $z_k > 0$, anions: $z_k < 0$). The relationship has to hold for each type of ion k, hence for a binary salt for both the anions and the cations. If we assume ideal conditions ($\gamma_k = 1$), take the example of a CEM (**Figure 4-12a**) and look at the anions: they are coions and therefore their concentration in the membrane $c_{-}^{(m)}$ is very small compared to their concentration $c_{-}^{(s)}$ in the solution. The logarithm in Eq. 4-38 will therefore be negative, and with $z_{-} < 0 E_D$ will be negative, i.e., the phase potential in the membrane $\phi^{(m)}$ will be lower than that in the solution $\phi^{(s)}$. For the cations / counter-ions, $c_{-}^{(m)} > c_{-}^{(s)}$, since the concentration in the membrane corresponds to the concentration of the fixed ions plus the excess electrolyte. Using analogous arguments for an AEM, we find that $E_D > 0$ in this case.



Figure 4-12. (a) Illustration of Donnan equilibrium between an ion exchange membrane and the adjacent electrolyte solution, shown here for a cation exchange membrane (CEM). The potential difference between the membrane (m) and the solution (s) is the Donnan potential E_D . \bigcirc : fixed ion, \bigoplus : counter-ion, \bigcirc : co-ion, \bigoplus & \bigcirc : free ions in solution. (b) Distribution of phase potential across a membrane. The membrane potential E_{LJ} in the membrane. Example here: CEM, $c_\beta > c_\alpha$, $t_- > t_+$ (e.g. KOH).

The ionic charges are balanced in the bulk of the electrolyte and membrane, yet there is a region with excess positive and negative charge ρ , respectively, on either side of the interface (same situation as in the electrochemical double layer, cf. Chapter III), causing the potential φ to change from φ_m to φ_s , which is described by the Poisson equation: $\nabla^2 \varphi = -\rho / \varepsilon \varepsilon_0$. The magnitude of E_D

depends on the difference in concentration of the fixed ions in the membrane and the solution concentration. With a solution of low ionic strength, E_D will be large and co-ion exclusion very effective. With a highly concentrated solution, E_D will approach zero and co-ion / Donnan exclusion will break down. For a 1-1 salt with a solution concentration that is a tenth of that of the fixed ions in the membrane E_D is ca. (–)60 mV at 25°C. The concentration of co-ions in the membrane is then about a tenth of the solution concentration and, consequently, a hundredth of the fixed ion concentration. For a detailed analysis, see **Appendix A**.

The uptake of water by an IEM when it is immersed in electrolyte is largely an osmotic effect, since water has the tendency to dilute the fixed charges and counter-ions in the membrane. The water uptake is therefore highest when immersed in pure water. Upon increase of the ionic strength of the solution, for example by adding sulfuric acid (**Figure 4-13a**), the water content in the membrane decreases, because the osmotic pressure decreases. In pure water, NafionTM (cf. below) has a conductivity of around 80 mS/cm at room temperature. When immersed in dilute sulfuric acid, the conductivity increases with concentration up to ~2 M due to the sorption of electrolyte. However, with acid concentration further increasing, the conductivity starts to drop because of membrane dehydration. See **Appendix B** for details on the effect of osmotic pressure on the Donnan equilibrium.

A yet more complex situation is encountered if an IEM separates two solutions of different composition and / or concentration (**Figure 4-12b**). At both interfaces of the membrane with the solutions, a Donnan potential $E_{D,\alpha}$ and $E_{D,\beta}$, respectively, will form. In addition, a diffusion potential



Figure 4-2. (a) Uptake of water and sulfuric acid by a NafionTM 117 membrane as a function of acid concentration at room temperature and corresponding membrane conductivity (Data from J. Electrochem. Soc. 160(9), 2013, F1040). (b) Proton conductivity of perfluoroalkylsulfonic acid (PFSA) membranes from 3M with different equivalent weight (EW) compared to NafionTM 112 (EW of 1'100 g/mol) at fuel cell relevant temperature. (Source: S. Hamrock, 3M)

will develop in the membrane, because the concentration of ions in the membrane near the surface α will generally be different from that near surface β . The diffusion potential is analogous to the liquid junction potential discussed above (Section 1.6). Consequently, the difference in the electric potential φ between solution S' and solution S is given by the sum of the two Donnan potentials and the diffusion potential, yielding the *membrane potential E*_m:

$$E_{\rm m} = \varphi_{\rm S} - \varphi_{\rm S'} = E_{\rm D,g} - E_{\rm D,g} + E_{\rm diff} \tag{4-39}$$

So, the general representation of the membrane potential is rather complex. We can, however, look at two limiting cases.

- i) In case the fixed ion concentration in the IEM is much lower than the concentration of the solutions, Donnan exclusion is ineffective and the Donnan potentials E_{D,α} and E_{D,β} can be neglected, and E_m ≈ E_{diff}, which is given by Eq. 4-34. The magnitude of E_{diff} is influenced by the mobility of the ions (kinetic effect). In this limiting case, the ion exchange property of the IEM is not exploited and it behaves like a liquid junction or an uncharged polymer.
- ii) For very high fixed ion concentration or very low salt concentration in the solutions, the diffusion potential can be neglected and the membrane potential is then simply given by the difference of the two Donnan potentials, giving the ideal membrane potential, which is only dependent on the activity of ions in solutions S and S' (thermodynamic effect):

$$E_{\rm m} \approx -\frac{RT}{z_k F} \ln \frac{a_k^{\rm (S)}}{a_k^{\rm (S')}} \tag{4-40}$$

For *k* use counter-ions here, so we obtain $E_m < 0$ for a CEM and $E_m > 0$ for an AEM if $a_{\alpha} < a_{\beta}$. For a development of the corresponding expression for co-ions, see **Appendix C**.

The membrane potential will be revisited in Chapter VIII ('Analytical Methods & Sensors'). It is the basis of the working principle of ion-selective electrodes.

2.3 Perfluoroalkylsulfonic acid (PFSA) membranes

An important class of ion exchange membranes are based on perfluoroalkylsulfonic acid (PFSA) ionomers, which are used in a number of technically and industrially relevant applications, such as electrolyzers (cf. Chapter VI), fuel cells (cf. Chapter VII), and flow batteries. PFSA ionomers are perfluorinated copolymers of tetrafluoroethylene (TFE) and a vinyl ether comonomer with pendant sulfonic acid group, $-SO_3H$. Due to the attachment to a fluorocarbon, it is a superacid with $pK_a \leq 6$,

hence it readily dissociates, even at low degrees of hydration. Owing to the presence of polymerbound acid groups, PFSA membranes are called *proton exchange membranes* (PEMs). Yet the protons can be readily exchanged with other cations, for example Na⁺. A well known and widely used PFSA membrane product is Nafion[™] (originally from DuPont, now Chemours). Its first commercial success was in chlor-alkali cells¹ (cf. Chapter VI).

Due to the PTFE-like chemistry, PFSA ionomers and membranes have a very high chemical stability. The hydrated material has a very unique microstructure, consisting of a nano-phase separated morphology with water rich domains and a polymer rich matrix. Ion conduction takes place within the aqueous phase. In the absence of a liquid electrolyte, such as in a polymer electrolyte fuel cell (cf. Chapter VII), PFSA membranes are proton conductors with a transference number for H^+ of $t_+ = 1$. An important property of PFSA membranes is the content of sulfonic acid groups, characterized by the equivalent weight (EW), which is the mass of polymer per ion exchange site (unit: g/mol). Typical EW values for PFSA membranes are between 600 and 1'200 g/mol. The lower the EW, the higher the concentration of exchange sites and, thus, the higher the water uptake of the membrane. Below an EW of about 600 g/mol, the ionomer becomes water soluble. Often, for ion exchange membranes the inverse of the EW, the ion exchange capacity (IEC), is used to quantify the ion content (unit: mmol/g).

Example:

We calculate the theoretical EW and IEC for an Aquivion® (Solvay) PFSA ionomer, where 20% of the monomer units are the sulfonic acid bearing co-monomer with molar mass of 278 g/mol. The molar mass of TFE is 100 g/mol. The mass of ionomer per $-SO_3H$ site is therefore $1 \cdot 278$ g/mol + $4 \cdot 100$ g/mol = 678 g/mol. This is therefore the EW. The IEC is then 1 / 678 g/mol = 1.47 mmol/g.

At a practical EW of 1'100 g/mol, Nafion[™] shows a water uptake of about 30 wt-% when immersed in water at room temperature. In a water vapor atmosphere, the water content is considerably lower, depending on the relative humidity, but still sufficient for conductivities of 10 mS/cm and higher. This is important for the application in fuel cell powered cars. **Figure 4-13b** shows the conductivity of PFSA membranes with different EW at 80°C, a practical temperature for fuel cell operation, as a function of relative humidity (r.h.). The conductivity increases significantly with r.h. (note the semilogarithmic scale), owing to the increasing water content and thus improved hydration and proton mobility. Evidently, the conductivity increases with the concentration of ionic groups (decreasing EW), but, as already mentioned, low EW membranes show considerable swelling at high r.h. or in liquid water, which impairs their function in the fuel cell.

¹ This is where NafionTM derives its name from: Na-F-ion = Na⁺ conducting, fluorinated (F) IONomer.

3 Solid State Ion Conductors

Solid state ion conductors are a class of materials with ionic or mixed ionic-electronic conductivity, encompassing inorganic crystalline solids, glasses or composites. They offer the prospect of allsolid state electrochemical devices without liquids that can leak or evaporate or polymer membranes that may swell and shrink. Important applications involving solid ion conductors are high-temperature oxygen sensors (cf. Chapter VIII), solid oxide fuel cells (cf. Chapter VII), molten salt batteries, and solid-state lithium thin-film batteries.

The charge transport mechanism in solid state ion conductors is typically enabled by lattice defects that are mobile and allow the transport of ionic charges. From a materials science point of view, solid state ion conductors are classified into the following groups, characterized by their conduction mechanism:

- Superionic conductors: here, a sublattice is completely disordered ('molten'), often above a certain transition temperature. The corresponding charge carriers can freely move within the parent lattice. Example: β"-Al₂O₃.
- Intrinsic ion conductors: lattice defects are created by thermal activation, for example oxygen vacancies in non-stoichiometric oxides such as ceria (CeO_{2-δ}).
- Extrinsic ion conductors: lattice defects are deliberately introduced by doping with compounds of different valence, such as in yttria (Y₂O₃) doped zirconia (ZrO₂) (YSZ).
- **Ion conducting glasses**: the amorphous structure contains mobile ions, for example in sulfide and phosphate based compounds for solid-state lithium batteries. This class of materials is not further treated here.

We can identify a number of general characteristics and requirements for solid state ion conductors. A sizeable fraction of the anions or cations should display significant mobility. This requires a large number of empty sites in the lattice, either vacancies or accessible interstitial sites. The empty and occupied sites should have a similar potential energy with a low activation energy barrier for hopping between neighboring sites. A high activation energy decreases ion mobility, and very stable sites with deep potential energy wells lead to trapping of carriers. Moreover, the structure should have a solid, preferably 3D framework, permeated by open channels. Ideally, the migrating ion sublattice should be "molten", and a solid framework of the other ions is needed to prevent the lattice structure from collapsing or the material as a whole from melting. The framework ions should be highly polarizable. Such ions can deform to stabilize the transition state geometry of the migrating ion through covalent interactions.

3.1 Point defects

In crystalline solids, imperfections in the lattice in the form of point defects are the basis of ionic conductivity. In order for an ion to move through a crystal it must hop from an occupied site to a vacant site. Thus ionic conductivity can only occur if defects are present. The defects have a mobility that is thermally activated. Common defects are vacancies in the anion or cation sublattice, such as oxygen vacancies in YSZ. The movement of vacancies in one direction is associated with the transport of ions in the opposite direction. Other often encountered defects are interstitials. Here, an ion assumes a normally unoccupied site in the crystal structure. In **Figure 4-14**, the terminology of the different types of point defects is introduced. Schottky defects (anion and cation vacancy pairs) are found, for example, in NaCl. Frenkel defects can be found in AgCl and AgBr. The relatively large Cl⁻ ions allow a high mobility of the comparatively small Ag⁺ ions. The effect is even more pronounced in AgBr, hence its conductivity is higher. In AgI, superionic conduction is observed (see below). An example with Anti-Frenkel defects is CaF₂, where the fluoride anions are responsible for charge transport.



Figure 4-14. Overview of different point defects in crystalline solids. Schottky defect = anion-cation vacancy pair; Anti-Schottky defect = anion-cation interstitial pair; Frenkel defect = cation vacancy-interstitial pair; Anti-Frenkel defect = anion vacancy-interstitial pair. (Source: www.tf.uni-kiel.de/matwis/amat/def_en/index.html)

A conductivity chart of various solid ion conducting materials is shown in **Figure 4-15** in Arrhenius representation. The slope of the curve is indicative of the activation energy for ion conduction: the flatter the curve, the lower the activation energy. A jump in conductivity indicates a phase transition, as in AgI. The conductivity σ is governed by the charge *z* and concentration of defects, given here as number density *n* (unit: cm⁻³), and their mobility *u*: $\sigma = z e n u$. The mobility *u* is related to the diffusivity *D* via the Einstein relation (Eq. 4-21), and the diffusivity is thermally activated via

 $D = D_0 \exp(-E_a/kT)$, where E_a is the activation energy. Therefore, the temperature dependence of the conductivity σ is expressed as follows:

$$\sigma T = n \frac{(ze)^2}{k} D_0 \exp(-\frac{E_a}{kT})$$
(4-41)

We are using here 'per particle' quantities, i.e., *n* (unit: cm⁻³), *e* (1.602 \cdot 10⁻¹⁹ As), *E*_a (unit: eV), and *k* (1.381 \cdot 10⁻²³ J/K), as typically used in the materials science of high temperature ion conductors (and semiconductors). Essentially, to determine the activation energy for ion conduction, log(σT) should be plotted vs. 1/*T*, not log(σ). Figure 4-15 is therefore not quite correct, but merely a schematic representation.



Figure 4-15. Temperature dependence of the conductivity of selected solid-ion conducting materials, represented in an Arrhenius-plot. (Source: K. Conder, PSI)

3.2 Superionic conductors

A part of the lattice is completely disordered and 'liquid-like' in superionic conductors. Therefore, exceptionally high conductivities can be obtained for a solid ion conductor. A prominent example is silver iodide. Below the transition temperature of 146°C, β -AgI has a conductivity below 10⁻³ S/cm, yet it increases by 3 orders of magnitude to 1.3 S/cm upon the phase transition to α -AgI. The Ag⁺ sublattice is completely disordered and allows movement of the silver ions like in a liquid with a very low activation of 0.05 eV. The strongly increasing sublattice disorder of AgI can be understood based on the entropy change of 14.5 J mol⁻¹ K⁻¹ at the $\beta \rightarrow \alpha$ phase transition, which is even higher than the melting entropy of α -AgI of 11.3 J mol⁻¹ K⁻¹. The combination of the two entropy changes is similar to the melting entropy of a 'normal' salt, say NaCl (24 J mol⁻¹ K⁻¹). In modified materials, the high conductivity α -phase can be stabilized down to room temperature. For

example, RbAg₄I₅ shows a conductivity of 0.25 S/cm at 25°C, the highest room temperature ionic conductivity of any crystalline solid. The activation energy for ionic conduction is 0.07 eV.

Another class of superionic conductors of technical relevance is β "-Al₂O₃. Good sodium-ion conductors are of the composition (Na₂O)_x·Al₂O₃ with *x* ranging from 5 to 7 and can achieve a conductivity of 0.25 S/cm at 500°C. The crystal structure contains layers in which Na⁺ ions can move with little restriction. The material is used as solid electrolyte in Na-S and Na-NiCl ('Zebra') batteries, which have an operating temperature of around 350°C. Na⁺ ions can be exchanged with other ions, such as Ag⁺, Li⁺ or K⁺, yet conductivity decreases because their ionic radii do not match well with the lattice. Larger ions, such as K⁺, 'squeeze' less well through the structure, while smaller ions, e.g. Li⁺, tend to get trapped in low energy sites of the lattice.

3.3 Solid oxide ion conductors

An important class of materials are solid oxide ion conductors for oxygen ion transport. Such materials are used as electrolyte in the solid oxide fuel cell (SOFC) and potentiometric O₂ sensors (lambda probe). The O²⁻ ion conductivity is enabled by vacancies in the oxygen lattice. The conductivity σ is determined by the concentration of oxygen vacancies¹ [V₀^{••}] (unit: cm⁻³) and their mobility *u*, which is thermally activated as explained above:

$$\sigma = q \left[V_0^{\bullet \bullet} \right] u \tag{4-42}$$

One oxygen vacancy carries a formal +2 charge (q = 2e), because the vacancy replaces an O²⁻ ion in the oxygen lattice. The concentration of oxygen vacancies in a stoichiometric oxide is normally very small, thus also the conductivity. The content of oxygen vacancies can be increased by *doping*, where cations are partially replaced by other cations with lower valence. To compensate for the different charge, vacancies are formed in the oxygen lattice. A prominent example is zirconium oxide (= 'zirconia'), ZrO₂, where Zr-ions have the oxidation state +4. When zirconia is doped with yttrium oxide (= 'yttria'), Y₂O₃, Y³⁺ ions replace Zr⁴⁺ ions on their cation sites. To compensate the difference in charge, an oxygen vacancy is created per two Y-ions introduced (**Figure 4-16a**). Y₂O₃:ZrO₂ is called yttria stabilized zirconia (YSZ) because the high-temperature cubic structure is stabilized at low temperature by the presence of yttria. Other dopants can be used with ZrO₂, such

¹ In the Kröger-Vink notation of defect chemistry the type of defect, the location of the defect and its charge difference to the ideal lattice is indicated. For example, $V_0^{\bullet\bullet}$ describes a vacancy, V, in the oxygen lattice, O, which has a +2 charge compared to the site occupied by an O²⁻ ion. Ce_{Ce}['] is a Ce ion on a Ce lattice site with formal charge -1 compared to the undisturbed lattice. This is a Ce³⁺ ion on a Ce⁴⁺ lattice site.

as Sc_2O_3 or CaO. The influence on the doping level of YSZ on conductivity is shown in **Figure 4-17a**. The concentration initially increases due to the increasing concentration of oxygen vacancies, then goes through a maximum and decreases. This is related to a decreasing mobility of the vacancies as a result of the interaction between the defects. A maximum conductivity of YSZ is obtained at a Y₂O₃ content of 8 mol-%, attaining 0.2 S/cm at 1'000°C with an activation energy of 0.9 eV. This doping level corresponds to an yttrium-ion fraction in the cation lattice of ~15 % and a vacancy content of ~4 % in the oxygen lattice.



Figure 4-16. Defect chemistry of ZrO_2 : Y_2O_3 (= yttria stabilized zirconia, YSZ) and $CeO_{2-\delta}$ (ceria). (a) Doping of zirconia with oxides having cations of lower valence introduces oxygen vacancies, $V_0^{\bullet\bullet}$ (extrinsic defects). (b) Partial reduction of Ce(IV) to Ce(III) in ceria leads to oxygen release, non-stoichiometry (characterized by ' δ ') and the formation of oxygen vacancies (intrinsic defects). The presence of excess electrons leads to n-type electronic conductivity. The defect chemical reactions are given in Kröger-Vink notation.

In some oxides, the cations have the tendency to undergo partial reduction in an oxygen deficient atmosphere. In ceria, CeO₂, for example, a fraction of Ce⁴⁺ is reduced to Ce³⁺. To maintain charge balance, O₂ is evolved, leaving behind oxygen vacancies (**Figure 4-16b**). The result is a non-stoichiometric oxide, CeO_{2- δ}, where δ characterizes the extent of partial reduction of cerium and content of oxygen vacancies. Non-stoichiometric oxides are *intrinsic* ion conductors, because defects are formed through thermal activation. Therefore, the concentration of defects increases with temperature with a certain activation energy. In contrast, in *extrinsic* ion conductors, such as YSZ, defects are introduced by doping and their concentration is independent of temperature (their mobility, however, is thermally activated).

Also ceria can be doped, for example by gadolinia (Gd₂O₃) or samaria (Sm₂O₃), resulting in extrinsic oxygen vacancies and thus much higher conductivity. Both ceria and doped ceria are mixed ionicelectronic conductors (MIECs). In addition to oxygen vacancies providing ionic conductivity, the partially reduced cerium-ions cause n-type electronic conductivity, since the excess electrons can easily hop from Ce³⁺ to Ce⁴⁺ sites. The electronic conductivity increases with decreasing oxygen partial pressure and temperature, because the degree of non-stoichiometry and, thus, the concentration of electronic defects increases (**Figure 4-17b**). See **Appendix D** for an elaboration of the dependence of electronic conductivity on oxygen partial pressure. If used as an electrolyte, the electronic conductivity of doped ceria can lead to some degree of electron leakage across the cell. Nevertheless, MIECs can be used as electrolyte in, say, fuel cells, if temperature is below ~700°C and oxygen partial pressure not lower than 10^{-18} atm.



Figure 4-17. (a) Influence of doping level on the conductivity of yttria stabilized zirconia (YSZ) and scandia stabilized zirconia (SSZ). (Source: Solid State Ionics 162, 2006, 30) (b) Conductivity of samaria doped ceria, Ce_{0.8}Sm_{0.2}O_{1.9-8}, showing ionic conductivity at high $p(O_2)$ and increasing electronic conductivity at low $p(O_2)$. (Source: K. Conder, PSI, reproduced from J. Electrochem. Soc. 145, 1998, 414)

Appendix A: Donnan Potential

For an ion exchange membrane in a salt solution (**Figure 4-12a**), we formulate the equilibrium condition by requiring that the electrochemical potential $\tilde{\mu}_k = \mu_k^\circ + RT \ln a_k + z_k F \varphi$ of all the mobile ions *k* is the same in the membrane (m) and the solution (s) phase: $\tilde{\mu}_k^{(m)} = \tilde{\mu}_k^{(s)}$:

$$RT \ln a_k^{(m)} + z_k F \varphi^{(m)} = RT \ln a_k^{(s)} + z_k F \varphi^{(s)}$$
(4-A1)

We have assumed that the standard chemical potential μ_k° is the same in the membrane and the solution. This may be an oversimplification, because there may be specific chemical interactions of the ions in the membrane, for example with the ion exchange groups. Eq. 4-A1 leads to the definition of the Donnan potential $E_D = \phi^{(m)} - \phi^{(s)}$ (Eq. 4-38). Since Eq. 4-A1 needs to hold for the anions (-) as well as the cations (+) we can write

$$E_{\rm D} = \Delta \varphi = \varphi^{\rm (m)} - \varphi^{\rm (s)} = -\frac{RT}{z_+F} \ln \frac{a_+^{\rm (m)}}{a_+^{\rm (s)}} = -\frac{RT}{z_-F} \ln \frac{a_-^{\rm (m)}}{a_-^{\rm (s)}}$$
(4-A2)

which leads to

$$\left(\frac{a_{+}^{(m)}}{a_{+}^{(s)}}\right)^{\frac{1}{z_{+}}} = \left(\frac{a_{-}^{(m)}}{a_{-}^{(s)}}\right)^{\frac{1}{z_{-}}}$$
(4-A3)

where we remember that $z_+ > 0$ and $z_- < 0$. To simplify the discussion we assume a 1-1 electrolyte (e.g., NaCl) and ideal conditions ($\gamma_k = 1$). Thus, we obtain:

$$\frac{c_{+}^{(m)}}{c_{+}^{(s)}} = \frac{c_{-}^{(s)}}{c_{-}^{(m)}}$$
(4-A4)

For a CEM, the concentration of cations (= counter-ions) in the membrane $c_{+}^{(m)}$ is equal to the concentration of fixed ions c_F plus the concentration of excess ions in the membrane c_M . The concentration of anions (=co-ions) in the membrane $c_{-}^{(m)}$ is equal to the concentration of excess ions c_M . The concentration of anions and cations in the solution is $c_{+}^{(s)} = c_{-}^{(s)} = c_E$. We therefore obtain:

$$\frac{c_{\rm F} + c_{\rm M}}{c_{\rm E}} = \frac{c_{\rm E}}{c_{\rm M}} \tag{4-A5}$$

and by analogy for an AEM:

$$\frac{c_{\rm M}}{c_{\rm E}} = \frac{c_{\rm E}}{c_{\rm F} + c_{\rm M}} \tag{4-A6}$$

Eqs. 4-A5 and 4-A6 yield the same quadratic equation for c_M , which has the following solution (considering only the solution $c_M > 0$):

$$c_{\rm M} = \sqrt{\left(\frac{c_{\rm F}}{2}\right)^2 + \left(c_{\rm E}\right)^2} - \frac{c_{\rm F}}{2}$$
 (4-A7)

One limiting case is obtained at high concentration of fixed ions c_F / low concentration of excess electrolyte c_M : $c_M \ll c_F$. From Eq. 4-A5 or 4-A6 we thus obtain $c_M \approx (c_E)^2 / c_F$. In this case the concentration of excess electrolyte in the membrane c_M increases with the square of the external solution concentration c_E . Another limiting case is obtained for a high concentration of external electrolyte c_E compared to the fixed ion concentration in the membrane c_F : $c_E \gg c_F$. This situation is formally similar to the case where we have an uncharged membrane, where the concentration of the excess electrolyte in the membrane c_M is approximately equal to the concentration of the external electrolyte c_E : $c_M \approx c_E$.

For a real solution of a 1-1 electrolyte we rewrite Eq. 4-A4:

$$\frac{c_{+}^{(m)}\gamma_{+}^{(m)}}{c_{+}^{(s)}\gamma_{+}^{(s)}} = \frac{c_{-}^{(s)}\gamma_{-}^{(s)}}{c_{-}^{(m)}\gamma_{-}^{(m)}}$$
(4-A8)

With the definition of the mean activity coefficient for a 1-1 salt $(\gamma_{\pm})^2 = \gamma_{\pm}\gamma_{\pm}$ Eq. 4-A5 is rewritten as follows:

$$\frac{c_{\rm F} + c_{\rm M}}{c_{\rm E}} = \frac{c_{\rm E}}{c_{\rm M}} \left(\frac{\gamma_{\pm}^{(\rm s)}}{\gamma_{\pm}^{(\rm m)}}\right)^2 \tag{4-A9}$$

The solution of the quadratic equation then leads to:

$$c_{\rm M} = \sqrt{\left(\frac{c_{\rm F}}{2}\right)^2 + (c_{\rm E})^2 \left(\frac{\gamma_{\pm}^{(\rm s)}}{\gamma_{\pm}^{(\rm m)}}\right)^2 - \frac{c_{\rm F}}{2}}$$
(4-A10)

Sample data for an AEM immersed in NaCl solution are shown in **Figure 4-18**. At low concentration of the solution c_E , the concentration of counter-ions Cl⁻ in the membrane corresponds largely to the concentration of the fixed ions c_F of 3.58 M. Starting at an external concentration of around 0.2 M, significant excess electrolyte c_M is incorporated into the membrane. The concentration c_M of co-ions Cl⁻ and of excess counter-ions Na⁺ in the membrane is clearly below what would be expected from a non-selective, uncharged membrane with $c_M = c_E$. Thus, there is co-ion exclusion, yet the concentration c_M does not quite follow the ideal Donnan behavior. A number of arguments may be put forward in explanation of this. For example, it is unlikely that we can assume ideal conditions, especially in the membrane. A lower activity coefficient in the membrane than in the solution, $\gamma_{\pm}^{(m)} < \gamma_{\pm}^{(s)}$, is particularly likely at low solution concentration, which, according to Eq. 4-A10, will move the theoretical curve in **Figure 4-18** upwards toward the experimental values. Moreover, we have neglected osmotic pressure effects. Taking those into account (cf. **Appendix B**) will also move the theoretical curve at low solution concentration upward.



Figure 4-18. Concentration of counter-ions (Cl⁻) and co-ions (Na⁺) in mol per volume of sorbed water in an AR103 anion exchange membrane (fixed ion concentration: $c_F = 3.58 \text{ mol/L}$) as a function of the external NaCl concentration. The associated Donnan potential is calculated using Eq. 4-38. Ideal Donnan behavior is calculated using Eq. 4-A7. (Data: Macromolecules 48, 2011, 8011)
Appendix B: Osmotic Pressure

If an ion exchange membrane is in contact with an aqueous electrolyte, the osmotic pressure between the two phases is caused by the difference in the activity of water a_w :

$$\Delta \pi = p^{(m)} - p^{(s)} = -\frac{RT}{\bar{V}_{w}} \ln(\frac{a_{w}^{(m)}}{a_{w}^{(s)}})$$
(4-B1)

where \bar{V}_w is the partial molar volume of water (18 cm³/mol at room temperature). The value of RT/\bar{V}_w is 1'380 bar at 25°C. As an example, for a solution of pure water ($a_w = 1$) and a saturated NaCl solution of ~6 M concentration with $a_w = 0.753$, separated by a semipermeable membrane, we obtain a value for the osmotic pressure of $\Delta \pi = 390$ bar, showing that osmotic pressure can be appreciable. In case of an IEM with high concentration of fixed ions in a dilute solution, osmotic effects can lead to strong swelling pressure in the membrane. This swelling pressure is the balancing force between the opposing tendencies of dilution of the ionic charges in the membrane and the elasticity of the polymer matrix which opposes such dilution.

If we consider the effect of hydrostatic pressure p in a phase, an additional term $\bar{V}_k p$ needs to be added to the expression for the electrochemical potential of an ion: $\tilde{\mu}_k = \mu_k^\circ + RT \ln a_k + z_k F \varphi + \bar{V}_k p$. \bar{V}_k is the molar volume of the ion in solution. Eq. 4-A3 is therefore modified as follows:

$$\left(\frac{a_{+}^{(m)}}{a_{+}^{(s)}}\right)^{\frac{1}{z_{+}}} \cdot \left(\frac{a_{-}^{(s)}}{a_{-}^{(m)}}\right)^{\frac{1}{z_{-}}} = \exp\left(\frac{\Delta\pi}{RT}\frac{\overline{V_{s}}}{z_{+}V_{+}}\right) =: k_{\Delta\pi}$$
(4-B2)

 \overline{V}_{s} is the partial molar volume of the electrolyte (e.g., 16.7 cm³/mol for dilute NaCl solution) and $z_{\pm}v_{\pm}$ is the equivalence number of the salt (e.g., 1 for NaCl). The factor is only significant at elevated osmotic pressures. For NaCl solution at room temperature, $k_{\Delta\pi} = 1.07$ at $\Delta\pi = 100$ bar, and $k_{\Delta\pi} = 1.96$ at $\Delta\pi = 1'000$ bar. It is not unusual for ion-exchange material in equilibrium with pure water to develop swelling pressures on the order of 100 bar¹. Using Eq. 4-A1 to recalculate the Donnan potential $E_{\rm D}$, we observe that the osmotic pressure $\Delta\pi$ tends to increase the magnitude of $E_{\rm D}$, and solving the modified quadratic equation we find that the content $c_{\rm M}$ of excess electrolyte increases with $\Delta\pi$.

¹ J. Chem. Soc. Faraday Trans. 1 84(6), 1988, 2047

Appendix C: Ideal Membrane Potential

For the membrane potential discussed in Section 2.2 we studied the limiting case of a membrane with high fixed-ion concentration, such that the membrane potential is dominated by the two Donnan potentials at the two membrane-solution interfaces and the contribution of the diffusion potential in the membrane can be neglected. The ideal membrane potential is calculated using Eq. 4-40, where we have to insert the activities of the ions in solution α and β constituting the counterions in the membrane into the ln(...) term. However, the thermodynamic equilibrium described by the ideal membrane potential must also hold for co-ions. Hence, the corresponding expression is developed in this section.

We start by writing down explicitly the membrane potential $E_{\rm m}$ (Eq. 4-39) for the case that the diffusion / liquid junction potential $E_{\rm LJ}$ in the membrane can be neglected. The membrane potential pertaining to **Figure 4-12b** is then given by the difference of the Donnan potentials $E_{\rm D,\alpha}$ and $E_{\rm D,\beta}$:

$$E_{\rm m} \approx E_{{\rm D},\alpha} - E_{{\rm D},\beta} = \left(-\frac{RT}{zF}\ln(\frac{a_{\alpha}^{\rm m}}{a_{\alpha}^{\rm s}})\right) - \left(-\frac{RT}{zF}\ln(\frac{a_{\beta}^{\rm m}}{a_{\beta}^{\rm s}})\right) = -\frac{RT}{zF}\left(\ln(\frac{a_{\alpha}^{\rm m}}{a_{\alpha}^{\rm s}}) - \ln(\frac{a_{\beta}^{\rm m}}{a_{\beta}^{\rm s}})\right)$$
$$= -\frac{RT}{zF}\ln(\frac{a_{\alpha}^{\rm m}}{a_{\alpha}^{\rm s}} \cdot \frac{a_{\beta}^{\rm s}}{a_{\beta}^{\rm m}}) = -\frac{RT}{zF}\ln(\frac{a_{\beta}^{\rm s}}{a_{\alpha}^{\rm s}} \cdot \frac{a_{\alpha}^{\rm m}}{a_{\beta}^{\rm m}}) \cong -\frac{RT}{zF}\ln(\frac{c_{\beta}^{\rm s}}{c_{\alpha}^{\rm s}} \cdot \frac{c_{\alpha}^{\rm m}}{c_{\beta}^{\rm m}})$$
(4-C1)

where we have assumed ideal solutions in the last step for the sake of simplicity. This expression has to hold for counter-ions as well as co-ions. The concentration of ions in solutions c_{α}^{s} and c_{β}^{s} is known, yet the concentration of ions in the membrane c_{α}^{m} and c_{β}^{m} not *a priori*. We have to derive these based on the description of the Donnan equilibrium. We start with the counter-ions (•). At the limit of high fixed-ion concentration, the concentration of counter-ions c_{\bullet} is about equal to the concentration of fixed-ions c_{F} , because the uptake of excess electrolyte is very small, $c_{M} \ll c_{F}$. Therefore $c_{\bullet\alpha}^{m} \approx c_{\bullet\beta}^{m} \approx c_{F}$, hence $c_{\bullet\alpha}^{m}/c_{\bullet\beta}^{m} \approx 1$, and Eq. 4-C1 simplifies to

$$E_{\rm m} \approx -\frac{RT}{z_{\bullet}F} \ln(\frac{c_{\bullet\beta}^{\rm s}}{c_{\bullet\alpha}^{\rm s}}) \tag{4-C2}$$

which is identical to Eq. 4-40. In the example of a CEM, cations (z > 0) are counter-ions, hence for the case of $c_{\alpha}^{s} < c_{\beta}^{s}$ we obtain $E_{m} < 0$, in agreement with **Figure 4-12b**. Using an AEM in the same setting we get $E_{m} > 0$, because z < 0. In case of the co-ions (O), at the limit of high fixed-ion concentration Donnan exclusion of co-ions is very effective, $c_{\rm M} \ll c_{\rm F}$. We have seen in Appendix A that under these conditions we can write $c_{\rm M} \approx (c_{\rm E})^2 / c_{\rm F}$, where $c_{\rm E}$ is the ion concentration in the solution. For the argument of the ln() in Eq. 4-C1 we therefore obtain

$$\frac{c_{\mathsf{O}_{\mathsf{B}}}^{\mathrm{s}}}{c_{\mathsf{O}_{\alpha}}^{\mathrm{m}}} = \frac{c_{\mathsf{O}_{\mathsf{B}}}^{\mathrm{s}}}{c_{\mathsf{O}_{\alpha}}^{\mathrm{m}}} = \frac{c_{\mathsf{O}_{\mathsf{B}}}^{\mathrm{s}}}{(c_{\mathsf{O}_{\mathsf{B}}}^{\mathrm{s}})^{2} / c_{\mathrm{F}}} = \frac{c_{\mathsf{O}_{\mathsf{A}}}^{\mathrm{s}}}{c_{\mathsf{O}_{\mathsf{B}}}^{\mathrm{s}}}$$
(4-C3)

For the membrane potential we then obtain

$$E_{\rm m} \approx -\frac{RT}{z_{\rm o}F} \ln(\frac{c_{\rm oa}^{\rm s}}{c_{\rm o\beta}^{\rm s}}) \tag{4-C4}$$

As we can see, the expression yields the same result as Eq. 4-C2, because the argument of the logarithm is inverted and co-ions have opposite charge to counter-ions. The two effects cancel.

Appendix D: Mixed Ionic-Electronic Conductors

A mixed ionic-electronic conductor (MIEC) displays ionic as well as electronic conductivity. An example of such a material is ceria, $CeO_{2-\delta}$. As shown in **Figure 4-16b**, at low oxygen partial pressure, Ce^{4+} -ions can undergo partial reduction to Ce^{3+} according to the following defect chemical reaction:

$$2Ce_{Ce}^{x} + O_{O}^{x} \xrightarrow{CeO_{2}} V_{O}^{\bullet\bullet} + 2Ce'_{Ce} + \frac{1}{2}O_{2}$$

$$(4-D1)$$

which, essentially, describes an oxygen evolution reaction. Ce^{3+} sites carry an excess electron compared to the majority Ce^{4+} sites in the cation sublattice. This electronic defect is described as Ce'_{Ce} . It leads to n-type electronic conductivity σ_e :

$$\sigma_{\rm e} = q \, [{\rm Ce'}] \, u \tag{4-D2}$$

where *q* is the charge of the defect, here $1 \cdot e$, and *u* is the mobility (unit: $m^2 \cdot V^{-1} \cdot s^{-1}$) of the electronic defect. The unit of [Ce'] is cm⁻³. The concentration of Ce³⁺ and thus that of excess electrons is given by the law of mass action, as in conventional chemical reactions, with equilibrium constant *K*₁:

$$K_{1} = \frac{[V_{0}^{\bullet\bullet}][Ce']^{2}\sqrt{p(O_{2})}}{a(CeO_{2}) = 1}$$
(4-D3)

The left side of the chemical Reaction 4-D1 is defect-free CeO₂, which has unit activity. Oxygen vacancies, $V_0^{\bullet\bullet}$, are formed along with Ce³⁺, which leads to oxygen ion conductivity. The formation of these defects is thermally activated, hence the oxygen vacancies are called *intrinsic* defects. Electroneutrality requires that the oxygen defect concentration is stoichiometrically tied to Ce³⁺ concentration according to [Ce'] = 2 [V_0^{\bullet\bullet}]. Therefore, we can express the concentration of excess electrons and, consequently, electronic conductivity as a function of oxygen partial pressure $p(O_2)$ by solving Eq. 4-D3 for Ce':

$$[Ce'] = (2K_1)^{1/3} p(O_2)^{-1/6} = K'_1 p(O_2)^{-1/6}$$
(4-D4)

We see that electronic conductivity strongly increases at low oxygen partial pressure with the proportionality $\sigma_e \propto p(O_2)^{-1/6}$ for intrinsic defects.

In analogy to YSZ, ceria can be doped to introduce oxygen vacancies, for example with gadolinia, Gd₂O₃:

$$Gd_2O_3 \xrightarrow{CeO_2} V_0^{\bullet\bullet} + 2Gd'_{Ce} + 3O_0^{X}$$
(4-D5)

The concentration of these *extrinsic* defects is given by the doping level. In addition, intrinsic defects are created by thermal activation, yet their concentration is typically much smaller than that of the extrinsic defects. Since for extrinsic defects the concentration of oxygen vacancies is no longer stoichiometrically tied to the concentration of excess electrons, we obtain from Eq. 4-D3 a different relation between [Ce'] and $p(O_2)$:

$$[Ce'] = \left(\frac{K_2}{[V_0^{\bullet}]}\right)^{1/2} p(O_2)^{-1/4} = K'_2 p(O_2)^{-1/4}$$
(4-D6)

The dependence of electronic conductivity on the oxygen partial pressure is therefore different for doped ceria with extrinsic oxygen vacancies, $\sigma_e \propto p(O_2)^{-1/4}$. The conductivity of Ce_{0.8}Sm_{0.2}O_{1.9-δ} in **Figure 4-17b** shows this dependence, with ionic conductivity dominating at intermediate and high $p(O_2)$ and electronic conductivity dominating at low $p(O_2)$, the transition being a function of temperature.

Chapter V

Dynamic Electrochemistry

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So far, we have mostly studied electrodes and cells under thermodynamically ideal conditions, i.e. at equilibrium. This allowed us to describe and quantify the *possibility* for reactions to take place. Whether they actually do take place in the real world is a question of kinetics, which describe how easily reactions occur and at what rate. Take the example of metallic aluminium, which should readily corrode in air, yet is very stable, because it is covered by a dense, electronically insulating oxide film. The corrosion of the underlying Al metal is kinetically hindered. Iron is thermodynamically more stable, but actually readily corrodes ('rusts'), as we know. In most applications of electrochemistry, we are interested in cells that pass current, because we would like to use the flow of charge for our purpose, for example to produce compounds of commercial interest (cf. Chapter VI), propel an electric vehicle (cf. Chapter VII), or measure concentrations of toxic gases (cf. Chapter VIII). The description of the kinetics of electrochemical reactions is the main topic in this chapter. We will look at ways to describe electron transfer at the electrode-electrolyte interface and quantify the loss terms, called 'overpotentials', which are a measure of the deviation from the equilibrium. Therefore, 'dynamic electrochemistry' deals with the description of processes associated with the passage of charge in electrochemical systems. In addition, in Section 3, we will study mass transfer phenomena, which can limit electrochemical reactions at high current densities. We will study different mechanisms of mass and charge transport in the electrolyte, viz., diffusion, migration and convection.

1 Departure from Equilibrium

To start with, we consider a cell that is initially at equilibrium. As an example, we choose the H_2 -Cl₂ cell with hydrochloric acid electrolyte. The reaction equation is:

$$Cl_2 + H_2 = 2 HCl(aq)$$
 $U_{rev}^{\circ} = 1.36 V$ (5-1)

This invertible H₂-Cl₂ cell can be operated in galvanic as well as electrolytic mode. To operate it in galvanic mode, i.e., as a fuel cell, we supply hydrogen and chlorine gas to the electrodes. Then, we connect a load, for instance an ohmic resistor, between the electrodes. Current starts to flow and the cell voltage drops below the equilibrium value. H₂ and Cl₂ are reacting at a finite rate (cf. Chapter I, Faraday's laws) to HCl(aq). If we change the magnitude of the load, the current and corresponding voltage change. In this manner, we can record a polarization curve (**Figure 5-1**). This is a spontaneous reaction, meaning that the cell is generating electrical power. The more current we draw, the lower the cell voltage. The deviation of the cell voltage U from the reversible voltage U_{rev} is the loss term $\Delta U_{loss} = U_{rev} - U$, which results in waste heat production (cf. Chapter VII).

We can also operate this cell in electrolytic mode by driving a current through the cell in opposite direction with a power supply (or potentiostat / galvanostat). In this case, HCl(aq) decomposes to H₂ and Cl₂, which evolve at the electrodes. Reaction 5-1 is proceeding in backward direction. Forcing current through the cell will cause the cell voltage to increase above the thermodynamic equilibrium voltage of $U_{rev}^{\circ} = 1.36$ V (standard conditions, 25°C).¹ This is a thermodynamically 'uphill', i.e., non-spontaneous reaction, which we can force to take place using the energy provided by the power supply. The higher the current, the higher the cell voltage. Here, the loss term ΔU_{loss} describes the energy additional to the thermodynamic ideal we need to provide to make the reaction take place at a certain rate, i.e. current density.

5-3



Figure 5-1. Schematic polarization curve for a H₂-Cl₂ cell in HCl(aq) electrolyte that can be operated both in galvanic and in electrolytic mode. The departure of the cell voltage U from the equilibrium U_{rev} leads to the loss term $\Delta U_{loss.}$, which grows with increasing current density.

The departure from equilibrium is accompanied by a deviation of the cell voltage from the theoretical voltage described by thermodynamics. Next, let us look at what is happening at the two electrodes in a bit more detail. In the absence of current, i.e., at 'open circuit' conditions, the electrodes' potentials are at the values corresponding to the equilibrium under the prevailing conditions (temperature, pressure, activity of compounds involved in the reaction, cf. Chapter II, Nernst equation), at standard conditions we have $E^{\circ}(H^+/H_2) = 0.00 \text{ V}$ and $E^{\circ}(Cl_2/C\Gamma) = +1.36 \text{ V}$ at 25°C. In **Figure 5-2a** the electron energy (cf. also Chapter III) in the two electrodes, determined by the equilibrium formed with the respective redox couple in solution, is sketched. The electron energy is coupled to the Galvani potential φ of the electrode, $\tilde{\mu}_e = \mu_e - zF\varphi$ (cf. Chapter III). An increase in electron energy corresponds to a decrease in potential, and vice versa. First, let us look

¹ Actually, as we recall from Chapter II, U_{rev} is negative for a non-spontaneous (=electrolytic) reaction. For practical reasons, however, we often use the positive value to render the formalism less troublesome.

at the case when we operate the cell in galvanic (fuel cell) mode. The current that is observed as a result of the connection of a load to the electrodes must be the same on the anode and the cathode. The potential of the negative electrode is lifted to more positive values, which 'drains' electrons from the H⁺/H₂ redox couple and causes hydrogen to be oxidized to protons: $H_2 \rightarrow 2 H^+ + 2 e^-$ (Figure 5-2b). Concurrently, the potential of the positive electrode drops to more negative values, which 'pumps' electrons into the Cl₂/Cl⁻ redox couple and triggers chlorine to be reduced to chloride ions: Cl₂ + 2 e⁻ \rightarrow 2 Cl⁻. The opposite situation is encountered for the electrolytic reaction (Figure 5-2c). Electrons are 'pumped' into the negative electrode, forcing it to become even more negative, which causes the hydrogen evolution reaction to take place. The potential of the positive electrode is forced to even more positive potentials, which triggers the chorine evolution reaction. Also in this case, faradaic currents in both electrodes must be the same for conservation of charge.



Figure 5-2. Electron energy diagram for the H₂-Cl₂ cell, indicating the location of the Fermi level E_F (\triangleq the electrochemical potential of the electron) in the H₂ and Cl₂ electrode and the position of the half-cell equilibria corresponding to the redox couples H⁺/H₂ and Cl₂/Cl⁻. N.B.: an increase of the electrode potential leads to a decrease of E_F . a) equilibrium, b) galvanic cell mode, c) electrolytic cell mode. The cell voltage is given by $U = (E_F^+ - E_F^-)/e$.

Next, we look at the change in the potential of the electrodes as a function of the cell current in qualitative manner (**Figure 5-3**). In the fuel cell operation mode, the hydrogen electrode is *polarized* to more positive potentials than its equilibrium potential, the chlorine electrode is at a more negative potential compared to the equilibrium. The deviation of the electrode potential *E* from its equilibrium value E_{rev} is called *overpotential* η :

$$\eta \equiv E - E_{\rm rev} \tag{5-2}$$

According to this definition, positive values of η trigger an oxidation reaction, and the corresponding anodic current i_a is defined as positive current. Consequently, a reduction reaction is caused by a cathodic overpotential $\eta < 0$ with a negative, cathodic current i_c , where the absolute values of i_a and i_c need to be the same (provided the two electrodes have the same geometric area).



Figure 5-3. Effect of cell polarization on the potential of the H₂ and Cl₂ electrodes. The overpotential η indicates the deviation of the electrode potential from its equilibrium value. The current density on the two electrodes has to be the same (provided identical geometric area of the electrodes). (a) fuel cell mode, (b) electrolysis mode of operation.

Table 5-1. Relation between overpotential and type of reaction upon the polarization of an electrode.

Polarization	Overpotential η	Net reaction	Electrode
anodic	anodic, $\eta > 0$	oxidation, $i > 0$	anode
cathodic	cathodic, $\eta < 0$	reduction, $i < 0$	cathode

As we can see in **Figure 5-3**, the value of the overpotential increases monotonically as a function of the current flowing through the electrode. We can see the qualitative agreement of the resulting cell voltage with the cell voltage shown as a function of current density (polarization curves) in **Figure 5-1**. The anodic and cathodic currents have the same value, but the absolute values of the anodic and cathodic overpotentials are generally different. The way the overpotential changes with current depends on the type of reaction, the material of the electrode, the type of electrolyte, and a number other parameters, such as the pH of the solution, pressure and temperature (cf. below).

The overpotentials associated with an electrochemical reaction are categorized into the following types:

- η_a Activation overpotential η_a or charge transfer overpotential η_{CT} . It characterizes the driving force for charge transfer at the electrode-electrolyte interface, as illustrated in Figure 5-3, and is non-linear in the current density *i* (cf. Section 2).
- η_{Ω} Ohmic overpotential, also η_{iR} . This is the potential drop in cell components caused by the finite ohmic resistance of the electronically and ionically conducting materials, given by Ohm's law $\eta_{\Omega} = \Delta U_{\Omega} = i \cdot R$.
- η_{conc} Concentration or mass transport overpotential η_{mtx} is caused by the limited rate of transport of reactants to the reaction site, i.e., the electrode surface, which leads to a local concentration decrease or even depletion of the species (cf. Section 3).

In an electrochemical cell, we have a contribution of η_a and η_{conc} for each of the electrodes and an ohmic overpotential η_{Ω} . The latter is, in most cases, dominated by the resistance of the electrolyte R_i , since the ionic conductivity of the electrolyte is normally much lower than the electronic conductivity in the electrodes and other electron conducting phases. Nevertheless, ohmic resistance of electrodes R_e and contact resistances $R_{contact}$, which also follow an ohmic behavior, can often not be ignored. Consequently, the overall ohmic overpotential η_{Ω} is made up of contributions from those different sources: $\eta_{\Omega} = i \cdot (R_i + R_e + R_{contact})$.

The total overpotential η_{tot} includes all the overpotentials (charge transfer, ohmic, and concentration overpotentials) and is defined as a positive value:

$$\eta_{\text{tot}} \equiv \sum_{k} |\eta_{k}| = \Delta U_{\text{loss}}$$
(5-3)

This represents the voltage difference ΔU_{loss} of the cell voltage from the reversible voltage and is an expression for how much the cell reaction deviates from the thermodynamic ideal. In this definition, ΔU_{loss} is always ≥ 0 . We can now schematically draw the distribution of the (Galvani) potential across the cell from the negative H₂ electrode to the positive Cl₂ electrode with the electrolyte in between (**Figure 5-4**). At equilibrium, the potentials in the different phases are uniform, because no current is flowing, and the potential difference at the two electrode-electrolyte interfaces are at their equilibrium values. The drop of potential across the interface appears as a step here, but as we know, it follows the structure of the electrochemical double layer with a thickness in the range of Å to nm (cf. Chapter III). As elaborated in Chapter III, the potential of the electrolyte φ_s is experimentally



Figure 5-1. Schematic representation of the Galvani potential in the electrodes and electrolyte upon galvanic and electrolytic polarization of a cell (dotted blue lines: equilibrium conditions). The potential of the negative electrode is chosen as a reference potential. The arrow indicates the direction of current in the electrolyte. The position of the potential in the electrolyte q_k is arbitrarily chosen to lie between the two electrode potentials. The potential drop at the electrolyte interface and, hence, the activation overpotential is restricted to the dimension of the double layer, which is well below the macroscopic cell dimensions illustrated here.

inaccessible, therefore we arbitrarily choose to give it a value between those of the electrodes. As we polarize the cell, the potential difference at the interfaces changes, that is, an activation overpotential develops. In addition, we see a potential drop in the electrolyte, which is a consequence of its finite ionic conductivity σ . According to Ohm's law, $i = -\sigma \cdot \nabla \varphi$, where $\nabla \varphi$ is the potential gradient, hence the potential drops in the direction of charge flow¹. The potential drop in the electrodes is usually negligible due to the much higher electrical conductivity, as explained above.

2 Charge Transfer Reaction

In this section, we will develop a description of the relationship between overpotential and current density for the charge transfer process at the electrode-electrolyte interface, i.e. the half-cell reaction of one electrode. By 'charge' we mean 'electron' here. To start with, it is worthwhile to recall the various types of electrode processes, such as metal dissolution / plating, gas evolving / consuming reactions, electron transfer reactions between dissolved ions, etc. Any of those reactions involves not only the actual charge transfer process, but a number of additional chemical or physical steps, depending on the nature of the reaction, such as bond formation and cleavage. For the simple case of a redox reaction between species in solution, for example between Fe³⁺ and Fe²⁺, we can identify mass transport and adsorption processes for the reactant and product (**Figure 5-5**). In addition, the dipoles (ligands, solvent molecules) found in the solvation sphere of the species undergoing reaction are reoriented, because the oxidized and reduced form of the compound carry a different charge. All



Figure 5-2. Processes and reaction steps involved in a simple half-cell reaction in solution $S + e^- \Rightarrow S^-$. The characteristic time constants are taken from Brett and Oliveira Brett, Electrochemistry: Principles, Methods, and Applications, Oxford University Press, 1993. Adsorption and diffusion processes are even slower (>ns, μ s).

¹ Cations (+ charge) flow towards the cathode, anions (- charge) towards the anode. It is not the case that cations only flow toward the (-) electrode and anions only toward the (+) electrode. In the case of a galvanic cell (cf. **Figure 5-1**) the cations flow towards the (+) electrode and the anions towards the (-) electrode.

those processes are associated with different time constants. The electron transfer process itself is relatively fast (10^{-16} s) , whereas the other reactions are much slower. This essentially means that electron transfer takes place while the reacting centers and surrounding molecules are 'frozen' in place (Franck-Condon principle).



Figure 5-6. Differentiation between outer sphere and inner sphere reactions. Outer sphere reactions do not involve a chemical interaction of the reacting species with the electrode. In the reacting entity, typically a central metal ion surrounded by ligands, merely the bond length in the inner sphere changes between the reduced and the oxidized state. Inner sphere reactions involve the breaking of the ligand sphere and adsorption of the reacting compound.

2.1 Outer sphere reaction

In the following, we are going to describe the energetics of an electrode process. Many of the technologically relevant reactions involve chemical reaction steps. For example, in the hydrogen evolution reaction discussed above, a chemical bond between hydrogen atoms is formed. Such



Figure 5-3. Free energy of the reaction system $Ox + e^- \leftrightarrows Red$ during its transition from the Ox state via the transition state to the Red state, and vice versa. The increase of the electrode potential from φ_1 to φ_2 leads to a decrease in the energy of the electron and thus the energy of the (Ox + e⁻) state, thereby reducing the activation energy ΔG_a^{\ddagger} and favoring the anodic (backward) reaction. At the same time the cathodic (forward) reaction is disfavored, because the activation energy ΔG_c^{\ddagger} increases.

multi-step reactions are not straightforward to analyze and describe mechanistically. Therefore, in order to reduce complexity, we shall first consider an electron transfer process that does not involve a chemical interaction of the reacting species with the electrode, a so called *outer sphere* reaction (**Figure 5-6**). An outer sphere electron transfer process is characterized by weak interaction of the reacting species with the electrode surface, with the inner coordination sphere remaining intact during the process. A model type outer sphere reaction is that of a redox couple in solution, generically written as $Ox + e^- \leftrightarrows Red$, which describes an elementary reaction with a single e^- transfer. A well-known example is $[Ru(NH_3)_6]^{3+} + e^- \leftrightarrows [Ru(NH_3)_6]^{2+}$. The metal center, i.e. the reacting entity, is located at the outer Helmholtz plane (OHP) of the electrode surface, thereby minimizing chemical interactions. Another example is the reaction $[Fe(H_2O)_6]^{3+} + e^- \leftrightarrows [Fe(H_2O)_6]^{2+}$, but only in the absence of Cl⁻ or other halide ions ! Chloride ions modify the inner sphere and catalyze the reaction, turning it into an *inner sphere* reaction.

For the reaction $Ox + e^- \leftrightarrows$ Red we can schematically plot the free energy *G* of the reaction system as a function of the reaction coordinate, which represents progress along a reaction pathway (**Figure 5-7**). Here, the reaction coordinate may represent by the bond length to the ligands in the inner coordination sphere. We will assume that the electrolyte concentration is sufficiently high, such that the diffuse part of the double layer can be neglected and the solution phase potential φ_s just outside the Helmholtz layer is equal to the potential in the electrolyte bulk and thus unaffected by the electrode potential φ_m (here =: φ). The free energy curve shows the energy of the oxidized and the reduced side of the reaction and the energy trajectory to get from one to the other. The transition state (activated complex) is associated with the energy maximum. Hence the system must overcome the activation energy ΔG_c^{\ddagger} for the forward reaction (here the reduction reaction, c = cathodic), and ΔG_a^{\ddagger} for the backward reaction (here the oxidation reaction, a = anodic). The overall reaction rate v(unit: mol·cm⁻²·s⁻¹) is given as the difference of the anodic and cathodic reaction rate, $v = k_a \cdot c_{red} - k_c \cdot c_{ox}$, where k is the heterogeneous rate constant (unit: cm·s⁻¹) and c is the concentration of the reactant (unit: mol·L⁻¹). According to transition state theory, the rate constant depends on the activation energy in the following manner:

$$k_{\rm a} = k_{\rm a}^0 \cdot \exp(-\frac{\Delta G_{\rm a}^{\ddagger}(\varphi)}{RT})$$
(5-4)

$$k_{\rm c} = k_{\rm c}^0 \cdot \exp(-\frac{\Delta G_{\rm c}^{\ddagger}(\varphi)}{RT})$$
(5-5)

The crucial aspect here is that the two activation energies depend on the electrode potential φ , hence the rate constants of the cathodic k_c and anodic k_a reaction can be modified by changing the electrode potential φ . The reason for this dependence can be understood on the basis of the influence of the electrode potential on the energy of the system in its oxidized state $[Ox + e^-]$ and reduced state [Red], respectively. Ox and Red are located at the OHP, hence they do not 'feel' the influence of the electrode potential (recall the assumptions we made), yet the energy of the electron in the electrode changes by $-F \cdot \Delta \varphi$ if the electrode potential is changed from φ_1 to φ_2 , with $\Delta \varphi = \varphi_2 - \varphi_1$. Remember that when the electrode potential is increased (viz., made more positive), the energy of the electron decreases ('electron pressure' decreases), and vice versa. Therefore, the free energy difference between $[Ox + e^-]$ and [Red] changes by $-F \cdot \Delta \varphi$ (**Figure 5-7**). It is now reasonable to assume that the change in energy of the transition state is somewhere between that of $[Ox + e^-]$ and [Red], i.e. some fraction β of $-F \cdot \Delta \varphi$, where $0 < \beta < 1$. Hence, the energy of the activated state changes by $-\beta \cdot F \cdot \Delta \varphi$. Consequently, with a change of the electrode potential from φ_1 to φ_2 , the activation energies are modified as follows:

$$\Delta G_{a2}^{\ddagger} = \Delta G_{a1}^{\ddagger} - \beta \cdot F \cdot \Delta \varphi \tag{5-6}$$

$$\Delta G_{c2}^{\ddagger} = \Delta G_{c1}^{\ddagger} + (1 - \beta) \cdot F \cdot \Delta \varphi \tag{5-7}$$

which can be inferred from the energy balances shown in **Figure 5-7**. The parameter β is called *symmetry factor*, as it describes the location of the transition state on the reaction coordinate. Its value is generally around 0.5, which means that the transition state is half way between the reactant and the product state.

With this knowledge, we can now write down the current density of the forward and backward reaction. In general, the current density is given by $i = z \cdot F \cdot c \cdot k$, where here we can set z = 1, because we are dealing with an elementary one-electron process. Using Eqs. 5-4 to 5-7, we can write for the anodic and cathodic current densities, taking the situation at the equilibrium potential as reference point:

$$i_{a} = F \cdot c_{red} \cdot k_{a}^{0} \cdot \exp(-\frac{\Delta G_{a,eq}^{\ddagger} - \beta F(\varphi - \varphi_{eq})}{RT})$$
(5-8)

$$i_{\rm c} = -F \cdot c_{\rm ox} \cdot k_{\rm c}^0 \cdot \exp(-\frac{\Delta G_{\rm c,eq}^{\ddagger} + (1 - \beta)F(\varphi - \varphi_{\rm eq})}{RT})$$
(5-9)

where we have recalled that $i_a > 0$ and $i_c < 0$. The net current density is $i = i_a + i_c$. At equilibrium we have $\varphi = \varphi_{eq}$ and i = 0, hence $i_a = |i_c|$. Therefore we have

$$i_{a} = F \cdot c_{red} \cdot k_{a}^{0} \cdot \exp(-\frac{\Delta G_{a,eq}^{\ddagger}}{RT}) = \left| i_{c} \right| = F \cdot c_{ox} \cdot k_{c}^{0} \cdot \exp(-\frac{\Delta G_{c,eq}^{\ddagger}}{RT}) = i_{0}$$
(5-10)

and defined the *exchange current density* i_0 . What does this mean? The net current is zero, because the anodic and cathodic currents at the electrode cancel. We therefore have a dynamic equilibrium. The exchange current density i_0 is a measure for the ease with which the electrochemical reaction of interest is taking place. It is a key descriptor of the electrochemical activity of the reaction system.

Next, we will see what happens when the potential of the electrode departs from its equilibrium value φ_{eq} , i.e., we have an overpotential $\eta = \varphi - \varphi_{eq}$. Since this is a potential difference we can conveniently also use the electrode potential *E* (measured against some reference) to describe it: $\eta = E - E_{rev}$. Inserting η and the expression for the exchange current density 5-10 into equations 5-8 and 5-9, we find for the net current density:

$$i = i_{a} + i_{c} = i_{0} \cdot \left[\exp(\frac{\beta F}{RT} \eta) - \exp(-\frac{(1-\beta)F}{RT} \eta) \right]$$
(5-11)

This is the *Butler-Volmer equation*. It describes the kinetics of a charge transfer reaction at an electrode governed by the departure of the electrode potential from its equilibrium value expressed by the overpotential η . Most notably, it states that the current density increases exponentially with



Figure 5-4. Electrode kinetics described by the Butler-Volmer equation 5-11, consisting of the anodic and the cathodic branch. At $\eta = 0$, the reaction is at equilibrium, as no net current is passing, and the anodic and cathodic reaction take place at equal rate in opposite directions corresponding to the exchange current density i_0 .

the overpotential. The net current is the sum of the anodic and the cathodic branch (**Figure 5-8**). At the equilibrium ($\eta = 0$), the two contributions cancel. It is a dynamic equilibrium, since both the anodic and cathodic reaction take place with a rate corresponding to the exchange current density i_0 . Upon polarization, he current density increases monotonically with the overpotential. Evidently, in practice the absolute value of the current density will not increase to arbitrarily high values, because at some point the reaction will become mass transport limited (cf. below).

2.1.1 Concentration dependence of i_0

For the description of the concentration dependence of the exchange current density i_0 , we write the expression for the exchange current density differently¹, using the reversible potential E_{rev} as reference point:

$$i_{a} = F \cdot c_{red} \cdot k_{a} \cdot \exp(\frac{\beta F}{RT} E_{rev}) = i_{0} = \left| i_{c} \right| = F \cdot c_{ox} \cdot k_{c} \cdot \exp(-\frac{(1-\beta)F}{RT} E_{rev})$$
(5-12)

Solving for E_{rev} yields:

$$E_{\rm rev} = \frac{RT}{F} \ln(\frac{k'_{\rm c}}{k'_{\rm a}}) + \frac{RT}{F} \ln(\frac{c_{\rm ox}}{c_{\rm red}}) = E_{\rm rev}^{\circ} + \frac{RT}{F} \ln(\frac{c_{\rm ox}}{c_{\rm red}})$$
(5-13)

which is the Nernst equation ! Inserting this back into Eq. 5-12 yields

$$i_{0} = F \cdot k_{a}^{'} \cdot c_{ox}^{\beta} \cdot c_{red}^{1-\beta} \cdot \exp(\frac{\beta F}{RT} E_{rev}^{\circ}) = F \cdot k_{c}^{'} \cdot c_{ox}^{\beta} \cdot c_{red}^{1-\beta} \cdot \exp(-\frac{(1-\beta)F}{RT} E_{rev}^{\circ})$$
(5-14)

With this, we obtain the concentration dependence of the exchange current density as

$$i_0 = F \cdot k_0 \cdot c_{\text{ox}}^\beta \cdot c_{\text{red}}^{1-\beta}$$
(5-15)

$$i_{a} = i_{0} = F \cdot c_{red} \cdot k_{a}^{0} \cdot \exp(-\frac{\Delta G_{a,eq}^{\ddagger}}{RT}) = F \cdot c_{red} \cdot k_{a}^{\dagger} \cdot \exp(\frac{\beta F}{RT} E_{rev})$$

The relationship between the different parameters in the two expressions therefore is:

$$\ln(\frac{k_{a}}{k_{a}^{0}}) = -\frac{\Delta G_{a,eq}^{\dagger} + \beta F E_{rev}}{RT}$$

An analogous expression is obtained for the cathodic reaction.

¹ The change of the expression for the exchange current density i_0 is performed as follows: from Eq. 5-10 we write for the exchange current density, using the expression for the anodic reaction:

5-13

where we have defined

$$k_{0} \coloneqq k_{a}^{\prime} \cdot \exp(\frac{\beta F}{RT} E_{rev}^{\circ}) = k_{c}^{\prime} \cdot \exp(-\frac{(1-\beta)F}{RT} E_{rev}^{\circ})$$
(5-16)

Based on the analysis of Eq. 5-15¹, we can discuss some specific cases. Since β often has a value of around 0.5, inserting $\beta = 0.5$ yields $i_0 = Fk_0\sqrt{c_{ox}c_{red}}$, and for equal concentrations $c_{ox} = c_{red} =: c$ the expression is simply $i_0 = Fk_0c$, also for $\beta \neq 0.5$. For a total concentration of $c_0 := c_{ox} + c_{red}$ with variable concentrations of oxidized species, $c_{ox} = X_{ox} \cdot c_0$, and reduced species, $c_{red} = X_{red} \cdot c_0$, where $X_{red} = 1 - X_{ox}$, the maximum of i_0 is at $X_{ox} = X_{red} = 0.5$ for $\beta = 0.5$, but 'off-center' for $\beta \neq 0.5$.

2.1.2 Temperature dependence of i_0

For the analysis of the temperature dependence of the exchange current density, we take Eq. 5-10 and replace ΔG_{eq}^{\ddagger} with $\Delta H_{eq}^{\ddagger} - T\Delta S_{eq}^{\ddagger}$ and obtain

$$i_0 = i_a = F \cdot c_{\text{red}} \cdot k_a^0 \cdot \exp(-\frac{\Delta H_{a,eq}^{\ddagger}}{RT}) \cdot \exp(\frac{\Delta S_{a,eq}^{\ddagger}}{R})$$
(5-17)

for the anodic branch. For the cathodic branch an analogous expression is obtained. Neglecting the temperature dependence of k, ΔH and ΔS we obtain the temperature dependence of i_0 from an Arrhenius analysis as

$$\frac{\partial \ln i_0}{\partial (1/T)} = -\frac{\Delta H_{a,eq}^{\ddagger}}{R} = -\frac{\Delta H_{c,eq}^{\ddagger}}{R} = -\frac{\Delta H_{eq}^{\ddagger}}{R} = -\frac{\Delta H_{eq}^{\ddagger}}{R}$$
(5-18)

The anodic and cathodic activation enthalpy are the same (need to be the same !), because the exchange current density represents a quantity that is defined based on the combination of the anodic and cathodic partial reactions. It is important to note that the activation energy of i_0 is composed of contributions of the activation energy for the forward and backward reaction, which in general, evidently, have different activation energies. We have also assumed here that ΔH_{eq}^{\ddagger} is independent of the potential difference $\Delta \varphi_{eq}$ between electrode and electrolyte. This is a reasonable assumption for outer sphere reactions, as elaborated initially, but may not be applicable to inner sphere reactions.

¹ Note that we can keep the unit of $c \pmod{L}$ in Eq. 5-15, even though we are raising c_{ox} and c_{red} to the power of β and $1-\beta$, respectively, because the 'fractional' units cancel if we rearrange $c_{ox}^{\beta} \cdot c_{red}^{1-\beta} = c_{ox}^{\beta}/c_{red}^{\beta} \cdot c_{red}$, so we are left with the unit of $c_{red} \pmod{L}$.

2.2 Inner sphere reaction

Outer sphere reactions are a bit of an oddity, most electrochemical reactions of technical interest are of the inner sphere type and involve some sort of specific interaction between the electrode and the reacting compounds. The relationship between current density and overpotential for an inner sphere reaction is generally complex and not straightforward, as the charge transfer process is coupled with other reaction steps, such as the formation and cleavage of chemical bonds, adsorption of intermediates, etc., one of which may be rate limiting. For example, the reaction of Cl_2 to Cl^- and vice-versa (cf. Figure 5-1) involves an adsorbed intermediate Cl_{ad} and the formation / cleavage of the Cl-Cl bond. In contrast to outer sphere reactions, the type of electrode material used has a pronounced effect on the kinetics of the reaction, owing to the specific interaction with Clad. The choice of a suitable *electrocatalyst* (cf. Chapter VII) helps to decrease the activation energy ΔG^{\ddagger} for the reaction and, thereby, increase the exchange current density i_0 . Furthermore, many electrochemical reactions involve the transfer of several electrons, e.g. $O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O_*$ typically one at a time. It is likely that one of those charge transfer processes is rate limiting. Despite the more complex situation, for inner sphere reactions the polarization behavior can often also be described by a Butler-Volmer type relation, possibly only in a limited potential / current range. As before, and in general, the energy of the electron in the electrode changes by $-F \cdot \eta$ with respect to the equilibrium for an overpotential η . Unlike for an outer sphere reaction, a reactant, product, or intermediate is adsorbed on the electrode surface and, hence, located within the region of potential drop in the electrochemical double layer. Therefore, the compound also 'feels' the change in electrode potential and / or the structure of the double layer is modified. The activation energy for the anodic and cathodic reaction then changes by $-\alpha_a \cdot F \cdot \eta$ and $+\alpha_c \cdot F \cdot \eta$, respectively, where α_a and α_c are the anodic and cathodic *transfer coefficients*. This is a purely phenomenological parameter determined experimentally, it is not a priori accompanied by an underlying mechanistic understanding. The value of α can range from ~0.2 to 2. A value >1 means that the change in activation energy is even higher than the change in electron energy, possibly because of an overwhelming chemical contribution. Therefore, unlike the symmetry parameter β , the transfer coefficient α is temperature dependent. The sum of α_a and α_c corresponds to the number of electrons transferred *n* divided by the number of occurrences of the rate determining step $v(rds)^1$: $\alpha_a + \alpha_c =$ n / v. Hence, for the general case we use the *phenomenological Butler-Volmer equation*:

¹ This relationship holds only if the rds is the same for the forward and backward reaction. We will not go in more depth here, for details cf. for example *Pure Appl Chem* **86**(2) (2014) 245, but only provide an example: consider the hydrogen evolution reaction (HER) in acid: $2 \text{ H}^+ + 2 \text{ e}^- \rightarrow \text{H}_2$, so z = 2. The reaction proceeds via an adsorbed hydrogen atom H_{ads} as intermediate (cf. Chapter VII). For the case where the electron transfer $\text{H}^+ + \text{e}^- \rightarrow \text{H}_{ads}$ is the rds, we have v = 2, because this reaction takes place twice in the overall reaction. Therefore, we have $\alpha_a + \alpha_c = n / v = 2 / 2 = 1$.

$$i = i_{a} + i_{c} = i_{0} \cdot \left[\exp(\frac{\alpha_{a}F}{RT}\eta) - \exp(-\frac{\alpha_{c}F}{RT}\eta) \right]$$
(5-19)

This equation, and the simplifications derived below, is widely used in applied electrochemistry to describe electrochemical reactions. Yet the expression with the two exp() functions is often somewhat unwieldy¹. We can, therefore, use simplified relationships between current density and overpotential for the two following limiting cases:

High $|\eta|$, i.e. $|\eta| \gg \frac{RT}{aF}$

In this case, one of the branches can be neglected. For example, for a high anodic overpotential we can drop the cathodic branch to obtain

$$i \approx i_0 \cdot \exp(\frac{\alpha_a F}{RT} \eta)$$
 (5-20)

and an analogous expression for the cathodic reaction. After taking the logarithm, change to base 10, and rearrangement we obtain the *Tafel equation*:



Figure 5-5. At high positive or negative overpotential, the Butler-Volmer equation can be approached by the Tafel equation (5-21). Tafel representation of (a) an anodic reaction and (b) a reaction with anodic and cathodic branch, where the overpotential is given by $\eta = E - E_{rev}$. Regression analysis yields the exchange current density as intercept at $\eta = 0$ or $E = E_{rev}$, and the Tafel slope(s).

¹ which you will easily recognize if you wish to rearrange and express η as a function of *i*.

The parameter *b* is the *Tafel slope*, given by $b = \ln(10) \cdot \frac{RT}{aF}$, where $\ln(10) \cong 2.303$. It has the unit volt per decade of current density, often written V/decade or just V. Note that the Tafel slope is temperature dependent. Values for *b* at room temperature can range from ~30 to 120 mV/decade. When using the Tafel equation, be aware that for cathodic currents, one has to use |i| for the logarithm to make sense. Also, the associated overpotential η will be positive (since $|i| \gg i_0$). To be consistent with the definition $\eta < 0$ for a cathodic reaction, we may write the Tafel equation for a cathodic reaction as $\eta_c = -b_{-}\log(|i|/i_0)$. The logarithmic current-potential relationship was discovered empirically by Julius Tafel (1862-1918) in 1905. The Tafel representation of current-voltage data (**Figure 5-9**) is a popular method to determine exchange current density i_0 and Tafel slope *b* by regression analysis. A typical example for the use of the Tafel equation is the oxygen reduction reaction (ORR) in acid, because it has a low exchange current density of ~10⁻⁹ A/cm² (room temperature value), even on noble metals (cf. below).

Low $|\eta|$, i.e. $|\eta| \ll \frac{RT}{aF}$

A Taylor expansion of exp(x) about x = 0 yields $exp(x) \approx 1 + x$, hence the Butler-Volmer equation simplifies to

$$i \approx i_0 \cdot (\alpha_a + \alpha_c) \frac{F}{RT} \eta$$
(5-22)

In this regime, we observe a linear relation between current and overpotential. Such a situation can, for example, be encountered for the hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) on noble metals in acid (cf. Chapter VII), as the exchange current density is on the order of 0.1 A/cm^2 (at room temperature).

2.3 Roughness factor

So far, we have assumed that the electrode is flat and infinitely smooth, which entails that the microscopic current density is identical to the macroscopic current density given by the geometric area of the electrode. In reality, however, electrodes possess a certain degree of roughness, which effectively leads to an increase in the microscopic surface area of the electrode (**Figure 5-10**). The ratio of the microscopic surface area to the geometric surface area is called the *roughness factor r*. Consequently, the relationship between the microscopic current density *j* and the geometric current density *i* is given by: j = i/r. This means that for a rough electrode (r > 1), the microscopic current density *j* will be lower than the geometric current density *i*. Since the overpotential is determined by the microscopic current density *j*, an increase in the roughness factor essentially leads to a

decrease in overpotential. Therefore, for many technical applications (e.g. fuel cells, cf. Chapter VII), one is interested in increasing the roughness factor by one to two orders of magnitude. This can be accomplished by using porous electrodes with a high internal surface area. To maximize utilization of the microscopic surface area, it is important that the electrode particles are well connected electronically and the pores filled with electrolyte to ensure a continuous ionic phase. However, the likelihood of mass transport limitations increases with the roughness factor, and in practice a trade-off has to be made between mass transport and electrode activation losses.



Figure 5-10. Definition of the roughness factor *r*: ratio of the true, microscropic surface area divided by the geometric area of the electrode. In porous electrodes with co-continuous electronic and ionic phase, the roughness factor can be over 100, which is, for example, used in fuel cells.

The exchange current density for a given reaction on an electrode material is quoted with respect to the microscopic area, because it is a material specific quantity. In tabulated values of j_0 , (cf. examples in **Table 5-2**), the type of surface is often indicated, such as whether the surface is polycrystalline or of a specific crystallographic orientation, e.g. Pt(111). The determination of the microscopic surface area of an electrode can be cumbersome. In Chapter VIII, we will see which analytical techniques can be used to quantify the roughness factor r for (porous) electrodes.

Reaction	Electrode	Electrolyte	j o
			(A·cm ^{−2})
$Zn + 2 OH^- \rightarrow Zn(OH)_2 + 2 e^-$	Zn	Zn(OH) ₂ (aq)	0.06 ^a
$Fe^{2+} / Fe^{3+} (5 \text{ mM})$	Pt	$1 \text{ M H}_2 \text{SO}_4$	0.002 ^b
$Ag / Ag^{+} (1 mM)$	Ag	1 M HClO ₄	0.15 ^b
H_2 / H^+	Pt	0.1 M H ₂ SO ₄	0.03 °
H_2 / OH^-	Pt	0.1 M KOH	7·10 ^{-4 d}
H_2 / H^+	Hg	1 M H ₂ SO ₄	10^{-12} b
O_2 / H^+	Pt	1 M H ₂ SO ₄	10 ^{-9 e}

 Table 5-2.
 Selected exchange current densities j_0 (r.t. values).

 Densities
 Elected densities

^a T.F. Fuller, J.N. Harb, Electrochemical Engineering, Wiley, 2018, Tab. 3.1, p47

^b C.H. Hamann, A. Hamnett, W. Vielstich, Electrochemistry, 2nd Edition, Wiley-VCH, 2007, Tab. 4.1, p170

^c Electrochim. Acta 176 (2015) 763

^d J. Electrochem. Soc. 157(11) (2010) B1529

^e J.P. Hoare, The Elfectrochemistry of Oxygen, Interscience, 1968, Fig. 5.1, p144

2.4 Coupled and multi-step reactions

Electrochemical reactions are often coupled with other physical and/or chemical processes, which will probably influence the overall kinetics of the half-cell reaction. As we have seen above, adsorption phenomena are likely to accompany inner sphere reactions. It may well be that the kinetics of adsorption of reactants or desorption of products become rate limiting. In this case, the polarization (*i*-*E*) curve no longer follows the Butler-Volmer or Tafel equation, but will likely show limiting current behavior. For example, if an adsorption step in an electrochemical reaction is rather slow, the current density that can be obtained cannot be higher than the rate of adsorption of the reactant. Another limiting situation arises when the electrode surface is 'poisoned' by a strong adsorbate, which blocks the access of the reactant. An example of this type will be discussed in Chapter VII in the context of the poisoning of a platinum fuel cell electrocatalyst with carbon monoxide. In this situation, the coverage θ of the electrode surface by adsorbed species ($0 \le \theta \le 1$), be it as reactants, intermediates, products, or *spectator species*, i.e., a compound that does not appear in the overall reaction equation, can significantly influence the kinetics of the electrode reaction.

Another common situation is the coupling of a chemical (C) and an electrochemical (E) process, where the chemical reaction may precede the electrochemical reaction (CE reaction) or follow the electrochemical reaction (EC reaction). The chemical reaction may take place in solution (homogeneous process) or on the surface of the electrode (heterogeneous process). An example for a preceding homogeneous reaction would be the dissociation of a weak acid HA \leftrightarrows H⁺ + A⁻ followed by the reduction of protons $H^+ + e^- \rightarrow \frac{1}{2} H_2$, a CE type reaction. The reaction of protons would lead to a proton concentration gradient and a depletion layer near the electrode. In complex electrochemical reactions, in particular when several electrons are transferred, the mechanism may involve a number of different adsorbates, chemical and electrochemical reactions. Typically, electrons are transferred one at a time. Also, most of these processes and even the reaction mechanism itself may depend on the electrode material and the type of electrolyte used. The reduction of oxygen to water in a fuel cell is a prominent example (cf. Chapter VII), where 4 electrons are transferred per O₂ molecule and several adsorbates co-exisit on the catalyst surface. For such complex reactions, the current density at a given overpotential may not depend on the concentration of the reactant(s) in straightforward manner. To describe the relation between the current density i and the concentration c_k of a reactant k phenomenologically, we introduce the parameter γ_k and write the kinetic expression for a reaction in the Tafel regime as follows:

$$i = i_0 \cdot \left(\frac{c_1}{c_0}\right)^{\gamma_1} \cdot \left(\frac{c_2}{c_0}\right)^{\gamma_2} \cdot \exp\left(\frac{\alpha F}{RT}\eta\right)$$
(5-23)

where c_1 and c_2 are the concentrations of compounds 1 and 2, respectively, involved in the reaction, referenced to a standard concentration c_0 . γ_k is the *kinetic reaction order* with respect to the concentration of k, defined as $\gamma_k = (\partial \log(i) / \partial \log(c_k))$ at constant η , p, T, $c_{l \neq k}$. The mechanism may also change with the overpotential, with different reaction steps being limiting in different potential regimes. The reaction order may not even be an integer number. For example, the reaction order γ_{02} for the oxygen reduction reaction on Pt in acid is ~0.75¹. It may even be that the reaction kinetics depend on the concentration of a spectator species. For instance, in the hydrogen oxidation reaction, γ_2 H₂ \rightarrow H⁺ + e⁻, in the presence of CO (in a fuel cell operated on reformate, cf. Chapter VII), CO adsorbs on the surface of the Pt electrocatalyst with a high coverage θ_{CO} and limits the surface area accessible by hydrogen and thus impairs the kinetics of the hydrogen oxidation reaction. In this case, the reaction order γ_{CO} is even negative, because the higher the concentration of CO, the higher the CO coverage of the catalyst and the lower the rate of the hydrogen oxidation reaction at a fixed overpotential.

2.5 Charge transfer resistance

Given the fact that the activation overpotential represents a kinetic limitation of a reaction, one can assign a resistance to the charge transfer reaction, the charge transfer resistance R_{CT} . Formally, it is defined in analogy to the ohmic resistance as

$$R_{\rm CT} = \left(\frac{\partial \eta_{\rm CT}}{\partial i}\right) \tag{5-24}$$

However, unlike for an ohmic resistance, the charge transfer overpotential η_{CT} is not a linear function of the current density (as we already know). Hence, the charge transfer resistance is not a constant and generally changes with current density. For a reaction in the Tafel regime ($|\eta| >> b$) R_{CT} is obtained by differentiating Eq. 5-21 to yield an inversely proportional relationship with the

Table 5-1. Charge transfer resistance R_{CT} for a Butler-Volmer process with approximations at high and low overpotentials, respectively. For large η , R_{CT} depends on the current density, whereas at small η , R_{CT} approaches a constant value.

Regime	Equation no.	
$ \eta >> b$	$R_{\rm CT} \approx \frac{RT}{\alpha F} \cdot \frac{1}{ i } = \frac{b}{\ln(10)} \cdot \frac{1}{ i }$	1
$ \eta \ll b$	$R_{\rm CT} \approx \frac{1}{\alpha_{\rm a} + \alpha_{\rm c}} \cdot \frac{RT}{F} \cdot \frac{1}{i_0}$	2

 ¹ H.A. Gasteiger et al., in: Handbook of Fuel Cells - Fundamentals, Technology and Applications, Vol. 3, W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.), John Wiley & Sons, Chichester, 2003, 593-610

current density *i* (**Table 5-3**, Eq. 5-25). Hence, the charge transfer resistance decreases with increasing current density. Often, an equivalent circuit is used to represent a charge transfer reaction, consisting of the resistance R_{CT} in parallel to the double layer capacitance C_{DL} (**Figure 5-11**). Since R_{CT} varies with current density, it would be more appropriate to represent R_{CT} as a varistor.



Figure 5-11. Equivalent circuit describing a charge transfer process, comprising the double layer capacitance C_{DL} and, in parallel, the charge transfer resistance R_{CT} , which is represented as a variator rather than a resistor to emphasize that its value is not a constant but, in most cases, a function of the current density.



Figure 5-12. (a) Polarization curve following a Butler-Volmer description, (b) corresponding charge transfer resistance $R_{\rm CT}$. Parameters: $i_0 = 10^{-3}$ A/cm², $\alpha_a = \alpha_c = 1$. The maximum of $R_{\rm CT}$ is at $\eta = 0$ with a value of 13 $\Omega \cdot \text{cm}^2$.

The situation is, however, different under the conditions of low overpotential ($|\eta| \ll b$). In this case, the overpotential varies linearly with current density (cf. Eq. 5-22), hence R_{CT} is constant (**Table 5-3**, Equation 26). Values for the charge transfer resistance of an example process described by the Butler-Volmer reaction is shown in **Figure 5-12**, with the two regimes described above being apparent in Panel b. Close to the equilibrium, R_{CT} is a function of the exchange current density i_0 . Hence, for a large i_0 , R_{CT} is low in this regime. This means that the electrode 'passes current easily', or: its potential only changes little upon the passage of current. An electrode with very low charge transfer resistance $R_{CT} \approx 0$ is called an *ideal non-polarizable electrode*. An example is the hydrogen electrode using Pt or Pd, which is the reason for its choice as a reference electrode (cf. Chapter II). On the other hand, an electrode with a very high charge transfer resistance, $R_{CT} \rightarrow \infty$, is called an *ideal polarizable electrode*. Implicitly, it has a very low exchange current density, and it is difficult to pass current through it, even at sizeable overpotentials. An example would be a Hg electrode in contact with an aqueous solution of KCl or NaF.

3 Transport Phenomena

The charge transfer kinetics according to the Butler-Volmer or Tafel equation describe an exponential increase of current density with overpotential, yet there are obviously practical limitations when the rate of reaction is approaching the rate of reactant supply to the electrode surface. This implies that mass transport limitations are associated with the properties of the electrolyte (e.g., concentration of reactant, viscosity), which is certainly true for most types of electrochemical reactions. *Mass transport limitations* are often experienced in electrochemical cells, the polarization curve of an electrode then starts to deviate from the behavior described by the charge transfer reaction alone. In this section, we will study the mechanisms of species transport, i.e. mass transport, and how they affect the electrochemical reaction.

Table 5-4. Classification of transport phenomena.

Mechanism	Driving force (gradient)
migration	potential φ
diffusion	concentration c (activity a)
convection	pressure p / density ρ

We distinguish 3 mechanisms for the transport of species: *diffusion*, *migration* and *convection* (**Table 5-4**), in which the transport is caused by different driving forces.

$$J = -\underbrace{D \cdot \nabla c}_{\text{diffusion}} - \underbrace{u \cdot c \cdot \nabla \varphi}_{\text{migration}} + \underbrace{c \cdot v}_{\text{convection}}$$
(5-27)

The flux density *J* describes the rate of transport of a species per unit time and cross-sectional area (unit: mol·cm⁻²·s⁻¹). *D* is the diffusion constant or coefficient (or: diffusivity, unit: cm²·s⁻¹), *u* the mobility (m²·V⁻¹·s⁻¹), and *c* the concentration (mol/L). Diffusion affects all species in a phase, yet migration only affects charged species, i.e. ions. Both diffusion and migration are transport phenomena on the atomic / molecular level, whereas convection is a bulk movement of a fluid, described by the fluid velocity *v*.

It is worth noting that the transport of species (ions, other solutes, solvent) in an electrolyte is independent of the motion of other species only in dilute solution. In concentrated solutions, the transport of one type of solute will influence the transport of other solutes and also the solvent. For example, water in the hydration sphere of an ion is dragged along with the ion during its movement down a concentration and / or potential gradient, which is called *electroosmotic drag* of water. Therefore, in general, we have to write the transport equation for a species k with a transport matrix

 L_{kl} with off-diagonal coupling parameters $L_{kl} \neq 0$ and the general driving force being a gradient in its electrochemical potential $\tilde{\mu}_k$ and that of the other species $l \neq k$:

$$J_k = -\sum_l L_{kl} \cdot \nabla \tilde{\mu}_l \tag{5-28}$$

3.1 Diffusion

If we consider an electrochemical reaction taking place at a flat electrode, we can imagine that the consumption of the reactant at the electrode surface leads to a local decrease in concentration compared to the concentration in the bulk of the solution. Conversely, the concentration of the product is higher at the surface and decreases towards the bulk of the electrolyte. The difference in the concentration of the species in different locations will lead to a diffusive flux J_d down the concentration gradient ∇c , i.e., from higher to lower concentration:

$$J_{\rm d} = -D \cdot \nabla c \tag{5-29}$$

This is Fick's first law of diffusion. To be precise, we should be using the activity *a* instead of the concentration *c* in the general case, the use of the concentration only applies to the case of a sufficiently dilute solution. In the one-dimensional case, the gradient ∇c reduces to the derivative dc/dx. For illustration, we consider a steady-state situation for a simple electrochemical reaction of a redox couple $Ox + e^- \rightarrow Red$, where the concentrations are fixed on the surface (x = 0) of the electrode by its potential and, at some distance $x = \delta$, in the solution at the value of the bulk



Figure 5-6. (a) Representation of the concentration profile of Fe^{2+} and Fe^{3+} near the electrode surface as a result of the reduction reaction $Fe^{3+} + e^- \leftrightarrows Fe^{2+}$, where the solution is stirred and a steady-state diffusion layer of thickness δ_N establishes. (b) Time-dependent change of the concentration profile of a reactant with constant concentration c_∞ in the bulk and c_0 at the electrode surface after switching on the potentiostat at t = 0 and showing the increase of the diffusion layer thickness δ_N with time. x = distance from the electrode surface.

concentration by stirring of the solution (**Figure 5-13a**). In this case, a linear concentration profile develops between x = 0 and $x = \delta$, and a steady flux *J* of particles to and from the surface is established. The particles react at the electrode surface with a steady-state current density *i* given by $i = z \cdot F \cdot J$. Hence, the concentration gradient dc/dx at the surface of the electrode for any of the species involved in the reaction is proportional to the current density *i*.

Next, we are looking at the non-stationary case when the concentration profile is time-dependent. For the analysis, we do a mass balance for the species in a control volume¹, which leads to 2nd Fick's law:

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \cdot \nabla c) \stackrel{D=\text{const.}}{=} D \cdot \nabla^2 c = D \cdot \Delta c$$
(5-30)

where Δ is the Laplace operator $(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$ in Cartesian coordinates). As an example, imagine an electrode surface at x = 0 and electrolyte in the semi-infinite space x > 0. We assume that initially, the reaction is at equilibrium (i = 0) and the concentration of the reactant is homogeneous throughout an unstirred solution, c_{∞} . For simplicity, we only focus on the reactant and disregard the concentration of the product. Then, at t = 0, the electrode potential is changed to a value that leads to a decrease of the reactant at the electrode surface to a concentration $c(x=0, t\geq 0) = c_0 < c_{\infty}$. Over time, the depletion zone moves gradually into the electrolyte (**Figure 5-13b**). The concentration c(x, t) obeys 2^{nd} Fick's law, and for this problem of diffusion into semi-infinite space the solution can be looked up in a textbook:

$$c(x,t) = c_0 + (c_{\infty} - c_0) \cdot \operatorname{erf}(-\frac{x}{\sqrt{4Dt}})$$
(5-31)

¹ For the derivation of the time-dependent diffusion equation $(2^{nd}$ Fick's law), we consider a control volume with one spatial dimension x, where a species is entering the volume at the position x with flux J(x,t) and leaving the volume at position x+dx with J(x+dx,t). Therefore the change of concentration of the species in the region between x and x+dx is given by:



$$\frac{\partial c}{\partial t}dx = J(x) - J(x + dx) = J(x) - (J(x) + \frac{\partial J(x)}{\partial x}dx) = -\frac{\partial J(x)}{\partial x}dx$$

After cancelling and inserting Fick's first law we obtain

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} (D \cdot \frac{\partial c}{\partial x}) = D \cdot \frac{\partial^2 c}{\partial x^2}$$
 for $D = \text{const.}$

For the general expression in 3D, we use the ∇ operator (Eq. 5-30).

where $\operatorname{erf}(x)$ is the error function¹. The reader may check if the result fulfils the diffusion equation (a bit tedious...). The corresponding concentration profiles as a function of time show that the depth of the depletion zone increases with time. Close to the electrode surface, i.e., for $x \ll \sqrt{4Dt}$, we can approximate the concentration profile with a linear function based on a Taylor series expansion:

$$c(x,t) \approx c_0 + (c_\infty - c_0) \cdot \frac{x}{\sqrt{\pi Dt}}$$
(5-32)

The width of the depletion zone is given by the characteristic length δ_N , the *Nernst diffusion layer* thickness, which is defined as

$$\delta_{\rm N} = \sqrt{\pi D t} \tag{5-33}$$

In the concentration profile of **Figure 5-13b**, the Nernst diffusion layer thickness appears as an extrapolation of the linearized concentration profile near x = 0 to the value of x where $c = c_{\infty}$. One can see that its value increases with the square root of time. We have seen above that the current is proportional to the concentration gradient at x = 0, explicitly:

$$i = zFJ = zFD \frac{\partial c}{\partial x}\Big|_{x=0} = zFD \frac{c_{\infty} - c_0}{\sqrt{\pi Dt}} = zFD \frac{c_{\infty} - c_0}{\delta_{\rm N}}$$
(5-34)

Therefore, we see that the current decreases with time, as we can observe from the slope of the concentration profiles at the electrode surface in **Figure 5-13b**. If for such a transient we plot the current density *i* as a function of the inverse square root of time *t*, i.e., *i* vs. $1/\sqrt{t}$ (Cottrell plot), we obtain a curve with a linear region, from which we can determine the diffusion coefficient *D*.

Next, we calculate the concentration overpotential η_{conc} caused by the local change in concentration of species involved in an electrochemical reaction. For this, we consider the simple reaction Ox + $z \cdot e^- \rightarrow$ Red. As a result of the difference in the concentration of the reactant Ox at the surface of

 $\operatorname{erf}(x) = \frac{1}{\sqrt{\pi}} \int_{-x}^{x} \exp(-b^{2}) db = \frac{2}{\sqrt{\pi}} \int_{0}^{x} \exp(-b^{2}) db$ with characteristic values $\operatorname{erf}(0) = 0$ and $\operatorname{erf}(\infty) = 1$. Furthermore: $\frac{d}{dx} \operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \exp(-x^{2})$

¹ The error function is defined as:

the electrode c_0 and the concentration in the bulk c_{∞} , a Nernst potential develops, which is the concentration overpotential:

$$\eta_{\rm conc} = -\frac{RT}{zF} \ln(\frac{c_0}{c_{\infty}}) \tag{5-35}$$

Since $c_0 < c_{\infty}$, η_{conc} will always be positive. The concentration c_0 is somewhat problematic, because it is not easily experimentally accessible. Therefore, we look to relate the concentration overpotential to the current density *i*, which is easily measured. The maximum current density that can be sustained is given by the rate of reactant diffusion to the electrode when the reactant at its surface (x = 0) is completely depleted, i.e. $c_0 = 0$. From Eq. 5-34 we can therefore obtain this *limiting current density i*_{lim}:

$$i_{\rm lim} = zFD\frac{c_{\infty}}{\delta_{\rm N}} \tag{5-36}$$

This allows us, after some algebra (cf. Appendix A), to express the concentration overpotential η_{conc} as a function of the current density *i* and *i*_{lim}:

$$\eta_{\rm conc} = -\frac{RT}{zF} \ln(1 - \frac{i}{i_{\rm lim}})$$
(5-37)

As *i* approaches i_{lim} , the concentration overpotential increases and eventually, at $i = i_{\text{lim}}$, diverges.¹ The reaction is then said to be mass transport limited, because no matter how much we increase (or decrease) the electrode potential, the current is not going to exceed the limiting value, given by the maximum rate of transport of reactant to the electrode surface. We notice that, unlike the ohmic overpotential and the charge transfer overpotential, the concentration overpotential increases disproportionately with current density and can dominate the overpotential at high current densities.

Next, we will look at an electrode reaction that is subject to activation as well as mass transport losses. This means that we have a combined activation and concentration overpotential. For illustration, we first consider those two limitations independently and then combine them to obtain an electrode reaction under mixed activation and mass transport control. **Figure 5-14** shows these

¹ Note that $i < i_{\text{lim}}$, therefore the ln(...) in Eq. 5-39 is always negative and, consequently, η_{conc} always positive.

three types of reaction. As we have seen earlier in this chapter, a reaction governed by activation losses shows, according to the Butler-Volmer equation, an exponentially increasing current density *i* with activation overpotential η_a . On the other hand, the overpotential of a reaction that is only limited by diffusion of the reactant to the electrode surface is given by Eq. 5-37. In this case, the current density *i* increases with the concentration overpotential η_{conc} to the limiting current density *i*_{lim} (see Appendix A, Eq. 5-43). Due to the different dependencies of current density and overpotential for activation and mass transport control, a reaction under mixed control is limited by activation at low overpotentials and by mass transport at high overpotentials. Mathematically, this is expressed as follows:

$$\frac{1}{i} = \frac{1}{i_{\rm kin}} + \frac{1}{i_{\rm mt}}$$
(5-38)

where *i* is the current density for a combined overpotential $\eta = \eta_a + \eta_{conc}$. The current densities *i*_{kin} and *i*_{mt} ('mt' = mass transport) are the values that would be obtained if the reaction were limited only by electrode kinetics or mass transport, respectively. For a derivation of Eq. 5-38, see Appendix B. In fact, we have written *i*_{mt} because the relation holds not only for reactions limited by diffusion but also for processes limited by a combination of diffusion and migration. We will revisit the situation with mixed control in Chapter VIII in the context of the rotating disk electrode (RDE) analytical method.



Figure 5-14. Current-overpotential relationship for an electrode affected only by activation limitation (only η_a), only diffusion limitation (only η_{conc}), and under mixed activation-diffusion control.

3.2 Migration

While all species, charged and uncharged ones, respond to a gradient in activity by diffusion driven flux, migration only affects charged species, i.e. ions. The flux of an ion in an electric field $\mathbf{E} = -\nabla \varphi$

is proportional to its charge z and mobility u. The total migrative current i_m is the sum of the contributions of the different types of ions k with respective concentration c_k :

$$i_{\rm m} = -\sigma \cdot \nabla \varphi = -F(\sum_{k} | z_k | c_k u_k) \cdot \nabla \varphi$$
(5-39)

Obviously, anions and cations migrate in opposite direction, but their fluxes add up to the overall current. As elaborated in Chapter IV, the mobility u is related to the diffusivity D of a species according to the *Einstein relation*: $D = (R \cdot T)/(|z| \cdot F) \cdot u$. Therefore, even when the transport of a species is governed by migration (because there is no gradient in its concentration), the diffusivity still describes the 'ease' with which it is transported. Recall the *Nernst-Einstein equation* describing the relationship between conductivity and diffusivity (Chapter IV).



Figure 5-15. Schematic representation of the transport of a positively charged particle (z > 0) in a crystal lattice with defects, moving from one low energy position to the next over an activation barrier. In the absence of an electric field **E**, the particle has the same probability to jump to the left or the right. The presence of an electric field $\mathbf{E} = -\nabla \varphi$ introduces a gradient in the energy of the particle, which increases the probability of the particle to jump in the direction of decreasing energy, here to the right. Therefore, on average over many jump events, positively charged particles are moving to the right, i.e. down the potential gradient. Negatively charged particles (z < 0), on the other hand, would move towards higher potentials, here to the left.

A case where there is no (or a negligible) concentration gradient of an ionic charge carrier in an electrolyte, and charge transport is governed by migration, is found in single-ion conductors, such as water-swollen ion-exchange membranes or solid-state ion conductors with a single type of mobile defect (cf. Chapter IV). An example is the superionic conduction of Na⁺ in β "-Al₂O₃. We can depict the free energy or the electrochemical potential of a Na-ion as a function of position by a periodic function (**Figure 5-15**). The minima correspond to Na⁺ positions of highest stability, i.e. lattice positions, such as 1 and 3. The maxima correspond to the configuration with the highest distortion of the lattice. In the absence of a potential gradient, the activation energies for Na-ion movement to

the left and the right are identical. Hence, on average over time, no net movement of species will be observed, because the probabilities of the ion to jump to the left or right are the same. The situation is different in the presence of a potential gradient. The potential curve modified by the superimposed contribution by the electric field leads to a different activation energy for the movement to the right and to the left. Consequently, a net flux of ionic charge carriers is observed, corresponding to an electric current.

For the general case where there is a concentration (activity) gradient in the electrolyte as well as a potential gradient, we have to take into account both the diffusive and the migrative flux term. The current density associated with a species k is then:

$$i_{k} = -F(z_{k}D_{k}\cdot\nabla c + |z_{k}|c_{k}u_{k}\cdot\nabla \phi)$$
(5-40)

This is the *Nernst-Planck* equation. In the case one is interested in controlling the transport of a species undergoing an electrochemical reaction to or from an electrode surface, for example in electroanalytical techniques (cf. Chapter VIII), the migrative term is suppressed by adding an excess of *supporting electrolyte* to minimize the potential gradient in the electrolyte. In this situation, transport of the species can be taken to be caused exclusively by diffusion. For example, in the study of the electrochemical behavior of the ferri-ferrocyanide redox couple, $[Fe(CN)_6]^{3-} + e^{-}$ [Fe(CN)₆]⁴⁻, a concentration of 4 mM of K₃Fe(CN)₆ (low analyte concentration) may be used in, say, 1 M KNO₃ as supporting electrolyte.



Figure 5-16. Schematic of a 3-electrode cell configuration with working electrode (WE), counter electrode (CE), and reference electrode (RE). The use of a Luggin capillary to probe the potential near the WE is essential to minimize effects of deviation of the measured potential by an ohmic drop $\Delta U_{\Omega} = I \cdot R$ in the electrolyte.

Nevertheless, the potential gradient in the electrolyte as a result of the cell current is not negligible, and, therefore, for the accurate determination of the potential of the working electrode (WE) using a reference electrode (RE) in a 3-electrode setup (**Figure 5-16**), a *Luggin* capillary (cf. Chapter III) is used to sense the potential close to the surface of the WE (but not too close to avoid interference

with the electrode reaction) to minimize the *IR*-drop associated with the measurement of the potential difference between WE and RE.

3.3 Convection

The bulk movement of electrolyte in an electrochemical cell causes convective flux of species (solvent and solutes). Convection can be driven by a pressure gradient, for instance if the electrolyte is actively mixed (e.g. by a paddle wheel or by bubbling gas through it) or pumped through the cell. Also, the electrodes can be moved, causing convective flux in the electrolyte. In the rotating disk electrode (RDE) technique, for example, a cylindrical electrode is rotated to create a defined velocity profile of the electrolyte to control mass transport to and from the electrode (cf. Chapter VIII). Also, differences in the local density of the electrolyte, e.g. as a result of heat generation at the electrode(s), leads to electrolyte convection caused by buoyancy.



Figure 5-17. (a) Convective (i.e., bulk) flow of electrolyte past an electrode leads, due to viscous forces, to the formation of a boundary layer with flow velocity decreasing towards the electrode surface (Source: D. Pletcher, F.C. Walsh, Industrial Electrochemistry, Kluwer, 2nd Ed., 1990, Fig. 1.14, p. 29). (b) The thickness of the boundary layer $\delta r_{\rm r}$ (r = Prandtl) relates to the Nernst diffusion layer thickness according to $\delta r_{\rm r} \approx \delta_{\rm N} \cdot (\nu/D)^{1/3}$, where ν is the kinematic viscosity. For water at room temperature ($\nu = 8.9 \cdot 10^{-3}$ cm²/s, $D = 2.3 \cdot 10^{-5}$ cm²/s) we find $\delta r_{\rm r} \approx 10 \cdot \delta_{\rm N}$ (Source: C.H. Hamann, W. Vielstich, Electrochemistry, Wiley, 2nd Ed., 2007, Fig. 4.16, p. 192).

In a stagnant electrolyte (no convection), the Nernst diffusion layer thickness δ_N can increase to a thickness of ~mm after an hour of cell operation¹. With natural convection, δ_N can be maintained below 1 mm. With active flow of electrolyte, δ_N can be controlled to be below 0.1 mm, as well as with gas bubbling. The latter also applies to electrodes that evolve gas during the electrochemical reaction. The flow of electrolyte past an electrode leads to the formation of a boundary layer (cf.

¹ typical diffusivity of solutes in water at r.t. $D \cong 10^{-6} \text{ cm}^2/\text{s}$. Hence, with $\delta_N = \sqrt{\pi Dt}$ and t = 1 h we obtain $\delta_N \cong 1$ mm.

Figure 5-17), in which the flow velocity drops to zero at the electrode surface due to the finite viscosity of the electrolyte. The Nernst diffusion layer thickness δ_N is related to the thickness of the boundary or Prandtl layer δ_{Pr} , hence to reduce effects of concentration overpotential it is important to actively mix the electrolyte.

5-31

Appendix A: Concentration Overpotential

To obtain the relationship between the concentration overpotential η_{conc} and the current density *i* and limiting current density *i*_{lim}, we first rearrange Eq. 5-35:

$$\frac{c_0}{c_{\infty}} = \exp(-\frac{zF}{RT}\eta_{\text{conc}})$$
(5-A1)

Inserting into Eq. 5-34 yields

$$i = zFD\frac{c_{\infty} - c_0}{\delta} = zFD(\frac{c_{\infty}}{\delta} - \frac{c_{\infty}}{\delta}\exp(-\frac{zF}{RT}\eta_{\text{conc}}))$$
(5-A2)

With the definition of the limiting current density, Eq. 5-36, we obtain:

$$i = i_{\rm lim} (1 - \exp(-\frac{zF}{RT}\eta_{\rm conc}))$$
(5-A3)

Solving for η_{conc} then yields Eq. 5-37.
Appendix B: Mixed Activation and Mass Transport Control

For a description for the overpotential of an electrode reaction under mixed activation and mass transport control, we assume for simplicity an anodic reaction in the Tafel regime:

$$i = i_0 \cdot \left(\frac{c}{c_\infty}\right) \cdot \exp\left(+\frac{\eta}{b'}\right) \tag{5-B1}$$

where b' is the Tafel slope in V/e-fold¹, c the concentration of reactant at the electrode, and c_{∞} the concentration of reactant in the bulk. We have also assumed a reaction order with respect to the concentration c of 1. Implicitly, the concentration c depends on the overpotential under mixed control, and for $c = c_{\infty}$ the well-known Tafel equation is obtained. A more general relationship with a reaction order different from one yields a qualitatively similar result, but cannot be expressed analytically. Also, for a more elaborate analysis, we could use the full Butler-Volmer equation. Next, the expression for the limiting current density (Eqs. 5-35 and 5-37) is inserted to yield

$$i = i_0 \cdot (1 - \frac{i}{i_{\lim}}) \cdot \exp(+\frac{\eta}{b'}) = (1 - \frac{i}{i_{\lim}}) \cdot i_{ct}$$
 (5-B2)

where the expression $i_{ct} = i_0 \cdot \exp(\eta/b')$ represents pure activation control. Dividing by $i_{ct} \cdot i$ and rearrangement yields Eq. 5-38 in the main text.

¹ $b' = b / \ln(10)$, where b is the Tafel slope in V/decade.

Chapter VI

Industrial Electrochemistry

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In this chapter we will be studying how electrochemistry is put into use in industrial applications. The latter suggests that the cells and hardware we are dealing with are of rather large size, well beyond that of common laboratory equipment. In fact, large electrochemical plants can occupy entire factories, such as an aluminium smelting facility. In many cases, the aim of an electrochemical process is to produce a certain chemical of commercial interest or an intermediate, which is further used elsewhere in the plant or outside. Typical compounds produced electrochemically are metals, such as Al, Na, Mg, or inorganic products, e.g., Cl₂, F₂ or O₃, that are difficult or uneconomical to produce with other methods. These are generally electrolytic processes, which require the input of electrical energy. The electrochemical splitting of water to produce H_2 (and O_2) deserves a short note: today (2022) hydrogen is produced almost exclusively from fossil feedstock (coal, oil, gas) by steam reforming, partial oxidation or a combination thereof. Electrolytic production of H₂ from water using electricity from renewable sources can help to defossilize carbon-intensive sectors, such as the chemical industry and transportation ('power-to-X' concepts). Voltage, generally in the range of 1 volt or a few volt for one cell, is a strong driving force for non-spontaneous reactions, recall (Chapter II) the comparison of thermolytic water splitting, requiring temperatures of a few thousand degrees, vs. electrolytic water splitting, requiring around 2 V at practical current densities. In addition, electrochemical methods are used in separation and purification applications, such as electrodialysis for water desalination, and some surface treatment processes, most notably electroplating, anodization and electropolishing.

This chapter does not provide an exhaustive overview of electrochemical processes in industrial applications, owing to the large diversity of processes and methods. Rather, we will study some general concepts in electrochemical engineering and subsequently look into selected processes of significant economic value. This, in addition, also allows us to apply some of the more fundamental aspects discussed in the earlier chapters in an application relevant setting and environment.

1 Electrochemical Engineering

In electrochemical processes of industrial scale, cells are engineered and operated for a specific duty, in the sense that they are designed to yield a certain output, e.g. a compound of interest produced per unit time, with a minimum input of resources, such as raw materials, energy, heat, and manpower. A key equation to describe the output of an electrochemical reactor is Faraday's law (cf. Chapter I), which relates the rate of product formation \dot{m} (unit: kg/s) with the current in one cell *I* and the number of cells # in the system (assuming identical current in all cells):

$$\dot{m} = \varepsilon_{\rm F} \frac{\#M}{zF} I \tag{6-1}$$

M is the molar mass of the compound of interest and $\varepsilon_{\rm F}$ the faradaic efficiency of producing it, *z* and *F* have their usual meaning. We see that the rate of product formation is only given by the current, the cell voltage does not enter the equation. The cell voltage $U_{\rm cell}$ is a measure for the departure from equilibrium characterized by $U_{\rm rev}$. We recall from Chapter II that the theoretical electrical energy input $W_{\rm e,th}$ to drive an electrolytic process is given by the free energy of the reaction: $W_{\rm e} = \Delta_{\rm r}G = zFU_{\rm rev}$. Under practical conditions, the reaction is driven at a certain cell voltage $U_{\rm cell}$, which, since we are dealing with an electrolytic process, is higher than $U_{\rm rev}$ by the sum of overpotentials $\Sigma |\eta|$. Therefore, the mass based specific electricity consumption $\omega_{\rm m}$ (unit: J or kWh per kg of product) of the process is higher than the theoretical minimum and given by:

$$\omega_{\rm m} = \frac{zFU_{\rm cell}}{\varepsilon_{\rm F}M} \tag{6-2}$$

where we also take into consideration the faradaic efficiency $\varepsilon_{\rm F}$. The cell voltage $U_{\rm cell}$ and the cell current *I* are obviously connected via the polarization characteristic of a cell at a given set of operating conditions (pressure, temperature, etc.), and the power input *P* (unit: W) is given by $P = U_{\rm cell} \cdot I$ for one cell, which is multiplied by the number of cells # for the entire facility. The aim of cell development and engineering is to maximize the current density i = I/A, where *A* is the active area of one cell, to maximize output, and minimize the cell voltage $U_{\rm cell}$ and thereby energy input at the same time.

The operating point of the cell, corresponding to a point (i, U_{cell}) on the polarization curve, determines, on the one hand, the electricity consumption per unit of compound produced via Eq. 6-2 and thereby the electricity cost of the process. On the other hand, the current density *i* determines

Example:

A water electrolyzer is operated at an average cell voltage of 1.8 V at a current density of 2.0 A/cm². It consists of a total of # = 60 cells, each with an active area of A = 1200 cm². We can calculate directly the total power input as $P = \# \cdot U \cdot i \cdot A = 259$ kW. We assume a faradaic efficiency of 100 % to calculate the total rate of H₂ production using Eq. 6-1 with z = 2 and $M(H_2) = 2$ g/mol and obtain $\dot{m} = 5.4$ kg(H₂)/h. The specific electricity consumption is calculated with Eq. 6-2, for which we get $\omega_m = 48$ kWh/kg(H₂).

the size of the facility, because it determines the total cell area required to yield a certain output of product. If, for example, the current density is doubled, the required cell area is halved. Therefore, the investment cost of the facility decreases, because fewer cells have to be installed for a desired output. An increase in current density, however, leads to an increase of U_{cell} , according to the polarization characteristics of an electrolytic cell (cf. Chapter V, Figure 6-1), which increases the specific electricity consumption and, thus, operating cost. The optimum operating point depends on a number of variables, such as the cost of electricity and the cost of cell components.

1.1 Process and reactor design

The design of an electrochemical process is often similar to the one of a regular chemical one. The electrochemical reactor comprises the electrochemical cells, which are built and arranged in a certain way. Reactants need to be fed, products extracted, mass flow, temperature, pressure etc. need to be adjusted and monitored, and so forth. First off, we look at the different possible configurations of electrochemical cells in a reactor, which features a negative and positive terminal, to which the DC power supply is connected (**Figure 6-1**). The module of cells is called a *stack*. Cells can be arranged *in parallel*, also referred to as *monopolar* configuration. In this case, all the negative electrodes are connected to the common negative terminal, and all positive electrodes to the positive terminal. The DC power supply provides low voltage, corresponding to the single cell voltage U_{cell} , and high current, because the currents of all the cells are added up. Effectively, this configuration is like a single cell with an active area made up of the sum of all cells. Alternatively, cells can be arranged *in series*, which is also called *bipolar* configuration. Here, the positive electrode of one cell is electrically connected to the negative electrode of the next cell. The same current passes through all the cells, and the individual cell voltages add up to the stack voltage. The power supply hence provides a high voltage and comparatively low current DC electricity.

The bipolar arrangement leads to the occurrence of bypass currents, also called shunt currents, if there is an electrolyte path between neighboring cells, for example when using a common electrolyte feed and exhaust ('manifold'). This is a leakage current between electrodes of neighboring cells. This only arises in a bipolar stack, because there is an increasing voltage difference between



Figure 6-1. Possible electrical configurations in a multi-cell stack. The direction of current is indicated by the red arrows. The inlet and outlet manifolds for the electrolyte are shown (only the inlet in case of the bipolar configuration for the sake of clarity). **Monopolar** configuration = parallel connection of cells. All cells have the cell voltage U_{cell} , the individual cell currents I_{cell} add up to the total current I_{tot} . All the positive and negative electrodes, respectively, are connected to the DC power supply, which has the voltage of a single cell. **Bipolar** configuration = series connection of cells. All cells have same current I_{cell} , the individual cell voltages U_{cell} add up to the total voltage U_{tot} . Only the end cells are connected to the DC power supply. In the bipolar configuration, bypass currents (also called 'leakage' or 'shunt' currents) may arise in the electrolyte manifolds (only shown for the inlet, the same situation prevails in the outlet). The distribution of the potential φ across the cell arrangement is shown in the lower part (the cell voltages in the bipolar case are compressed to save space). The current leads to a potential drop in the electrolyte, yet the electrodes are assumed to be equipotential (owing to the much higher conductivity).

electrodes along the stack and current can and will flow if there is an electrolyte bridge (ionic path) between cells. The potential distribution across the arrangement of cells sketched in **Figure 6-1** shows that in the case of the bipolar configuration a potential difference exists between electrolytes of different cells. This potential difference drives the shunt currents. This is not the case for the monopolar configuration. Shunt currents, on the one hand, cause a loss in faradaic efficiency, typically on the order of a few percent. On the other hand, they can also trigger corrosion reactions, since cathodes will have 'anodic' zones. Leakage currents can best be avoided by increasing the electrolyte resistance or path length between cells in the stack, or by interrupting the ionic path.

In an electrochemical facility individual cell stacks may be connected themselves in a series or parallel configuration. Overall, the topology of electrical connections may consist of different layers. In any case, cells always need to be fed with DC electricity, which is obtained from common AC electricity through a rectifier.

Having established the preferred arrangement of cells in the stack modules, we look at how the electrochemical reactor is fed with reactant and how the product is obtained. For this, the concepts of reactor design in traditional chemical engineering are considered (**Figure 6-2**). A batch reactor (BR) is operated discontinuously. It is charged with the reactants which are then well mixed and left for a period for the reaction to occur to some predetermined extent. The concentration of reactants and products changes continuously over time. The resultant mixture is discharged and worked up to obtain the product(s). A plug flow reactor (PFR) and continuously stirred tank reactor (CSTR) are operated continuously under steady-state conditions. In a PFR the concentration of the reacting mixture changes along the length of the reactor. In a CSTR the contents are well stirred and uniform throughout the reactor, reactant is added continuously and a product stream removed at the same rate for post-treatment. The exit stream has the same composition as the fluid in the reactor. After separation of the product or a part thereof, the mixture may be sent back to the reactor with added reactants for another pass (recirculation).



Figure 6-2. Schematic of different reactor types used in chemical engineering.

Often, the electrochemical reactor is but one element of many in an industrial plant and the overall process needs to be optimized as a whole towards a specific *figure of merit*. This may be, for a production process, the output of product per unit time, the energy invested per amount of product and, consequently, the cost per unit of product, etc. For a purification process, it may be the energy invested to obtain a certain target final concentration of toxic constituents. **Table 6-1** provides an overview of key parameters to be considered for the design of an electrochemical reactor.

Table 6-1. Important parameters of an electrochemical process and system

Quantity	Symbol	Unit	Comment
Production rate	'n	kg/s, t/a	determines plant size
Current density	i	$A \cdot m^{-2}$	
Single cell voltage	$U_{\rm cell}$	V	i, U_{cell} and \mathcal{E}_{F} need to be optimized
Faradaic efficiency	<i>€</i> F	%	simultaneously (cell operating point)
Area of single cell	A	m ²	determines current I for a given current density i
Voltage of DC power supply	$U_{\rm DC}$	V	AC grid electricity is rectified to DC
Number of cells	#	-	series, parallel or mixed configuration

There are many different design features of electrochemical reactors beyond what we have discussed so far, for example whether the reactor is open or closed, electrodes are flat plates or porous 3D electrodes, how reactants are fed, etc. In **Figure 6-3a** an example of a lab-scale plate-and-frame type cell is presented, which features a feed and exit port for a common electrolyte ('undivided cell'), flat plate electrodes and a turbulence promoter to ensure that the fluid is well mixed in the cell. The design is stackable, meaning that it can be composed of multiple cells. A single cell arrangement is shown in **Figure 6-3b** with an ion exchange membrane separating the two electrode compartments containing *anolyte* and *catholyte*¹, respectively ('divided cell'). Here, 3D mesh electrodes are used, which provide a higher surface area than flat plate electrodes.



Figure 6-3. (a) Design and components of a typical lab-scale multi-purpose electrochemical cell with modular design and interchangeable components, such as electrode type, flow plate, and number of cells. (Source: Chem. Rev. 118, 2018, 4573) (b) Detail of single cell, comprising a plastic mesh turbulence promoter, a 3D electrode and a membrane to separate anode and cathode compartment. (Source: Electrochim. Acta 63, 2012, 47)

1.2 Current density distribution

In technical applications of electrochemistry, especially in industrial processes, the cell components are often of macroscopic scale. Electrodes can have dimensions on the order of meters. Therefore, it is very likely that the current distribution across the electrode will not be homogeneous. Inhomogeneities in current density may be caused by a number of phenomena, such as the ohmic resistance of components or mass transport limitations. Of course, it may also be that the source of uneven activity are local materials defects or impurities. Understanding current density distribution will give us an indication how well designed a process is and what the cell performance limiting factors are. It is typically not a goal to make current density distribution as uniform *as possible*, but as uniform *as necessary*, given by the technical and techno-economical requirements of the process.

In this section, we will discuss exemplary situations where non-uniform current density distributions may be encountered. The conceptual approaches are often of generic nature and can, in principle,

¹ anolyte = electrolyte in the anode compartment, catholyte = electrolyte in the cathode compartment

be transferred to other configurations. The focus is on the one hand on the qualitative description of current inhomogeneities, yet also quantitative relationships will be developed based on governing equations and boundary conditions.

In the first situation, we consider a flat, rectangular electrode immersed in an electrolyte, where the nominal current I_0 is entering the plate from the top face (**Figure 6-4a**). The electrochemical reaction is assumed to take place only on the right face of the electrode (the example shows an anodic reaction). Due to the finite (electronic) conductivity σ of the electrode material, the reaction current density i_n , which is perpendicular to the surface of the electrode, will be a function of the position x from the entry point of the current (we assume that the counter electrode is not influencing the current density distribution here).

The current I_0 is entering at the top of the electrode, which yields a current density of $I_0/\delta w$ on this electrode face, where δ is the thickness of the electrode and w its width. The current density i(x) in a cross-sectional area of the electrode at a position x from the top surface decreases as a function of x, because at each position charge is supplied to the reaction, described by the reaction current density $i_n(x)$ (**Figure 6-4b**). The charge balance in the control volume $\delta w \, dx$ yields the following differential equation¹.

$$\delta \frac{di(x)}{dx} = -i_{\rm n}(x) \tag{6-3}$$

At the bottom of the electrode (x = L), all the current is 'used up', hence i(x=L) = 0, which is one boundary condition of the problem. The change in the (Galvani) potential φ of the electrode along x is given by Ohm's law: $i(x) = -\sigma \nabla \varphi(x)$ (cf. Chapter IV), where the operator ∇ simplifies to d/dxin 1D. Combining this with Eq. 6-3 yields the following 2nd order ordinary differential equation (ODE):

$$\frac{d^2\varphi(x)}{dx^2} = -\frac{1}{\sigma} \cdot \frac{di(x)}{dx} = \frac{1}{\sigma\delta} \cdot i_n(x)$$
(6-4)

We write the current density at *x*+*dx* as a differential change from the position *x* according to $i(x+dx) = i(x) + (\frac{d}{dx}i(x))dx$

and after insertion into the equation of current balance we obtain Eq. 6-3.

The current entering the control volume at position x is $I(x) = i(x) \cdot \delta w$, the one exiting at x+dx is $I(x) = i(x+dx) \cdot \delta w$. The difference is the faradaic reaction rate $I_n(x) = i_n(x) \cdot w \cdot dx$. Therefore the balance is: $\delta \cdot w \cdot (i(x) - i(x+dx)) = i_n(x) \cdot w \cdot dx$



Figure 6-4. (a) Current density distribution in a flat electrode, where the current I_0 enters from the top and the right side is in contact with electrolyte. The length of the electrode is L, the width w, and the thickness δ . The local reaction rate is given by the current density i_n on the electrode surface. (b) In case no other process is limiting, the reaction current density i_n is a function of position x. (c) The ordinary differential equation of the system is obtained from the current balance in a control volume, Ohm's law applied to the electrode and the boundary conditions at x = 0 and x = L.

for which we need two boundary conditions. The first one relates to the current I_0 entering the electrode at x = 0, the second one results from the electrode boundary at x = L:

$$\frac{d}{dx}\varphi(x=0) = -\frac{I_0}{\sigma w\delta} \qquad \frac{d}{dx}\varphi(x=L) = 0$$
(6-5)

If we provide a relationship between the electrode potential φ and the reaction current density i_n (for example, a Butler-Volmer type relation, cf. Chapter V) we can solve the ODE (analytically or numerically). In **Appendix A**, this is done exemplarily for the simple case of linear kinetics. **Figure 6-4c** shows qualitatively the distribution of the reaction current density $i_n(x)$. It is highest at x = 0, because here the electrode is connected to the external power supply. Along x, i.e., with increasing distance from the external connection, the driving force for the reaction fades, and hence the reaction rate decreases. As we can infer from Eq. 6-4, the thinner the electrode and the lower its conductivity, the more pronounced will be the drop of i_n along x. In an extreme case, only the upper part of the electrode will be utilized. For the design of an electrochemical reactor, it is therefore important to take such phenomena and possible limitations into account. We have only considered one electrode here to illustrate the case, yet the conceptual approach for a full cell with two electrodes would be similar. With added complexity, it is often not possible to find analytical solutions. Computational tools are therefore widely used to treat situations of technical relevance.

In the previous example the current density was determined by limitations of the electrode. Next, we will focus on the current density distribution caused by the finite conductivity of the electrolyte and the geometry of the electrodes. We stipulate that the electrode phase has a uniform (Galvani) potential due to its (electronic) conductivity being much greater than the conductivity of the electrodes is determined by the ohmic resistance of the electrolyte only, i.e. we neglect activation and concentration overpotentials. Consequently, the geometry of the electrodes and cell will determine the current distribution on the surface of the electrodes. An example in 2D is shown in **Figure 6-5a**.



Figure 6-5. (a) Primary current distribution for the electrode geometry shown. Both electrodes have a uniform potential. The dashed blue lines indicate equipotential contours $\varphi = \text{const.}$ in the electrolyte, the red lines are streamlines along which the current flows. In the electrolyte, the Laplace equation $\nabla^2 \varphi = 0$ holds. (b) Primary and secondary current distributions on an electrode with a serrated profile. (Adapted from: D. Pletcher, F.C. Walsh, Industrial Electrochemistry, Springer, 1993)

To find the current density distribution, we need to know the distribution of the potential φ in the electrolyte. Everywhere in the electrolyte, including the boundaries, the local current density is given by Ohm's law: $i = -\sigma \nabla \varphi$, where σ is the conductivity of the electrolyte¹. The current distribution on the electrodes thus corresponds to the current density in the electrolyte at the respective boundary. The negative gradient of the potential is the electric field: $\mathbf{E} = -\nabla \varphi$. Since the interior of a phase is free of current sources and sinks, the divergence of φ is zero everywhere in the electrolyte: $\nabla \cdot \mathbf{E} = 0$. Therefore, by combining the last two expressions, we arrive at the following important equation:

$$\nabla^2 \varphi = 0 \tag{6-6}$$

¹ Actually, as we recall from Chapter IV, to be precise we should write the current density as a vector **i**, because the gradient $\nabla \varphi$ of the scalar field φ is a vector field. What is meant here with *i* is the magnitude of the vector, i.e. $i = |\mathbf{i}|$.

This is the *Laplace equation*¹. With boundary conditions given, we can calculate the distribution of the potential φ in the electrolyte (analytically or numerically), here in 2D and in general in 3D. In **Figure 6-5a** the equipotential contours $\varphi = \text{const.}$ are shown. Close to the electrodes, they follow the geometry of their surface. The closer spaced the contours are, the higher the potential gradient $\nabla \varphi$ and hence the field strength *E*, and thus the higher the current density *i*. The current follows the streamlines (provided that the conductivity σ is isotropic), which are perpendicular to the equipotential lines. From this it follows that the current is always perpendicular to the electrode surface. Qualitatively, we can get an idea of the current density distribution by looking at the different lengths of the streamlines between the two electrodes. The potential drop $\Delta \varphi$ is the same for all streamlines. Ohm's law for a streamline is $\Delta \varphi = i \cdot R$ (remember that we are neglecting activation and concentration overpotentials). The (area) resistance *R* (unit: Ohm·cm²) between the two endpoints of a streamline is proportional to its length *L* according to $R = L / \sigma$. Therefore, we see that the longer the streamline, the lower the current density (we assume σ also to be homogeneous), *L* and *i* are inversely proportional. This results in the current density being highest where the separation between the electrodes is the smallest, which is intuitive.

Next, we study the situation depicted in **Figure 6-5b** and again only consider ohmic losses in the electrolyte as overpotential to start with. We consider two current paths between the left flat electrode and the right serrated electrode. Having only ohmic overpotential, we write $\Delta \varphi = i_1 \cdot R_1 =$ $i_2 \cdot R_2$, and since the path is shorter at position 1 than at position 2, we have $R_1 < R_2$ and thus $i_1 > i_2$, to be precise: $i_1 / i_2 = R_2 / R_1$, in analogy to the situation discussed for **Figure 6-5a**. In the next case, we also take the activation overpotential of the electrode reactions into account. We combine the contributions of the two electrodes into one effective (positive) overpotential η . The loss term is now $\Delta \varphi = i_1 \cdot R_1 + \eta_1 = i_2 \cdot R_2 + \eta_2$. Generally, η_1 and η_2 will be different owing to the different current densities at positions 1 and 2, yet if we assume the activation overpotentials η_k to be much larger than the ohmic drop, i.e. $\eta_k \gg i_k R_k$, then we obtain in the limiting case $\eta_1 \approx \eta_2$ and thus $i_1 \approx i_2$. We therefore see that the prevalence of an activation overpotential leads to a smoothening of the current density distribution. This is exploited, for example, in electroplating baths, where additives are used to artificially increase the activation overpotential. This renders the current distribution more uniform and allows the plating of irregular shapes. The Wagner number Wa, a dimensionless quantity, is used to characterize the relative magnitudes of the charge transfer resistance $R_{\rm CT}$ and the ohmic resistance of the electrolyte R_{Ω} . It is defined as:

¹ We could have also written $\nabla^2 \varphi \equiv \Delta \varphi$, where Δ is the Laplace operator (cf. Chapter V), yet this would be a bit confusing here, because we also use $\Delta \varphi$ to designate the potential difference between the two electrodes.

$$Wa = \frac{R_{\rm CT}}{R_{\rm O}} \tag{6-7}$$

The larger Wa, the more even is the current distribution in spite of non-uniform geometry.

The types of current density distribution determined by the different overpotentials are classified into 3 categories:

- Primary current distribution: activation and concentration overpotentials are negligible, the current distribution is only determined by the ohmic losses in the electrolyte and cell geometry. As elaborated above, to obtain the current density distribution, we have to solve the Laplace equation in the region of relevance with corresponding boundary conditions.
- 2. Secondary current distribution: in this case, the concentration overpotential is negligible, but both the activation and ohmic overpotential are governing the current distribution, as illustrated above in Figure 6-5b.
- 3. **Tertiary current distribution**: here, all the overpotentials are considered, also mass transport limitations. This is obviously the general case.



Figure 6-6. (a) Current distributions for a parallel-plate reactor in fully developed laminar flow. Above: definition sketch, below: normalized current as a function of dimensionless distance along the electrode. (b) The effect of electrode surface profile on the tertiary current distribution, showing the size of the surface roughness *y* compared to the Nernstian diffusion layer thickness δ_N and the relative limiting-current density *i* on the peaks and valleys. (Adapted from: D. Pletcher, F.C. Walsh, Industrial Electrochemistry, Springer, 1993)

To further elaborate on these different cases and illustrate the differences, a parallel-plate flow cell with electrodes of length L, separation s, and fully developed laminar flow is considered (**Figure 6-6a**). The primary current distribution shows the current to be approximately uniform over most of

the electrode but with considerable edge effects at x = 0 and x = L, where the current increases to very high values. In fact, the current theoretically diverges at these points, as we shall see below. The secondary distribution is more uniform, as we have already seen, and determined by the Wagner number of the system. At the limit of $Wa \rightarrow \infty$, a perfectly uniform current density is obtained. Conversely, for $Wa \rightarrow 0$ the primary current distribution prevails. The tertiary current distribution also takes into account the changes in the concentration of electroactive species in the cell. In our example the drop in reactant concentration in the electrolyte in the direction of flow leads to a decrease in limiting current density along x.

We have so far considered the overall electrode geometry. However, the electrode surface profile must also be looked at (**Figure 6-6b**). If the electrode surface roughness *y* is large in comparison to the Nernst diffusion layer thickness δ_N (cf. Chapter V), $y \gg \delta_N$, the latter follows the surface profile, giving rise to a uniform limiting-current density distribution. When the roughness is small, $y \ll \delta_N$, a non-uniform tertiary-current distribution arises, as the high points are favored with a larger limiting current density.



Figure 6-7. (a) 2D representation ('top view') of a Hull cell, comprising an anode (potential φ_h) and cathode (potential φ_h) electrode plate immersed in an electrolyte. $\varphi(x,y)$ is the potential in the electrolyte. The boundary condition $\partial \varphi / \partial n$ for the wall of the electrolyte tank is indicated. In the electrolyte the Laplace equation $\nabla^2 \varphi = 0$ holds. (b) Influence of the Wagner number on the current distribution in the Hull cell for Tafel kinetics. The ratio i/i_{av} is represented as a function of the dimensionless cathode length *z*. (Source: J. Electrochem. Soc. 134(12), 1987, 3015)

For electroplating applications it is desired to characterize the deposition behavior qualitatively and quantitatively to establish optimum electrolyte composition and cell current. For empirical studies, specifically designed cells are used to study electroplating behavior. One of them is the *Hull cell*, which consists of an electrolyte bath, into which the two electrodes are placed (**Figure 6-7a**). The anode A-D is placed at a right angle to the side walls, the cathode B-C, which is the test electrode, is placed opposite the anode, yet at an angle. This means that there is a continuous variation of the

path length between anode and cathode, which, in general, leads to different current densities along the test electrode coordinate *z* and different thickness and quality of the electrodeposited layer.

The primary and secondary current distribution in the Hull cell can be determined numerically. As elaborated above, to obtain the primary current distribution, the Laplace equation $\nabla^2 \varphi = 0$ has to be solved in the electrolyte domain, here with the coordinates *x* and *y*, since the situation is the same at all bath heights. The boundary conditions are a constant potential of the anode φ_a and cathode φ_c . The current and thus the potential gradient $\nabla \varphi$ has to be parallel to the side walls A-B and C-D, hence the potential does not change perpendicular to it, expressed as $\partial \varphi / \partial n = 0$, where *n* is the normal vector perpendicular to the side wall (n = y at the side walls for the situation here). For the primary current distribution, which corresponds to Wa = 0, the current density approaches zero in C, the 'far corner', ($z \rightarrow 0$) of the test electrode. In B, the 'near corner', ($z \rightarrow 1$) the current tends towards infinity. Actually, it can be shown (cf. **Appendix B**) that theoretically the current always tends to zero in corners with an acute angle (<90°) and to infinity in corners with an obtuse angle (>90°). Only for a right angle between electrode and side wall the current density is finite. The secondary current density distribution in the Hull cell depends on the Wagner number (**Figure 6-7b**). The higher *Wa*, the more uniform the current distribution, as we have already seen before.

1.2.1 3D electrodes

Electrochemical reactions take place at the interface of electrode and electrolyte, and it is often in the interest of the scientist or engineer to maximize this interfacial area. With the use of flat electrodes or electrodes with a rough surface or added structural features, such as ridges, the roughness factor (cf. Chapter V) can be increased by a factor of 2 to 5, maybe 10. For higher roughness factors, 3D electrodes may be used. These are porous electrodes made of stacked mesh, foam, cloth, paper or felt material, or packed bed electrodes containing fibers, granules, flakes, etc.



Figure 6-8. (a) Schematic illustration of a 3D electrode with projected surface area *A* and thickness *L*. (b) Example of carbon felt electrodes with a thickness of about 5 mm (source: AvCarb). (c) Example of a reticulated vitreous ('glassy') carbon electrode (source: redox.me).

Metal and carbon based 3D electrodes are most common (**Figure 6-8**). Due to the high surface area of the electrode, the roughness factor may be as high as 100 or more. This allows a high cell current for a given activation overpotential, or a small overpotential for a given cell current. Evidently, mass transport limitations may become appreciable in this case and may need to be taken into consideration in the analysis of the reaction limitations and cell engineering.

Aside from the roughness factor r, the *specific interfacial area a* is used to characterize porous electrodes, which is defined as the internal surface area of the electrode S (unit: cm² of microscopic interfacial area) divided by the geometric volume V (unit: cm³, macroscopic dimensions) of the electrode:

$$a = \frac{S}{V} = \frac{S}{A \cdot L} = \frac{r}{L} \tag{6-8}$$

A is the projected surface area of the electrode and L its thickness perpendicular to the current collector plate. The unit of a is $cm^2/cm^3 = cm^{-1}$.

Example:

An electrochemical reactor comprising a packed bed cathode consisting of carbon chips is used to recover platinum from an aqueous solution. The graphite chips have an average particle diameter d of 725 µm and there are n = 104'000 particles in the bed. The bed volume V is 66 cm³ and the projected electrode surface area A is 55 cm². First, we calculate the surface area of all particles, assuming a spherical geometry: $S = n \cdot 4\pi \cdot (d/2)^2 = 1'700$ cm². The roughness factor is therefore r = S/A = 31. The thickness of the bed is L = V/A = 1.2 cm, and the specific interfacial area a = 26.

In 3D electrodes imbibed with a liquid electrolyte, a co-continuous electrode and electrolyte phase is imperative to maximize the electrochemically active interfacial area. If a zone is disconnected from either of the two phases, the charge (ions or electrons) cannot be transported to or away from



Figure 6-9. (a) Schematic of a porous electrode (cathode) filled with electrolyte in an electrochemical flow-through cell with flat anode. (b) Charge balance in a control volume of the 3D electrode, considering current in the electrode phase, i_m , and in the electrolyte phase i_s . The local electrochemical reaction rate is given by the volumetric current density i_v . (Currents are negative, since a cathode reaction is considered here.)

it, rendering this portion of the electrode electrochemically inactive. In general, in porous electrodes all types of overpotential should be expected to be prevalent, which, in addition, may vary as a function of position in the electrode. Due to the confinement of the electrolyte in the porous structure of the electrode, mass transport effects are very likely to influence the kinetics. Often, the electrolyte is actively forced through the porous electrode to supply reactants and remove products. This will lead to variations in current density in the direction of flow through the 3D electrode. In the analysis to follow, we consider a cell consisting of a 3D cathode and a flat anode (= counter electrode) through which electrolyte is flown (Figure 6-9a). We only study the variation along x, i.e. in thickness direction of the electrode, and assume the electrolyte flow to be sufficiently high not to cause any variation along the direction of flow. The 3D electrode is assumed to be macrohomogeneous, meaning that we do not resolve the structural features (fibers, beads, etc.) of the electrode but define averaged parameters, such as the effective electronic conductivity of the electrode phase $\sigma_{\rm m}$, and effective ionic conductivity of the electrolyte phase $\sigma_{\rm s}$, which we assume to be uniform over the electrode volume. Note that $\sigma_{\rm m}$ and $\sigma_{\rm s}$ are not the conductivities of the bulk electrode material and electrolyte, but corrected for porosity and tortuosity of the respective phase in the 3D electrode¹.

If we now imagine a position somewhere in the electrode, the local reaction rate, expressed by the real current density j (unit: A/cm²) related to the microscopic interfacial area, translates into a local volumetric reaction rate / current density i_v (unit: A/cm³) in the 3 D electrode according to $i_v = a \cdot j$. The local reaction is associated with charge transfer between electrode and electrolyte phase, and we can therefore perform a charge balance in a control volume of the 3D electrode consisting of a thin slice of thickness dx at position x (**Figure 6-9b**). The local geometric current density in the electrode and electrolyte phase are i_m and i_s , respectively (unit: A/cm²). The electrochemical reaction converts electronic current into ionic current (anodic process) or vice-versa (cathodic process). Charge balance² yields the following relation:





 $\sigma = \sigma_0 \frac{\varepsilon}{\tau}$

where ε is the porosity (<1), and σ_0 the conductivity of the bulk phase.

² We write: $i_m(x) - i_m(x + dx) = i_s(x + dx) - i_s(x) = i_v \cdot dx$ and, again, introduce the differential

$$i(x+dx) = i(x) + (\frac{d}{dx}i(x))dx$$

$$i_{v}(x) = -\frac{d}{dx}i_{m}(x) = \frac{d}{dx}i_{s}(x)$$
 (6-9)

The change of the current in the electrode corresponds to the change of the current in the electrolyte (considering the direction of charge flow via the sign). If we move in the electrode from the front face (x = L) to the back face (x = 0), the cathodic reaction gradually converts ionic current into electronic current. If we integrate the volumetric current density i_v over the thickness of the electrode L, we obtain the *projected current density* i_a (unit: A/cm²), which is the macroscopic cell current I we measure divided by the projected surface area A of the electrode:

$$i_{\rm a} = \int_{0}^{L} i_{\rm v}(x) \, dx = i_{\rm m}(x=0) = i_{\rm s}(x=L) \tag{6-10}$$

Due to the conservation of charge, electronic and ionic current density always add up to the projected current density at any position x: $i_m + i_s = i_a$. Also, the electronic current density i_m equals i_a at the back of the electrode (x = 0), where it is in contact with the current collector, and the ionic current density i_s equals i_a at the front of the electrode (x = L).

As in the problem analyzed at the beginning of this sub-section (**Figure 6-4**), the local reaction rate depends on the local potential difference between electrode and electrolyte phase. In case of the 3D electrode, in general there are limitations due to the finite conductivity of both phases. Therefore, the potential will change for both as a function of *x*. Again, the governing equation describing the local change in the phase potential φ is Ohm's law $i_k = -\sigma_k \cdot \nabla \varphi_k = -\sigma_k \cdot d\varphi_k/dx$ applicable to both phases (k = m, s).¹ After differentiating with respect to *x* and inserting Eq. 6-9 we obtain the following differential equations, relating the electrode and electrolyte phase potentials to the reaction rate:

$$\frac{d^2 \varphi_{\rm m}(x)}{dx^2} = \frac{1}{\sigma_{\rm m}} i_{\rm v}(x) \qquad \qquad \frac{d^2 \varphi_{\rm s}(x)}{dx^2} = -\frac{1}{\sigma_{\rm s}} i_{\rm v}(x) \tag{6-11}$$

The boundary conditions are as follows:

which yields Eq. 6-9.

¹ For anisotropic compounds, which is a very likely case for a carbon fiber based electrode, owing to the preferential orientation of the carbon fibers, the (effective) conductivity value to choose here is the conductivity in x-direction.

$$\frac{d\varphi_{\rm m}(x=L)}{dx} = 0 \qquad \qquad \frac{d\varphi_{\rm s}(x=0)}{dx} = 0 \tag{6-12}$$

$$\frac{d\varphi_{\rm m}(x=0)}{dx} = -\frac{i_{\rm a}}{\sigma_{\rm m}} \qquad \frac{d\varphi_{\rm s}(x=L)}{dx} = -\frac{i_{\rm a}}{\sigma_{\rm s}}$$
(6-13)

Note that, in general, $d\varphi_m/dx \neq d\varphi_s/dx$, because $\sigma_m \neq \sigma_s$. Again, if we find a kinetic relationship between the potentials and the reaction rate (Butler-Volmer, Tafel, or linear kinetics), the volumetric current density i_v can be expressed as a function of the phase potentials φ_m and φ_s and the differential equations solved. This has been done exemplarily assuming linear kinetics (cf. **Appendix C**) with a specific set of parameters for a cathodic as well as an anodic process, the results of which are presented in **Figure 6-10**. In this example, we see a notable variation of local reaction rate i_v as a function of position *x* in the electrode. We can qualitatively discuss selected other cases, where one of the parameters is limiting:

- i. If the electrode is very thin (small *L*), the specific interfacial area *a* high, or the conductivities σ_m and σ_s very high, then the distribution of the potentials φ_m and φ_s in the electrode is nearly uniform and so is the local reaction rate i_v . The current densities i_m and i_s in the two phases change linearly between x = 0 and x = L.
- ii. If the effective ionic conductivity of the electrolyte, σ_s , is much smaller than that of the electrode, σ_m , which is often the case, then the reaction is confined to an area close to the front of the electrode at $x \approx L$. This may be a practical scenario in a battery electrode (cf. Chapter VII). A flipped situation is encountered with the reaction confined to the back of the electrode at $x \approx 0$ if the electronic conductivity is poor, for example for oxide based electrode material.



Figure 6-10. Calculated potential φ , current density *i*, and volumetric current density *i*_v for a 3D electrode imbibed with electrolyte, assuming linear kinetics, for (a) an cathodic reaction, and (b) an anodic reaction. The solid lines indicate the potential φ_m and current density *i*_m in the electrode phase, the dashed lines the corresponding quantities φ_k and *i*_s in the electrolyte phase. The red circles in the graphs depicting the potential φ indicate the boundary condition given by Eq. 6-12 (\bigcirc) and Eq. 6-13 (\bigcirc). The values are calculated (cf. **Appendix C**) using following parameters: *a* (specific interfacial area) = 30 cm²/cm³, *R*_{CT} (charge transfer resistance) = 22.5 $\Omega \cdot \text{cm}^2$, *L* (electrode thickness) = 1 cm, σ_s (ionic conductivity of electrolyte) = 0.1 S/cm, σ_m (electronic conductivity of electrode) = 0.5 S/cm, $\Delta \varphi_{eq}$ (= $\varphi_m - \varphi_s$ at equilibrium) = 0.3 V, *i*_a (projected current density) = ± 0.1 A/cm². The potential of the electrode φ_m is arbitrarily pinned to 0 V at *x* = 0.

2 The Chlor-Alkali Process

The chlor-alkali process is an industrial process consisting of the electrolysis of sodium chloride solution (brine) to produce chlorine and sodium hydroxide (caustic soda), two indispensable commodities in the chemical industry. It is one of the largest electrochemical technologies in the world, along with the Hall-Héroult process for aluminium production (see Section 3.1). In 2019, 88 Mt of chlorine were produced worldwide, most of it electrolytically. Primary uses of chlorine are in the pulp and paper industry and in water treatment as a disinfectant. Other uses include the production of organic and inorganic chemicals, notably polyvinyl chloride (PVC) and titanium dioxide (a widely used pigment). Sodium hydroxide is used in many industries, such as pulp and paper manufacture, textiles, drinking water, soaps and detergents.

The electrolytic production of Cl_2 and NaOH(aq) was established in the late 19th century. Before that, chorine was produced chemically, for example through gas phase oxidation of hydrogen chloride at 400-450°C over a copper catalyst according to 4 HCl(g) + $O_2 \rightarrow 2 Cl_2 + H_2O$ (Deacon process). There are 3 chlor-alkali electrolysis technologies (**Table 6-2**). The amalgam and diaphragm process were the first ones to be industrialized. The membrane process was introduced in the 1970s and has since then been gradually replacing the other two processes, not only because it is less energy intensive, but also as a result of the amalgam process (involving mercury) and the diaphragm process (using an asbestos separator / diaphragm) being problematic from an environment and health standpoint. Due to the importance of the membrane process today and in the future, we will limit ourselves to this technology in the sub-sections to follow.

Property (unit)	Amalgam	Diaphragm	Membrane
$U_{\rm rev}^{\circ}$ (V)	3.11	2.19	2.19
$U_{\rm cell}$ (V)	~4	~3.5	3.0-3.2
$i (A/cm^2)$	1.0	0.25	0.3-0.4
$W_{\rm e}$ (kWh/t(Cl ₂))	3'100-3'400	2'300-2'900	2'100-2'600
$W_{\rm e}$ (kWh/t(Cl ₂)) tot	3'100-3'400	3'200-3'800	2'400-2'900
NaCl purification	simple	simple	expensive ^a
NaOH quality	50 wt% from cell,	ca. 12 wt% from cell,	ca. 32 wt% from cell,
	low Cl ⁻ content	<1 % Cl ⁻ in 50 wt% NaOH	low Cl ⁻ content
Cl ₂ quality	<1 % O ₂ ,	2-3 % O ₂ ,	1-3 % O ₂ ,
· ·	no further cleanup	further cleanup required	further cleanup required ^b
Environmental issues	Hg used as cathode material	Asbestos used for diaphragms	none

Table 6-2. Comparison of the different chlor-alkali processes. (Source: J. Appl. Electrochem. 38, 2008, 1177)

^a $Ca^{2+} + Mg^{2+} < 20 ppb$

 b 0.5 % O₂ with HCl addition to anolyte

2.1 Membrane cell process

In 1975, Asahi Kasei (Japan) began the first commercial chlor-alkali production using the membrane electrolysis process, see **Figure 6-13a** for a modern facility. All industrial scale chlor-alkali plants incorporate the plate-and-frame cell design, where membranes and electrodes are assembled together with spacers and gaskets in a stack. The cells in the stack are arranged in bipolar configuration and the cell area can easily be on the order of square meters. The feed is brine, a concentrated solution of NaCl with a concentration of around 300 g/L. It is introduced to the anode compartment of the cells, where the chloride ions are oxidized to chlorine gas (**Figure 6-13b**). At the cathode water reacts to hydroxide ions and hydrogen, which traditionally has been regarded as a waste product. The cathode feed is 30% NaOH solution, whose concentration increases to 32% towards the cathode outlet. The half-cell reactions and overall cell reaction are as follows:

(+) anode	2 Cl^-	\rightarrow	Cl ₂ + 2 e ⁻	$E_{\rm C}^{\circ} = +1.36 {\rm V}$	(6-14)
(-) cathode	$2 H_2O + 2 e^-$	\rightarrow	$H_2 + 2 OH^-$	$E_{\rm H}^{\circ} = -0.83 \text{ V} \text{ (pH 14)}$	(6-15)
overall	$2 \text{ Cl}^- + 2 \text{ H}_2\text{O}$	→	$Cl_2 + H_2 + 2 \ OH^-$	$U_{\rm rev}^{\circ} = (-)2.19 {\rm V}$	(6-16)

As the name of the process implies, a polymer membrane, specifically a cation exchange membrane (cf. Chapter IV), is used as electrolyte and transports Na⁺ ions from the anode to the cathode. Detailed features and properties of the membrane will be discussed below. From the standard potentials of the two half-cell reactions at 25°C, we obtain a standard reversible cell voltage of $U_{rev}^{\circ} = -2.19$ V. The negative value confirms that the reaction is non-spontaneous and needs to be driven with a power supply. For convenience we will normally use a positive cell voltage in the discussions here. The reaction is carried out at a temperature of 80°C to 95°C at a current density of 0.3 to 0.4 A/cm². Newer designs can operate at somewhat higher values of 0.6 A/cm². The operating voltage is around 3 V, which, according to Eq. 6-2 and a faradaic efficiency of 97 %, yields a



Figure 6-11. (a) Modern chlor-alkali membrane cell electrolyzers from Asahi Kasei (source: chemanageronline.com, 10.07.2017). (b) Schematic of the membrane cell process for chlor-alkali production.

specific electricity consumption for cell operation of 2'300 kWh/t(Cl₂), which is in agreement with the range reported in **Table 6-2**. Considering additional energy input for balance-of-plant components, such as pumps, dryers, etc., the total energy consumption is 2'400 - 2'900 kWh/t(Cl₂). This shows that, like in many other electrolytic processes, for example water electrolysis or aluminium production, electricity is the largest contributor to the energy input and, hence, cost.

Historically, graphite anodes were employed in the brine electrolysis process. Their use was abandoned due to oxidation to carbon dioxide in the process. During the production of 1 t of chlorine, 2 kg of carbon was oxidized. In the 1960s, the *dimensionally stable anode* (DSA) based on titanium was introduced. Initially, it was coated with platinum, which on the one hand reduced the overpotential to 200 mV at 0.3 A/cm² (graphite anode: 400 mV) and, on the other hand, reduced the corrosion of the anode to 0.6 g per ton of chlorine produced. Further improvements were made by using a RuO₂ based coating (**Figure 6-12a**), which reduced the overpotential to 70 mV. A coating of 10 μ m lasts for over 5 years.

Nickel is used as cathode material for the hydrogen evolution reaction under the prevailing strongly alkaline conditions. The reaction has a relative high overpotential of up to 300 mV. It can be significantly decreased if coatings of, e.g., ruthenium oxides, are applied on the cathode surface.



Figure 6-12. (a) Image of a dimensionally stable anode (DSA), consisting of a titanium expanded metal mesh coated with a layer of RuO₂. (Source, above: W. Grot, Fluorinated Ionomers, 2^{nd} Edition, Elsevier, 2011; below: Z. Phys. Chem. 227, 2013, 651) (b) Schematic of cation exchange membrane, consisting of a perfluorocarbon polymer with sulfonate fixed groups on the positive side and a thinner layer with fixed carboxylate groups facing the negative compartment. The carboxylate layer improves the OH⁻ barrier properties and reduces OH⁻ transport towards the anode (+) favored by the potential gradient $\nabla \varphi$ in the membrane.

The cation exchange membrane used as polymer electrolyte deserves a bit of our attention, as it is a fine example of dedicated material and component design towards a specific application. The material used for the membrane is a perfluoroakyl ionomer (cf. Chapter IV). The most widely known representative is Nafion[™], originally developed by DuPont in the 1960s as a spin-off from the fuel cell research performed in the context of the US space program. Nafion™ membranes were found to have good ion-exchange properties as well as high chemical resistance to the harsh environment of the chlor-alkali cell. In fact, the name 'Nafion' derives from its ability to conduct Na⁺ ions. The first thing to realize is that the solution in the two electrode compartments that the membrane is separating have markedly different composition: concentrated NaCl solution (brine) on the anode side and concentrated NaOH solution (caustic soda) on the cathode side. The cation exchange membrane is supposed to only pass Na⁺ ions. However, as we recall from Chapter IV, it is challenging to maintain co-ion exclusion, here Cl⁻ and OH⁻, at high electrolyte concentrations, because Donnan exclusion is weak. The crossover of chloride ions to the cathode is undesired, as it leads to a contamination of the NaOH product stream, whereas the crossover of hydroxide ions to the anode should be prevented to avoid unwanted side reactions, such as the formation of hypochlorite according to $Cl_2 + OH^- \rightarrow ClO^- + Cl^- + H_2O$. The pH in the anode compartment is maintained at mildly acidic conditions (pH ~3) through the addition of HCl to minimize this reaction. To understand how transport selectivity in the membrane (Figure 6-12b) is achieved, we look at the driving forces for transport of the different ions:

- Na⁺ ions: sodium ions are readily taken up by the cation exchange membrane and are transported from anode to cathode by migration driven by the potential gradient in the membrane. Na⁺ ions carry most of the charge in the membrane, hence its transference number is close to unity.
- Cl⁻ ions: there is a strong concentration gradient for chloride ions, as the cathode compartment is virtually chloride free. However, being negatively charged, they are largely rejected by the membrane. In addition, the potential gradient in the membrane is such that they are driven towards the anode. Therefore, the crossover of chloride ions through the membrane is very small.
- **OH**⁻ **ions**: there is an equally strong concentration gradient for hydroxide ions, and their uptake by the membrane is equally disfavored by the Donnan potential. Yet co-ion exclusion is not complete, and the potential gradient actually drives OH⁻ towards the anode. The avoidance of OH⁻ crossover is the most challenging task for the membrane. To improve selectivity, the side of the membrane facing the cathode contains carboxylate exchange groups instead of sulfonate ones. The lower water uptake of the carboxylate layer leads to a reduction in conductivity but increases the exclusion of hydroxide ions.

Next, we look at the reactions taking place at the electrodes, their standard potential at 25°C and the polarization characteristics (Figure 6-13). At the negative electrode, the hydrogen evolution reaction (HER) takes place at alkaline conditions. At pH 14, the HER has a standard reversible potential of -0.83 V (cf. Chapter II). The overpotential at practical current densities is in the range of a few hundred millivolt. At the positive electrode, the chlorine evolution reaction (CIER) takes place, which has a standard reversible potential of +1.36 V, independent of the pH. The overpotential here is around 100 mV. The major challenge on the anode is to suppress the parasitic oxygen evolution reaction (OER), which impairs the faradaic efficiency of the anodic reaction and leads to contamination of the chlorine product stream. At pH 7, the standard potential of the OER is +0.82 V. Therefore, the OER is thermodynamically favored over the CIER, and the selectivity for the chlorine reaction is effectively achieved by choosing an anode catalyst material (RuO₂ based) that is highly active towards the chlorine reaction but has low activity towards the oxygen reaction. In terms of electrocatalysis, the OER has an exchange current density (cf. Chapter V) that is several orders of magnitude lower than that of the CIER. We have seen above that the pH on the anode side is maintained at around 3. Therefore, compared to pH 7, the equilibrium potential of the OER increases by 59 mV at 25°C for each unit of pH decrease, hence the value is +1.05 V at pH 3. Consequently, a low anode compartment pH actually helps to improve the selectivity of the CIER, because the driving force / overpotential for the OER decreases with decreasing pH for a given operating potential of the anode. The pH should not be too low though, as this would lead to an increasing fraction of H⁺ being transported across the membrane instead of Na⁺.



Figure 6-13. Electrode polarization diagram for a chlor-alkali cell, with hydrogen evolution reaction (HER) at the negative electrode. At the positive electrode the chlorine evolution reaction (CIER) is desired, yet the oxygen evolution reaction (OER) is thermodynamically favored, but, owing to the choice of catalyst, kinetically hindered.

Taking the reversible potential of the reaction¹ and adding the anode and cathode overpotentials, we obtain a cell voltage of around 2.7 V. The difference to the effective cell voltage of \sim 3 V in a technical cell is made up of the ohmic overpotential of the cell, which is not included in **Figure 6-13**.

2.2 Oxygen depolarized cathode (ODC)

In most cases, the hydrogen produced in the cathode reaction of the traditional chlor-alkali process (**Figure 6-13**) is regarded as an undesired side product. In search for an alternative cathodic reaction, the oxygen reduction reaction (ORR) suggests itself. This is the background of the *oxygen depolarized cathode* (ODC). The anodic chlorine reaction is unchanged. The cathodic ORR at pH 14 has a standard potential of +0.40 V at 25°C, which reduces the absolute value of the reversible voltage by 1.23 V compared to the standard process with hydrogen cathode:

(+) anode	2 Cl ⁻	\rightarrow	Cl ₂ + 2 e ⁻	$E_{\rm C}^{\circ} = +1.36 {\rm V}$	(6-17)
(-) cathode	$H_2O + \frac{1}{2}O_2 + 2 e^{-1}$	\rightarrow	2 OH-	$E_0^{\circ} = +0.40 \text{ V} (\text{pH 14})$	(6-18)
overall	$2 \text{ Cl}^- + \frac{1}{2} \text{ O}_2 + \text{H}_2 \text{O}$	→	$Cl_2 + 2 \text{ OH}^-$	$U_{\rm rev}^{\circ} = (-)0.96 {\rm V}$	(6-19)

With the ODC the desired products, i.e. chlorine and caustic soda, remain the same, yet the production of hydrogen is avoided (**Figure 6-14a**). The membrane and DSA also are unchanged. The ODC consists of a porous carbon fiber based gas diffusion layer (GDL), which is coated with a mixture of a silver catalyst and PTFE as binder (**Figure 6-14b**). This electrode design is similar to the one used in a polymer electrolyte fuel cell (cf. Chapter VII). Pure oxygen is fed to the cathode



Figure 6-14. (a) Chlor-alkali membrane cell with oxygen depolarized cathode (ODC). Instead of hydrogen evolution (Figure 6-13) the oxygen reduction reaction (ORR) takes place here, which leads to a drop in cell voltage by \sim 1 V. (b) Schematic of the cell with ODC, which consists of a gas diffusion layer (GDL) and a catalyst layer containing an Ag based catalyst.

¹ The reversible voltage of the chlor-alkali reaction 6-16 has a temperature dependence of 0.4 mV/K, therefore the U_{rev}° value at 90°C differs only by about 30 mV from the value at 25°C.

as well as NaOH solution, whose concentration increases in the compartment due to the reaction. This requires an intricate design of the cathode to manage the flow of these two phases. In principle, air could be used as reactant, yet this would lead to a higher kinetic and concentration overpotential, which is considered excessive.



Figure 6-15. Electrode polarization curves for the chlor-alkali process with and without oxygen depolarized cathode (ODC). Replacing the hydrogen evolution reaction (HER) by the oxygen reduction reaction (ORR) reduces the cell voltage by $\sim 1 \text{ V}$. (Adapted from: Electrochem. Soc. Interface 26, 2017, 73)

A diagram of the electrode potentials and polarization is shown in **Figure 6-15**, showing the standard cathode process (HER) and the ORR associated with the ODC. The activation overpotential of the ORR is about 200 mV higher than that of the HER, which leads to the overall reduction of the operating cell voltage from \sim 3 to \sim 2 V. The corresponding specific electricity consumption drops from 2'100 kWh/t(Cl₂) to 1'600 kWh/t(Cl₂).

2.3 Hydrochloric acid electrolysis

A process related to the chlor-alkali reaction is the hydrochloric acid electrolysis. It yields hydrogen and chlorine gas. In particular, it is a route for recovering Cl_2 from HCl(aq), because hydrogen chloride is a side product of numerous processes in the chemical industry involving chlorine. In the standard HCl(aq) electrolysis process H⁺ and Cl⁻ react to form H₂ and Cl₂ at the cathode and anode, respectively. In addition, in analogy to the chlor-alkali process, the HER can be replaced by the ORR in the process with an ODC:

conventional 2 HCl(aq)
$$\rightarrow$$
 H₂ + Cl₂ $U_{rev}^{\circ} = (-)1.36 \text{ V (pH 0)}$ (6-20)
with ODC 2 HCl(aq) + $\frac{1}{2} O_2 \rightarrow$ H₂O + Cl₂ $U_{rev}^{\circ} = (-)0.13 \text{ V (pH 0)}$ (6-21)

Hydrochloric acid electrolysis is a relatively simple process, because the same electrolyte, hydrochloric acid with a concentration of around 15%, is used in both electrode compartments, other than in the chlor-alkali electrolysis with two very different electrolytes. The strongly acidic conditions increase the reversible potential for the OER to higher values than what is observed in brine electrolysis (pH \sim 3, see above). Therefore, a high faradaic efficiency of chlorine evolution is obtained and the oxygen content in the anode gas is negligible.



Figure 6-16. Electrode polarization curves for the HCl(aq) electrolysis process with and without oxygen depolarized cathode (ODC). (Adapted from: Electrochem. Soc. Interface 26, 2017, 73)

The half-cell polarization characteristics relevant for the HCl(aq) electrolysis reaction are shown schematically in **Figure 6-16**. The standard reversible cell voltage of the regular process (with H_2 cathode) is 1.36 V at 25°C. With the ODC, the value decreases by 1.23 V to a mere 0.13 V. The overall reaction with the ODC is formally identical to the Deacon reaction (cf. above), except that the latter is a gas phase reaction with gaseous HCl and water vapor as product.

A regular Nafion[™] type membrane with sulfonic acid exchange sites is used as polymer electrolyte in the HCl electrolysis cell. The cell temperature is in the range of 70 to 90°C and the current density is between 0.5 and 1.0 A/cm². The conventional process features a cell voltage of ~2.2 V, which yields a specific electricity consumption of 1'700 kWh/t(Cl₂). The overpotential is therefore around 0.8 V. In the ODC process, the cell voltage is typically around 1.4 V, which corresponds to 1'060 kWh/t(Cl₂). In this case, the overpotential is around 1.3 V, which is a result of a higher overpotential of the ORR compared to the HER in the conventional process. It is interesting to note that the ODC process was introduced earlier in industrial HCl electrolysis (2003) than in brine electrolysis (2011).

3 Other processes

There is a wide range of electrochemical processes of technical and industrial relevance, which cannot all be treated here. The variety of electrochemical applications for chemical synthesis, water treatment, surface treatment and forming, etc., was outlined at the beginning of the chapter. In this sub-chapter, selected other electrochemical processes are discussed, which are deemed of particular importance.

3.1 Molten salt electrolytic processes

A number of metals are produced from their respective ores, often oxides, by electrochemical reduction. Many other metals are produced by chemical reduction, such as iron. In the blast furnace iron oxide reacts with coke (carbon) to yield ('pig') iron and carbon dioxide at a temperature of around 1'200°C. The chemical reduction of aluminium oxide, which is thermodynamically more stable than iron oxide, with carbon to yield aluminium metal would require much higher temperatures, which is impractical and uneconomical. Electrolytic aluminium production ('smelting') from aluminium oxide is carried out in a molten salt reactor containing a mixture of Al_2O_3 and Na_3AlF_6 (cryolite) at a temperature of around 950°C (**Figure 6-17**).



Figure 6-17. Schematic of the aluminium smelting process, through which Al^{3+} ions in a fused salt mixture (cryolite) are reduced to metallic, molten aluminium at a temperature of around 950°C. The reaction at the anode is the oxidation of graphite to carbon dioxide. The cell voltage is ~4 V.

This is the *Hall-Héroult process*, introduced in the late 19th century. The half-cell reactions are as follows:

$$\begin{array}{lll} (-) \text{ cathode} & Al^{3+} + 3 e^{-} \rightarrow Al \\ (+) \text{ anode} & C + 2 O^{2-} \rightarrow CO_2 + 4 e^{-} \end{array}$$

$$\begin{array}{lll} (6-22) \\ (6-23) \end{array}$$

The first large-scale aluminium production plant was opened in 1888 by Hall in Pittsburg, Ohio (USA). The cell voltage is around 4 V and the current several hundred kA in one cell. This causes liquid aluminium metal to be deposited at the cathode, while the oxygen ions from the alumina combine with carbon from the anode to produce mostly carbon dioxide. Aluminium smelting is therefore a major source of global CO_2 emissions, even if electricity from renewable sources is used for driving the electrolysis, because the carbon anode obtained from fossil sources is gradually converted to CO_2 in the process. A major overpotential in the cell is associated with the ohmic resistance of the electrolyte. The Joule's heat produced upon passing of current through it helps to maintain the reaction at the temperature close to 1'000°C. A selection of other molten salt electrolytic processes is described in **Table 6-3**.

1	1	(
Metal	Feedstock	Temp. (°C) Voltage			
sodium	NaCl with CaCl ₂ and BaCl ₂	600	7		
potassium	KCl	360-380	4-7		
magnesium	MgCl ₂ , KCl, 1 % CaF ₂	670-730	12		
calcium	CaCl ₂ , CaF	680-800	25-40		
beryllium	5 % BeF ₂ , 2 BeO	600	55		
rare earth metals $(Ce La Nd)$	chlorides, NaCl	800-900	8-15		

Table 6-3. Selected processes for electrochemical production of metals. (Source: P. Novák, Lecture notes)

3.2 Copper refining

Electrorefining is a process to remove impurities from a metal, for example copper. The anode consists of the impure metal to be refined. The impure metallic anode is oxidized and the metal dissolves into solution. The metal ions migrate through the electrolyte towards the cathode where the metal is plated at high purity onto the cathode (**Figure 6-18a**). The mechanism of electrorefining is illustrated in **Figure 6-18b**, based on the polarization curves for stripping and plating of the target metal (here: copper) and selected metals representing different classes of impurities. At the anode, copper is oxidized along with other metals that are easier to oxidize, i.e. metals that have a lower equilibrium potential, such as nickel, zinc and iron. Metals that are not going into solution, such as gold, silver and tellurium, are left behind and accumulate at the bottom of the reactor as 'anode sludge'. At the cathode potential is not too low to avoid redeposition of these metals. Technically, copper refining cells are operated at a cell voltage of 0.1 to 0.2 V and a current density of 100 to 300 mA/cm². Similar electrorefining processes have also been developed for the purification of nickel, cobalt, lead and other metals.





Figure 6-18. (a) Cell schematic of the copper electrorefining process, whereby copper is oxidized from an inpure copper electrode and deposited as high purity copper at the cathode. Metal ions going into solution and slag metals accumulating at the bottom are indicated. (b) Working principle of copper electrorefining. The numbers indicate the standard reversible potential of nickel, copper and silver, respectively.

Appendix A: Edge Supply of Current to Electrode

For the problem depicted in **Figure 6-4**, we develop the equations for the potential φ of the electrode, the current density i(x) in the electrode, and the reaction current density $i_n(x)$ for the case of linear kinetics with a constant charge transfer resistance R_{CT} . For linear kinetics, the interrelation of overpotential η and current density i_n is: $\eta(x) = \varphi(x) - \varphi_{eq} = i_n(x) \cdot R_{ct}$, where φ_{eq} is the potential of the electrode at $i_n = 0$. For convenience we set $\varphi_{eq} = 0$, because we are primarily interested in the change of φ along *x*. Inserting this kinetic expression into Eq. 6-4 we obtain:

$$\frac{d^2\varphi(x)}{dx^2} = \frac{\varphi(x)}{\sigma\delta R_{\rm CT}}$$
(6-A1)

We define $\alpha^2 = 1/\sigma \delta R_{CT}$. The solutions of the resulting ODE $\varphi''(x) = \alpha^2 \cdot \varphi(x)$ are exponential functions and combinations thereof, for example the hyperbolic functions. We choose an *ansatz* $\varphi(x) = A \cdot \cosh(\alpha(L-x))$ which already satisfies the boundary condition of $\varphi'(x=L) = 0$ (Eq. 6-5). With the boundary condition $\varphi'(x=0) = -I_0/\sigma w \delta$ we obtain

$$\varphi(x) = \frac{I_0}{w} \sqrt{\frac{R_{\rm ct}}{\sigma \delta} \frac{\cosh(\alpha(L-x))}{\sinh(\alpha L)}}$$
(6-A2)

Ohm's law yields the current density in the electrode:

$$i(x) = -\sigma \frac{d\varphi(x)}{dx} = \frac{I_0}{\delta w} \cdot \frac{\sinh(\alpha(L-x))}{\sinh(\alpha L)}$$
(6-A3)

We see that indeed i(x=L) = 0. The current density associated with the reaction rate $i_n(x)$ is obtained from Eq. 6-3 as

$$i_{\rm n}(x) = -\delta \frac{di(x)}{dx} = \frac{I_0 \alpha}{w} \cdot \frac{\cosh(\alpha(L-x))}{\sinh(\alpha L)}$$
(6-A4)

As we can expect intuitively, the reaction current density $i_n(x)$ decreases along x, because the driving force for the reaction fades, owing to the potential drop in the electrode caused by the finite conductivity of the electrode material.

Appendix B: Current Distribution and Edge Effects

Here we will deal with effects in the corner of a Hull-like cell and show that, depending on the angle the electrode forms with the wall of the electrolyte containing vessel, the theoretical current in the corner can be zero, finite, or infinite. We consider the following geometric situation:



Figure 6-B1. Geometry of the corner of an electrochemical cell bound by an electrode (with constant potential $\varphi =: 0$) and a wall (boundary condition: $\partial \varphi / \partial \theta = 0$) forming an angle α . Polar coordinates (*r*, θ) are used in the calculation.

We introduce polar coordinates r and θ . The electrode is located at $\theta = 0$ and has a constant potential of $\varphi = 0$. The wall extends from the left edge of the electrode (r = 0) at an angle α . Current cannot flow past the wall, hence we have the boundary condition $d\varphi/d\theta = 0$ here. In the electrolyte the potential φ obeys the Laplace equation¹

$$\nabla^2 \varphi(x, y) = \varphi_{xx} + \varphi_{yy} = 0 \tag{6-B1}$$

which we rewrite in polar coordinates:

$$\nabla^2 \varphi(r,\theta) = \varphi_{rr} + \frac{1}{r} \varphi_r + \frac{1}{r^2} \varphi_{\theta\theta} = 0$$
(6-B2)

To solve the Laplace equation, we make the following *ansatz* for $\varphi(r,\theta)$ (separation of variables):

$$\Delta \varphi(r,\theta) = R(r) \cdot \Theta(\theta) \tag{6-B3}$$

Inserting into the Laplace equation yields:

¹
$$\varphi_{xx} = \frac{\partial^2 \varphi}{\partial x^2}$$
, etc.

$$-\frac{\Theta''}{\Theta} = \frac{R'' + R'/r}{R/r^2} = k \tag{6-B4}$$

where k is a constant, and to simplify later expressions we define $k =: n^2$. We can first solve the equation with Θ :

$$\Theta'' + n^2 \Theta = 0 \tag{6-B5}$$

We choose the *ansatz*

$$\Theta(\theta) = A_n \cdot \cos(n\theta) + B_n \cdot \sin(n\theta)$$
(6-B6)

The boundary condition (b.c.) at $\theta = 0$ of $\varphi = 0$ yields $A_n = 0$. With the b.c. $d\varphi/d\theta = 0$ at $\theta = \alpha$ we obtain $n \cdot \alpha = \frac{1}{2\pi} (+m \cdot \pi)$ with m = 0, 1, 2, ... We limit ourselves to m = 0 without loss of generality, as results will be qualitatively analogous to the other periodic solutions with $m \ge 1$. We therefore have $n = \pi/(2\alpha)$ and

$$\Theta(\theta) = B_n \cdot \sin(\frac{\pi}{2\alpha}\theta) \tag{6-B7}$$

The factors B_n are left unspecified, they would be determined by the boundary conditions further away, which are not explicitly defined here.

Next, we tackle the radial function R(r). We rewrite Eq. 6-B4 as

$$R'' + \frac{R'}{r} - \frac{n^2}{r^2}R = 0 \tag{6-B8}$$

We choose the ansatz

$$R(r) = C_n \cdot r^n + D_n \cdot r^{-n} \tag{6-B9}$$

The function should not diverge for $r \to 0$, hence $D_n = 0$. We therefore obtain the expression for the potential φ , remembering $n \cdot \alpha = \frac{1}{2}\pi$:

$$\varphi(r,\theta) = B_n \cdot \sin(\frac{\pi}{2\alpha}\theta) \cdot C_n \cdot r^{\frac{\pi}{2\alpha}} = E_n \cdot \sin(a\theta) \cdot r^a$$
(6-B10)

where we have defined $E_n = B_n \cdot C_n$ and introduced $a = \pi/(2\alpha)$.

Caluclation of current density

The current density anywhere in the electrolyte is given by (Ohm's law)

$$i(r,\theta) = -\sigma \nabla \varphi(r,\theta) \tag{6-B11}$$

The gradient operator in polar coordinates is

$$\nabla f(r,\theta) = \left(\frac{\partial f}{\partial r}\right) \cdot \underline{e}_r + \frac{1}{r} \left(\frac{\partial f}{\partial \theta}\right) \cdot \underline{e}_{\theta}$$
(6-B12)

For our function $\varphi(r, \theta)$ we have

$$\frac{\partial \varphi(r,\theta)}{\partial r} = E_n \cdot \sin(a\theta) \cdot a \cdot r^{a-1}$$
(6-B13)

$$\frac{\partial \varphi(r,\theta)}{\partial \theta} = E_n \cdot a \cdot \cos(a\theta) \cdot r^a \tag{6-B14}$$

The current density at the surface of the metal electrode ($\theta = 0$) is then

$$i_{\rm m}(r) = i(r,0) = -\sigma \cdot E_n(\underbrace{\sin(0)}_{=0} \cdot a \cdot r^{a-1} \cdot \underline{e}_r + a \cdot \cos(0) \cdot r^{a-1} \cdot \underline{e}_{\theta}) = -\sigma \cdot E_n \cdot a \cdot r^{a-1} \cdot \underline{e}_{\theta} \quad (6-\text{B15})$$

As expected, the current is perpendicular to the surface of the electrode. Now, we study the behaviour of the current density when we approach the corner at r = 0. Remembering that $a = \pi/(2\alpha)$ we can distinguish 3 cases:

i) The wall forms a **right angle** with the electrode, $\alpha = \frac{1}{2}\pi$:

$$i_{\rm m}(r) \propto r^{a-1} = r^{\frac{\pi}{2\alpha}^{-1}} = r^{\frac{\pi}{2\alpha}^{-1}} = r^0 = {\rm const.}$$
 (6-B16)

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ii) The wall forms an **acute angle** with the electrode, $\alpha < \frac{1}{2}\pi$:

$$1 < \frac{\pi}{2\alpha} \to a > 1 \to x := n - 1 > 0 \to i_{\mathrm{m}}(r) \propto r^{x > 0} \to \lim_{r \to 0} (i_{\mathrm{m}}(r)) = 0$$
(6-B17)

iii) The wall forms an **obtuse angle** with the electrode, $\alpha > \frac{1}{2}\pi$:

$$1 > \frac{\pi}{2\alpha} \to a < 1 \to x = a - 1 < 0 \to i_{\rm m}(r) \propto r^{x < 0} = \frac{1}{r^{|x|}} \to \lim_{r \to 0} (i_{\rm m}(r)) = \infty$$
(6-B18)

Hence, we have shown that, theoretically, the current density becomes infinite at the edge of the electrode for an angle α larger than 90°, even if it is only slightly more than 90° ! Obviously, in reality the current density in such a point would be limited by other processes, such as activation or concentration overpotential. Furthermore, we find that the current goes to zero in any corner with angle α smaller than 90°.
Appendix C: Potential and Current Distribution in 3D Electrode

For simplicity we describe the relationship between overpotential η and reaction current density *j* using linear kinetics: $\eta = j \cdot R_{ct}$. The local reaction rate in the porous electrode (unit: A/cm³) is then $i_v = a \cdot j$. The activation overpotential is $\eta = \Delta \varphi - \Delta \varphi_{eq}$, where $\Delta \varphi = \varphi_m - \varphi_s$ and $\Delta \varphi_{eq}$ is the Galvani potential difference between electrode and electrolyte at equilibrium (we recall from Chapter III that this quantity is actually experimentally inaccessible). In the general case, both phase potentials φ_m and φ_s change as a function of position *x*. Therefore, we write for the volumetric current density

$$i_{\rm v} = a \cdot j = \frac{a}{R_{\rm ct}} (\varphi_{\rm m} - \varphi_{\rm s} - \Delta \varphi_{\rm eq})$$
(6-C1)

Inserting into Eq. 6-11 yields coupled ODEs for φ_m and φ_s . Solutions of 2nd order ODEs of the form $\varphi''(x) = \alpha^2 \cdot \varphi(x)$ are exponential or hyperbolic functions. We use the *ansatz* $i_v(x) = A \cdot \cosh(vx) + B \cdot \cosh(v(L-x))$. The values of the constants *A* and *B* are obtained by integration of the expression and taking into consideration the boundary conditions (Eqs. 6-12 and 6-13). The algebra is rather tedious, the reader is referred to Fuller & Harb, Electrochemical Engineering, Wiley, 2018, Chapter 5, for details. Here, we limit ourselves to providing the solution for $i_v(x)$, from which the current densities i_m and i_s and phase potentials φ_m and φ_s in the electrode and electrolyte, respectively, can be obtained through integration with appropriate boundary conditions.

$$i_{v}(x) = i_{a}\alpha \cdot \frac{\cosh(\alpha x) - \beta \cosh(\alpha (L - x))}{(1 + \beta)\sinh(\alpha L)}$$
(6-C2)

where the parameters α and β are defined as follows:

$$\alpha^{2} = \frac{aL}{R_{\rm ct}} \left(\frac{1}{\sigma_{\rm m}} + \frac{1}{\sigma_{\rm s}}\right) \qquad \beta = \frac{\sigma_{\rm s}}{\sigma_{\rm m}} \tag{6-C3}$$

Chapter VII

Energy Conversion & Storage

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Electrochemical energy conversion and storage technologies have been receiving increasing attention in the context of the *Energiewende* (Energy Transition). For decarbonization, there is considerable interest in 'electrifying', using renewable power, the transport sector, heating sector, and industrial processes that today have a large carbon footprint. Battery electric vehicles, for example, are showing a steep increase in market share, and the need for utility-scale storage batteries to balance the electricity grid with an increasing share of renewables is growing. Fuel cells have seen notable deployment in residential, industrial combined heat and power (CHP) and backup applications. Together with the use of hydrogen as an energy vector, fuel cells can furthermore play an important role in light and, in particular, heavy duty vehicles for freight transport, marine shipping and short-range air transport. We should not forget, though, that electrochemical energy conversion and storage technologies have been around for more than a century. The lead-acid battery, for example, invented in 1859 by *Planté*, is testimony of a remarkable success story. It is the oldest example of a rechargeable battery. Introduced into automobiles in the 1910s for starting, lighting and ignition (SLI), it is still the technology used to start internal combustion engine cars today. The fuel cell, originally invented in 1839 by Schönbein and Grove, took longer to mature: it has been an essential device in manned space missions since the 1960s.

The focus of this chapter is on electrochemical devices for energy applications with the purpose to store energy (batteries), or convert the chemical energy stored in energy carriers, such as hydrogen, into electricity (fuel cells) (**Figure 7-1**). The electrochemical splitting (electrolysis) of water to produce hydrogen and the electroreduction of carbon dioxide to intermediates relevant for the chemical industry (e.g., carbon monoxide) and value-added products are electrochemical conversion technologies receiving growing interest in power-to-X scenarios, yet these topics are beyond the scope of this course and will not be treated here. The main interest of electrochemistry in energy conversion and storage applications is the 'energy' aspect, unlike in industrial electrochemistry (Chapter VI), where the primary interest is the produced goods (e.g., chlorine), provided service or duty (e.g., water treatment, electropolishing).



Figure 7-1. Schematic of the architecture of (a) a battery (storage device) and (b) a fuel cell (conversion device).

7-2

1 Batteries

The birth of electrochemistry is generally associated with the first demonstration of a device producing electricity (voltage and current) in continuous manner by *Volta* in 1799. His voltaic pile is essentially a battery consisting of a number of Zn-Cu cells (or other metal pairs) arranged in series configuration. In fact, 'battery' refers to a number of connected electrochemical cells. The term was coined by *Franklin* in 1749 to describe a set of connected Leyden jars, which gave a stronger discharge than a single capacitor, in analogy to an artillery battery, where all the cannons are striking at the same time. Today, 'battery' is also used to describe a single galvanic cell.

Table 7-1. Overview of common primary and secondary battery chemistries. Representation: - electrolyte +.	
(adapted from: D. Linden, T.B. Reddy (eds.): Handbook of Batteries, 4th ed., McGraw-Hill, New York (USA), 20	011)

Primary batteries (non-rechargeable)	Secondary batteries (rechargeable)
Zn-carbon Leclanché: Zn NH ₄ Cl MnO ₂	Lead-acid: Pb H ₂ SO ₄ PbO ₂
Zn-carbon Zn chloride: Zn ZnCl ₂ MnO ₂	Valve-regulated lead-acid (VRLA):
Alkaline MnO ₂ : Zn KOH MnO ₂	Pb immobilized H_2SO_4 PbO ₂
Magnesium: Mg Mg(ClO ₄) ₂ -Li ₂ CrO ₄ MnO ₂	Ni-Cd: Cd KOH Ni oxide
Zinc-silver oxide: Zn KOH or NaOH Ag ₂ O	Ni-MH: metal hydride KOH Ni oxide
Mercury-zinc: Zn KOH or NaOH HgO	Li-ion: LiC ₆ aprotic organic Li _{1-x} CoO ₂
Mercad: Cd KOH or NaOH HgO	LiC ₆ aprot. org. Li _{1-x} Ni _{1/3} Co _{1/3} Mn _{1/3} O ₂
Zinc-air: Zn KOH O ₂	LiC ₆ aprot. org. Li _{1-x} Ni _{0.8} Al _{0.15} Co _{0.05} O ₂
Li-ion: Li LiAlCl ₄ -SOCl ₂ SOCl ₂	LiC ₆ aprotic organic FePO ₄
Li aprotic organic SO ₂	Edison (NiFe): Fe KOH-LiOH Ni oxide
Li aprotic organic MnO ₂	RAM*: Zn gelled KOH MnO ₂
Li aprotic organic FeS ₂	Sodium-sulfur: Na β"-alumina or NASICONs S
Li aprotic organic (CF) _n	Na-nickel chloride (ZEBRA):
Li LiI I ₂ •poly(2-vinylpyridine)	Na β "-alumina + NiAlCl ₄ NiCl ₂

* rechargeable alkaline manganese

The history of the battery therefore goes back to the 19th century. Landmarks of battery development are the Daniell cell (cf. Introduction), invented in 1836, the first practical source of electricity. It provided an operating voltage of around 1.1 V and was widely used, especially in connection with the growing telegraph network. The lead-acid battery has already been mentioned. Further battery chemistries of importance will be discussed below. First and foremost, we have to make the distinction between single-use (primary) batteries and rechargeable (secondary) batteries. **Table 7-1** lists the most important representatives of those two categories. Primary batteries are discharged once and cannot be recharged, because the electrochemical reactions occurring during the discharge cannot be reversed or only to a very limited extent. They come in a wide variety of different shapes and sizes for a very diverse range of applications, from calculators, remote controls, toys, etc., to medical implants. The chemistry of secondary batteries is designed for the cell to be repeatedly discharged and charged, although a loss in capacity is observed over many cycles. Their use has become ubiquitous today: in mobile phones, portable computers, power tools and electric vehicles, to name just a few key applications.

A battery for a given use case is chosen such that its stored energy can be converted to electrical energy with adequate current and voltage attributes for a period of time that is suitable for the application at hand. For example, batteries for laptops should power the computer for ~5h, ideally of course longer, but space is limited. On the other hand, a battery for a heart pacemaker should last for 5 to 10 years, because replacing it requires a surgical procedure.

The most important parameters of a battery are its nominal voltage U_0 (unit: V), which is given by the battery chemistry, and the stored charge Q (unit: Ah), determined by the amount of *active mass* it contains (basically, the battery's size), which according to Faraday's laws (cf. Chapter I) corresponds to a certain nominal charge. These quantities are often printed on the battery casing, e.g., 3.7 V and 4'200 mAh. The nominal stored electrical energy is given by

$$W = U_0 \cdot Q \tag{7-1}$$

In our example, this would be 15.5 Wh. This means that nominally a device requiring 15 W could be operated for ~1 h until the battery is completely discharged, or one requiring 5 W for around 3 h, and so forth. The delivered energy under practical conditions is obtained by measuring the battery's electrical output during a discharge experiment, which is typically performed at a constant current *I*, starting from the fully charged state. **Figure 7-2a** shows a schematic discharge curve of a lithiumion cell with a nominal voltage of $U_0 = 3.7$ V. We see that the actual cell voltage is around 4.2 V



Figure 7-2. (a) Schematic discharge curve of a lithium-ion cell at constant current *I*, also referred to as 'rate' in battery terminology. The end of discharge at t_d is marked by a steep drop in cell voltage *U*. The delivered charge is Q_d , and the delivered electrical energy *W* is given by the area under the curve (green painted area). (b) Representation of a single battery cell providing electrical energy and a series and parallel connection of cells, respectively.

7-4

initially, then it continuously decreases as the discharge reaction proceeds, until the voltage drops steeply after time t_d , which marks the end of discharge. Since we have a constant current *I*, we can plot the time *t* on the horizontal axis as well as the delivered charge *Q*, which are connected by $Q = I \cdot t$. The energy delivered by the battery is obtained as the area under the curve, mathematically:

$$W = \int U(t) \, dQ = \int U(t) \, I(t) \, dt = (I = const.) = I \int U(t) \, dt \tag{7-2}$$

In the general case (during practical battery operation), the current also varies as a function of time, I = I(t). With the average cell voltage during discharge, \overline{U} , we can obtain the electrical energy delivered upon discharge as $W = \overline{U} \cdot Q_d = \overline{U} \cdot I \cdot t_d$, where Q_d is the discharge capacity. We will see below in Section 1.2 that the delivered charge and energy of a battery will strongly decrease at high discharge rates (=current) due to overpotentials and limited extraction of capacity. The delivered power at any point during the discharge process is given by $P = U \cdot I$.

The theoretical limit for charge and energy stored by a battery is given by its chemistry and the amount of active mass it contains. The active masses of the negative and positive electrode determine the maximum amount of charge that can be stored and extracted. The theoretical specific energy w (unit: Wh/kg) and specific charge q (unit: Ah/kg) are calculated as follows:

$$w = U_0 \cdot q = U_0 \cdot \frac{zF}{\Sigma M_k} \tag{7-3}$$

where U_0 is the nominal cell voltage and ΣM_k is the sum of the molar masses of the active materials. The commonly used unit of the specific charge is Ah/kg and that of the specific energy Wh/kg. The practical specific energy and charge, however, are much lower, because the battery obviously contains not only the active masses, but also binder, conductive carbon, separator, electrolyte, current collector, and a casing.

Example:

The Zn-Ag₂O chemistry is often used in primary button cells (cf. **Table 7-1**). The cell reaction is Zn + Ag₂O \rightarrow ZnO + 2 Ag (z = 2). The nominal cell voltage is $U_0 = 1.55$ V. The active masses are Zn (negative electrode) and Ag₂O (positive electrode) with respective molar masses of M(Zn) = 65.4 g/mol and $M(Ag_2O) = 231.7$ g/mol. We calculate the specific charge as $q = zF / (M(Zn) + M(Ag_2O)) = 180$ Ah/kg. For the specific energy we therefore obtain $w = U_0 \cdot q = 280$ Wh/kg. The practical specific energy of a Zn-Ag₂O button cell is 130 Wh/kg. In the theoretical value, we have only accounted for the active materials, the cell evidently comprises additional components making up the battery.

Many batteries used in the household come as single cells. Most technical applications, however, require a higher voltage and / or capacity than one cell can deliver. Therefore, cells are often combined in a series or parallel configuration (**Figure 7-2b**). In the series configuration, the overall voltages of the single cells add up to the total voltage of the battery. In the well-known 9 V single-use battery, for example, 6 cells with an individual voltage of 1.5 V are arranged in series. Large batteries, for example for electric vehicle traction, often contain thousands of individual cells, which are arranged on different topological levels to produce the overall battery system:

- Cell: basic, sealed electrochemical functional unit.
- **Module**: an assembly of cells, connected in parallel or in series or a combination thereof, placed in a frame to protect the cells from external shocks, heat or vibration.
- **Pack**: battery system consisting of a number of modules plus control, protection, and cooling system, including a battery management system (BMS).

Example:

The battery of the 2018 Nissan LEAF contains 192 pouch type Li-ion cells¹. A battery module consists of 8 cells, with 2 parallel strings of 4 cells in series. The battery pack contains 24 modules $(24 \times 8 = 192 \text{ cells})$ with a rated voltage of 350 V, a nominal energy storage capacity of 40 kWh, and a total weight of 303 kg.

1.1 Primary batteries

Single-use batteries have to be primarily inexpensive, convenient, lightweight, and have a good shelf life. Obviously, as for batteries in general, they should have high energy density and be safe to use. Ideally, in addition their chemistry should be non-toxic. Many primary batteries are of the 'dry cell' type, i.e. their electrolyte is not a liquid but a paste or similar. Generally primary batteries have a higher capacity and initial voltage than rechargeable batteries. We will study exemplarily a selected number of battery types in the following. The limited scope of this text does not allow us to discuss the wide variety of primary battery chemistries (**Table 7-1**) in detail.

The batteries using Zn and MnO_2 as active materials on the negative and positive electrode, respectively, are the oldest type of battery that is still very commonly used today, because it is of very low cost. The cell using an ammonium chloride paste electrolyte (hence 'dry cell') was invented by *Leclanché* in 1866. The overall reaction occurring during discharge is:

$$Zn + 2 MnO_2 + 2 NH_4Cl \rightarrow 2 MnOOH + [Zn(NH_3)_2]Cl_2$$
(7-4)

¹ https://www.marklines.com/en/report all/rep1786 201811, accessed 20-Oct-2022

It has a nominal voltage of 1.5 V, and its specific energy is 65 Wh/kg. In the reaction on the positive electrode, hydroxide ions are formed: $MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^-$. The hydroxide ion reacts with the NH_4^+ of the mildly acidic electrolyte to produce water and ammonia, and the latter precipitates with zinc and chloride ions to $[Zn(NH_3)_2]Cl_2$. In the well-known cylindrical cell, a carbon rod in the center serves as current collector on the positive, manganese side. It is connected with the steel top cover, which forms the positive terminal of the battery. The Zn cup is connected with the bottom cover, the negative terminal. A coarse paper serves as a separator between the Zn can and the paste consisting of a mix of MnO_2 , carbon powder (to provide electronic conductivity) and the NH₄Cl electrolyte. In a version of the battery for extra heavy-duty applications, the electrolyte is zinc chloride mixed with a small amount of ammonium chloride.

The most common primary battery used today uses an alkaline electrolyte based on KOH, which has a good conductivity, resulting in a low internal (=ohmic) resistance of the cell. The first modern alkaline cell was developed in the 1960s. The cell reaction is:

$$Zn + 2 MnO_2 + 2 H_2O \rightarrow 2 MnOOH + Zn(OH)_2$$
(7-5)

The zinc is not used as a can here, like in the Leclanché cell, but as compacted powder electrode (for higher surface area) in the center of the cylindrical case. This allows high discharge rates and continuous discharge, also at low temperatures. Its nominal voltage is also 1.5 V, its specific energy 95 Wh/kg.

Also the next two cell types to be discussed are based on zinc as the negative active mass. They are typically used as button cells for applications such as watches, calculators, hearing aids and other such applications that require small batteries and long service life. The discharge reaction of the Zn/Ag_2O cell is:

$$Zn + Ag_2O + H_2O \rightarrow Zn(OH)_2 + 2 Ag$$
(7-6)

It has a nominal cell voltage of 1.5 V and a specific energy of 130 Wh/kg. The Zn/air battery does not need positive active material stored in the cell, it uses oxygen from the air as oxidant:

$$Zn + \frac{1}{2}O_2 + H_2O \rightarrow Zn(OH)_2$$
(7-7)

It has therefore a higher specific energy of 290 Wh/kg. The nominal cell voltage is 1.4 V. As the access of O_2 / air is required, it is an open cell design.

Lithium based primary batteries have gained importance starting in the 1980s. There are a number of cell chemistries (**Table 7-1**). Their typical cell voltage is around 3 V, and they have high specific energy of >200 Wh/kg and a long shelf-life.

A major disadvantage of primary batteries is the large amount of waste that has to be recycled. Batteries disposed into landfill sites have severe environmental impact. From an energy point of view, the life cycle energy efficiency of primary batteries is in the low percent range, which means that it takes around 100 times more energy to produce the battery than it can deliver.¹

1.2 Rechargeable (secondary) batteries

The chemistry of rechargeable batteries is chosen such that discharge and charge reactions can be repeatedly carried out for hundreds or thousands of cycles. This means that the redox reactions of the active electrode materials have to be highly reversible² in order to maintain the battery's capacity from cycle to cycle and avoid side reactions that lead to capacity fading. The life cycle energy efficiency of secondary batteries is much higher than that of primary batteries, as over its lifetime a rechargeable battery can store and deliver more energy than is used for its production.

Туре	Cell voltage	Practical specific energy	Charge- discharge efficiency	Self-discharge	Cycle life
	(V)	(Wh/kg)	(%)	(%/day)	(10 ³ cycles)
Pb-acid	2.0	30 - 50	70 - 80	0.1 - 0.3	0.5 - 1.0
NiCd	1.2	50 - 75	60 - 70	0.2 - 0.6	2.0 - 2.5
NiMH	1.2	60 - 120	70 - 90	1	1.0
NaS	2.0	150 - 240	75 - 90	0	2.5
NaNiCl ₂	2.5	100 - 120	85 - 90	0	2.5+
Li-ion	$2.4-3.8^{\rm a}$	75 - 200	85 - 98	0.1 - 0.3	$1.0 - 10^{a}$

 Table 7-2.
 Most widely used rechargeable battery types. (adapted from: Annu. Rev. Chem. Biomol. Eng. 2, 2011, 503 and the Battery University: https://batteryuniversity.com/article/bu-107-comparison-table-of-secondary-batteries)

^a depending on cell chemistry

The desired properties of rechargeable batteries are, in addition to the general requirements (high energy and power density, low toxicity, safe operation, etc.), a long cycle life with minimal capacity fading, high charge-discharge efficiency, and low self-discharge. With the strong increase in battery production capacity in the last decade (2010-2020), additional important aspects have become increasingly important, such as the reduction of the use of critical³ elements (such as cobalt in lithium-ion batteries) and the recyclability of the used materials.

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¹ https://www.doitpoms.ac.uk/tlplib/batteries/primary.php

² We should use the term 'invertible' here, because in the context of electrochemistry 'reversible' is used to describe an electrochemical reaction that occurs very easily in forward and backward direction, i.e. with fast kinetics (cf. Chapter VIII).

³ critical in terms of scarcity, environmental impact or human health during mining

Key properties of the most important secondary battery types are listed in **Table 7-2**. The lead-acid and lithium-ion battery will be discussed in more detail below. The nickel-cadmium battery has been the main rechargeable battery in the late 20^{th} century, used widely in grid-independent applications (portable power tools, photography equipment, flashlights, hobby RC, etc.) as well as grid-scale energy storage. A disadvantage of NiCd batteries is the toxicity of cadmium as well its adverse 'memory effect'. NiCd batteries were largely supplanted by nickel-metal-hydride batteries, owing to their higher specific energy, in consumer applications, although their cycle life is not as good. Before the advent of lithium-ion batteries, NiMH batteries were the main type of battery used in mobile phone, laptop and (hybrid) electric car applications. The sodium-sulfur and sodiumnickel-chloride battery are high-temperature batteries that operate at a temperature of around 350°C. They employ a solid Na⁺ containing ceramic electrolyte (β'' -Al₂O₃, cf. Chapter IV). They have been used in grid-scale storage and, to some extent, in heavy-duty electric vehicle applications. A key advantage for these uses is their low self-discharge rate and long cycle life. They are, however, in increasing competition with lithium-ion batteries.



Figure 7-3. Charge-discharge curves of a lithium-ion cell with a nominal capacity of ~3 Ah at different rates. The voltage during charge is limited at 4.2 V, afterwards charging continues at constant voltage with decreasing current ('taper charge'). (adapted from: J Electrochem Sci Technol 9(4), 2018, 330)

The operational characteristics of secondary batteries are described by their charge-discharge curves, which depend not only on the cell chemistry, but also on cell and battery engineering, and notably the rate (=current) of charge/discharge and the temperature. **Figure 7-3** shows different charge-discharge curves of a lithium-ion cell as a function of current, expressed as *C-rate*. The C-rate characterizes the current at which a battery is charged or discharged relative to its nominal capacity. The rate of 1C corresponds to a current that (dis)charges the battery in 1 hour. For example, for a battery with a capacity of 3 Ah, this equates to a current of 3 A. A rate of 5C for this battery

would be 15 A, and the battery would be nominally (dis)charged in 12 min. It is important to realize though that at high C-rates, the available capacity decreases significantly below the nominal capacity, owing to polarization effects. Together with the increasing effect of ohmic losses, this leads to a strong drop in the energy that can be extracted from the battery. The charging behavior is affected analogously. However, if the upper voltage limit is reached (4.2 V in the example of **Figure 7-3**), the battery management system usually switches to a constant voltage charging mode, thus the battery is further charged with decreasing current ('taper charge') to a certain target state-of-charge. The ability to handle high-rate charging currents is especially important for battery electric vehicles. Using fast-charging stations, charging a significant fraction of the battery capacity is desired in much less than an hour. The battery cell, module and pack have to be engineered to make this possible. For example, waste-heat has to be managed and the safety of the battery system and vehicle ensured.

1.2.1 The lead-acid battery

The lead-acid battery is a true success story of electrochemistry. Its use in a wide variety of applications is explained by its low price, high reliability, and good performance. Its cycle life is a few hundred charge–discharge cycles, and for some cell types even more than thousand cycles. It has been used commercially already in the late 19th century. In the early 20th century it became an integral part of automobiles: it enabled engine starting with an electric motor, whereas before it had to be hand-cranked. In addition, it is used to drive the ignition system of the engine, and provide electricity for lights and other functions of the car when the engine is not running. The battery is charged by the engine during operation using a generator.

The chemistry of the lead-acid battery is based on the use of lead as negative electrode material (oxidation number: 0) and lead-oxide, PbO₂, as positive electrode material (oxidation number: IV). Aqueous sulfuric acid with a concentration of about 30% is used as electrolyte. The half-cell reactions and overall reaction are as follows:

	charged		discharged	$E^{\circ}, U_{rev}^{\circ}(V)$
negative electrode	$Pb + SO_4^{2-}$	ţţ	$PbSO_4 + 2 e^-$	-0.356
positive electrode	$PbO_2 + SO_4^{2-} + 4 H^+ + 2 e^-$	ţ	$PbSO_4 + 2 H_2O$	+1.685
overall	$Pb + PbO_2 + 2 SO_4^{2-} + 4 H^+$	ţţ	$2 PbSO_4 + 2 H_2O$	2.041

We see that the product of the reaction is lead sulfate, PbSO₄, on both electrodes. The sulfate is provided by the sulfuric acid electrolyte. Acid is consumed on the positive electrode during the discharge reaction, and formed again during charge. Therefore, the concentration of sulfuric acid,

measured for example by probing the density of the solution, can be used to characterize the state of charge of the battery. The nominal voltage of a lead-acid cell is 2 V.

A common lead-acid battery, as used in a car, and its components is displayed in **Figure 7-4**. It consists of 6 cell blocks arranged in series configuration, hence the battery has a nominal voltage of 12 V. Each component cell (block) is composed of several negative and positive electrode plates. The plates, connected in parallel, are packed together in a comb-like structure and immersed in the electrolyte. Cellulose, porous PVC or polyethylene is usually used as separator sheets between each positive and negative plate. The complete battery consists of a series of cell blocks, sitting in separate electrolyte compartments.



Figure 7-4. Exploded view of the components of a 12 V starting, lighting and ignition (SLI) battery for a car, consisting of 6 cell compartments connected in series configuration. (Source: Varta)

Considering the reversible potential of the two half-cell reactions, from a thermodynamic point of view one may expect water splitting (H₂O \rightarrow H₂ + $\frac{1}{2}$ O₂) to occur as a side reaction, since hydrogen evolution is expected to take place at potentials below 0 V and oxygen evolution at potentials above 1.23 V at 25°C. These values apply to standard conditions, and with an activity of water below 1 in the sulfuric acid electrolyte¹ the stability window of water increases somewhat (Le Chatelier's principle). The main reason for negligible water splitting, however, is that the hydrogen and oxygen evolution reactions are strongly kinetically limited on the used electrode materials, i.e. these half-cell reactions have a very low exchange current density. However, as a result of the high voltage during charging of 2.4 V or more, water splitting *can* actually take place at measurable rates, and

¹ water activity $a_w \approx 0.74$ at 25°C for a sulfuric acid concentration of 30% (Drying Technology, 2021, DOI: 10.1080/07373937.2020.1869037).

gaseous hydrogen and oxygen are readily formed, leading to the consumption of electrolyte and a potentially explosive conditions. Batteries are made safer by incorporating a catalyst, which allows the gases to recombine within the cell to water.

1.2.2 The lithium-ion battery

Research into the lithium-ion battery technology started in the 1970. It was introduced into the market by Sony in 1992. In 2019, the Nobel Prize in chemistry was awarded to three researchers 'for the development of lithium-ion batteries'¹. It became the most important battery technology in consumer electronics within a decade. Furthermore, in the context of the boom of electric vehicle technology, the production capacity of lithium-ion cells has been massively increased over the past decade. Owing to the concomitant tremendous drop in production cost, Li-ion batteries are of increasing interest for stationary energy storage. Especially in view of the transition of power generation from coal and nuclear power to wind and solar power, the requirement of stationary energy storage capacity is expected to increase enormously in the next decade(s).



Figure 7-5. Operating principle of a Li-ion cell. Lithium is reversibly intercalated into the lattice structure of the graphite at the negative electrode and the oxide on the positive electrode. The electrolyte is a non-aqueous (organic) solvent (e.g., a mixture of ethylene carbonate and dimethyl carbonate) with dissolved lithium-salt (e.g., LiPF₆). Copper and aluminium are used as current collector materials.

Lithium metal has a density of 0.54 g/cm³ and a low standard potential of $E^{\circ}(\text{Li}^{+}/\text{Li}) = -3.05 \text{ V}$. This makes it an attractive negative electrode material. However, it is difficult to us metallic lithium in a rechargeable battery, because of dendrite formation during Li plating in the charging process, which leads to shorting of the cell after a few cycles. Therefore, Li-ion batteries use graphite as negative electrode material, as it serves as a host to take up lithium by inserting – 'intercalating' –

¹ https://www.nobelprize.org/prizes/chemistry/2019/press-release/

it between its graphene layers. Thus, stripping and plating of bulk lithium does not take place, which makes the battery much safer to use. The low electrode potential of lithium also means that we cannot use an aqueous electrolyte, hydrogen evolution would readily take place. In fact, organic solvents, such as cyclic carbonates, containing a dissolved lithium salt, e.g. LiPF₆, are used in Liion cells (cf. Chapter IV). Also the active material on the positive electrode is an insertion compound. Mostly, oxides with a layered structure are used, which can accommodate the lithiumions in the lattice structure. The operating principle of a Li-ion battery is illustrated in **Figure 7-5**. Lithium-ions are moving towards the negative electrode during the charging reaction, where they are intercalated into the graphite. On the positive electrode, they are de-inserted from the oxide. The opposite processes take place during the discharge reaction: Li-ions move from the graphite through the electrolyte to the oxide. Due to this back-and-forth movement of Li^+ during charge and discharge, the Li-ion battery is also referred to as a 'rocking chair' battery.

The archetypical oxide material that was used in the first generation of Li-ion batteries is LiCoO₂. The half-cell and overall cell reactions can be written as follows:

	charged		discharged
negative electrode	LiC ₆	ţţ	$C_6 + Li^+ + e^-$
positive electrode	$2 \text{Li}_{0.5}\text{CoO}_2 + \text{Li}^+ + \text{e}^-$	ţ	2 LiCoO ₂
overall	$\text{LiC}_6 + 2 \text{Li}_{0.5}\text{CoO}_2$	ţţ	$2 \operatorname{LiCoO}_2 + \operatorname{C}_6$

The graphite can be lithiated up to a maximum stoichiometry of LiC_6 . At the same time, lithium is de-inserted from the oxide in the charging reaction. However, only about half of the lithium can be removed from $LiCoO_2$, the oxide structure otherwise becomes unstable, as Li is an integral part of the lattice. The oxidation number of cobalt is a mixture of +III and +IV as a function of the state of charge. The nominal cell voltage of this lithium-ion cell is 3.7 V.

Example:

We calculate the theoretical specific charge and energy of a graphite / LiCoO₂ cell. From the overall reaction above we obtain $q = zF / \Sigma M = 1 \cdot 26.8$ Ah/mol / $(M(C_6) + 2 \cdot M(\text{LiCoO}_2)) = 100$ Ah/kg. For the specific energy we get $w = q \cdot U_0 = 370$ Wh/kg. Practical specific energy is ~150 Wh/kg on the pack level.

The lithium-ion cell chemistry and engineering has greatly improved over the last three decades. A number of different oxide materials have for example been established, with the aim of increasing the specific charge, the potential vs. Li^+/Li , the cyclability and rate capability. Furthermore, the content of cobalt has been sought to be reduced, as it is a scarce material and often mined under questionable conditions. For example, today lithium nickel cobalt aluminium oxide (NCA), such as $LiNi_{0.8}CO_{0.15}Al_{0.05}O_2$, is widely used in Li-ion cells.

2 Fuel Cells

In 1838 *Schönbein*, professor for physics and chemistry at the University of Basel, wondered whether the chemical energy of hydrogen and oxygen could be converted directly into electricity (and water) in a suitable galvanic cell. In an experimental setup, he immersed two platinum wires into an electrolyte and could measure an electric potential difference if hydrogen was bubbled over one and oxygen over the other wire. Shortly thereafter *Grove*, a Welsh lawyer and scientist, used the setup to produce electrical energy. He called this type of cell 'gas voltaic battery'. Only at the end of the 19th century was the concept revisited for a practical application, namely the direct conversion of coal and oxygen to electricity. *Mond* and *Langer* introduced the term *fuel cell* (in German 'Brennstoffzelle'). However, realizing practical performance and stable cells proved to be challenging. Only in the 1930s it was realized that the most promising approach for a practical fuel cell is the use of hydrogen as fuel and an alkaline electrolyte. Bacon built the first practical H_2/O_2 fuel cell with power output in the kW range. This alkaline fuel cell technology was later introduced into aerospace applications in NASA's Apollo program.

Around the same time, development of other fuel cell technologies gained momentum. The different types of fuel cell are named after the material used as their electrolyte, a distinctive feature that defines its operating temperature range. **Figure 7-6** shows the ionic conductivity of a range of



Figure 7-6. Ionic conductivity as a function of temperature for selected classes of materials considered for the application in fuel cells. The temperature range of operation for fuel cells with liquid electrolyte (grey boxes) and solid electrolytes (yellow boxes) is indicated (cf. **Table 7-3**). A minimum conductivity for fuel cell application of 0.01 S/cm is typically considered. (Source: DOI 10.3929/ethz-b-000190017, based on figures by K.-D. Kreuer and T. Norby).

materials used in or considered for the use in different fuel cell types as a function of temperature. The names and key features of the different fuel cell types are given in **Table 7-3**. The cells using a liquid electrolyte are the molten carbonate fuel cell (MCFC), the phosphoric acid fuel cell (PAFC), and the already mentioned alkaline fuel cell (AFC). In their respective cell constructions, a porous material, made of a suitable material that is stable in the corresponding electrolyte and prevailing temperature range, is infused with the liquid electrolyte and serves as a separator. A general issue of an alkaline environment, in contrast to an acidic one, is the carbonation of the electrolyte in the presence of CO_2 , which precludes or at least aggravates the use of air as oxidant.

Туре	Operating temperature (°C)	Fuel	Ionic charge carrier
Solid oxide fuel cell (SOFC)	750 - 1'000	H_2 , CO, CH_4	O ^{2–}
*Molten carbonate fuel cell (MCFC)	630 - 700	H ₂ , CO	CO3 ²⁻
*Phosphoric acid fuel cell (PAFC)	180 - 210	H ₂ (1% CO)	H^{+}
* [‡] Alkaline fuel cell (AFC)	60 - 220	H ₂	OH⁻
Polymer electrolyte fuel cell (PEFC)	60 - 90	H ₂ (~ppm CO)	H^{+}
High-temperature (HT-) PEFC	160 - 200	H_2 (1% CO)	
Direct methanol fuel cell (DMFC)	60 - 120	CH ₃ OH	H^{+}

Table 7-3. Overview of common and commercialized fuel cell technologies

* with liquid electrolyte

[‡] not CO₂ tolerant, requires pure O₂ or purified air

The ion conducting solids indicated in **Figure 7-6** are mechanically sufficiently robust to be used as a self-standing electrolyte. Polymeric ion conductors, such as NafionTM (cf. Chapter IV), have sufficiently high conductivity at low temperature to be used at room temperature or even below. The polymer electrolyte fuel cell (PEFC) will be discussed in detail in Section 2.1. A high temperature (HT-) version operates in the temperature range of 160 to 200°C and uses a polybenzimidazole (PBI) membrane doped with phosphoric acid as polymer electrolyte. At temperatures above 500°C, ceramic ion conductors are used as electrolyte, for example oxygen-ion conductors, such as yttria stabilized zirconia (YSZ) (cf. Chapter IV), in the solid oxide fuel cell (SOFC) (cf. Section 2.2). Low temperature (LT-)SOFCs are developed with a view to reducing cell material costs and temperature-activated aging phenomena. This is the temperature range where proton conducting ceramics have promising conductivities. There is a gap between around 200 and 400°C where there are no technically mature ion conducting materials. Some materials classes, such as solid acids or pyrophosphates, have been considered but they have not reached technical readiness.

Fuel cells are often discussed in conjunction with hydrogen as fuel, since it is a carbon-free energy carrier that can be produced from renewable sources. In addition, the electrochemical oxidation of hydrogen is a very fast reaction using an adequate *electrocatalyst* (cf. Chapter V), which is

important in particular at low temperatures where the thermal activation barrier for (electro)chemical reactions is high. The high temperature fuel cells (SOFC, MCFC) can use methane (natural gas) as a fuel. At sufficiently high temperatures of \gtrsim 700°C, it can be directly used in the cell, where it breaks down to H₂ and CO (and CO₂), which is then electrooxidized. At lower temperature, methane or other carbonaceous fuels have to be *reformed*, i.e., catalytically broken down, into a mixture of H₂, CO and CO₂, which is then fed to the fuel cell. Also low temperature fuel cells can be operated on *reformate*, yet the poisoning of the anode catalyst by CO becomes increasingly pronounced as the temperature decreases. The PAFC can tolerate CO in the percent level, yet CO content needs to be decreased to the ppm level for the PEFC. In the direct methanol fuel cell (DMFC), a variant of the PEFC, methanol is electrooxidized directly at the anode.

Fuel cell use cases are categorized into stationary, mobile and portable applications. All fuel cell types (except the DMFC) have been used or are used in stationary power generation, where often also the waste heat is used, for example for space heating (combined heat and power, CHP, application). In particular the high-temperature fuel cells generate high-grade heat for secondary processes in industry. For mobile applications, such as in forklifts or passenger cars, the PEFC is mostly the technology of choice. A PEFC can be started-up in straightforward manner from room temperature¹ and operated intermittently and with variable load profile. Rapid start-up is also of interest in backup power systems. Portable applications allow clean on-site power generation, for example for camping.

2.1 The polymer electrolyte fuel cell (PEFC)

The basic electrochemical element of the PEFC is the membrane electrode assembly (MEA), consisting of an ion conducting membrane sandwiched between two gas diffusion electrodes (**Figure 7-7a**). The membrane is a proton exchange membrane (PEM), mostly of the perfluoralkylsulfonic acid (PFSA) ionomer type, such as NafionTM (cf. Chapter IV).² The primary function of the membrane is that of an electrolyte and separator to prevent the passage of reactant gases and electrons. Its thickness is in the range of 10 to 50 µm (**Figure 7-7b**). The electrochemical reactions take place in the catalyst layer, which is about 10 µm thick and composed of a mixture of the noble metal catalyst and ionomer. On the anode, the hydrogen oxidation reaction (HOR) is taking place: $H_2 \rightarrow 2 H^+ + 2 e^-$. The protons are transported across the membrane to the cathode,

¹ and, with proper operating strategy, also from temperatures below 0°C.

² Interest in fuel cells using an anion exchange membrane (AEM) as polymer electrolyte for OHconduction have gained considerable interest starting ~2010. The alkaline cell conditions allow the use of non-noble metal catalyst, such as silver and nickel based materials. In this case, however, the HOR is associated with considerable overpotential. A main challenge is the limited stability of the AEM against chemical degradation initiated by nucleophilic attack by hydroxide.

where the oxygen reduction reaction (ORR) is taking place: $O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$. The water produced on the cathode side helps to keep the membrane hydrated, which is required to maximize proton conductivity of the ionomer (cf. Chapter IV). The catalyst layer on both sides is in contact with a gas diffusion layer (GDL), porous carbon fiber based components with a thickness of about 200 µm. Their function is to i) conduct electrons to and from the catalyst layer, ii) conduct waste heat away from the reaction zone, iii) allow the access of reactants, H₂ and O₂, to the catalyst layer, and iv) transport the water produced on the cathode side out of the MEA. To prevent the blocking of the pores of the GDL with water ('flooding'), the carbon fibers are wet-proofed with polytetrafluoroethylene (PTFE) (e.g., TeflonTM). Carbon fibers are stable against corrosion in the acidic environment of the cell, unlike many metal fibers.



Figure 7-7. (a) Membrane electrode assembly (MEA) of a PEFC. The electrodes consist of a carbon fiber based gas diffusion layer (GDL) and a catalyst layer containing the noble metal based electrocatalyst. The proton exchange membrane (PEM) serves as the polymer electrolyte. Hydrogen is oxidized at the anode, oxygen is reduced at the cathode, where water is produced. (b) Electron microscope cross-sectional image of a catalyst coated membrane (CCM). The dissimilar thickness of the anode and cathode catalyst layers reflects the different catalyst loadings (Source: J. Electrochem. Soc. 157, 2010, B425). (c) Transmission electron microscope image of the electrocatalyst used on both anode and cathode, consisting of a high-surface area carbon support onto which Pt (or Pt-alloy) nanoparticles are deposited (Source: E-TEK).

The catalyst consists of Pt or Pt-alloy nanoparticles supported on carbon black particles with a high surface area (**Figure 7-7c**). In this way, a high *dispersion* of the catalyst is obtained, i.e. a high catalyst surface area per volume of the particle. Since the electrochemical reaction takes place at the surface of the Pt, small particles maximize the catalyst utilization and therefore minimize the requirement of Pt mass. The dispersion of the Pt catalyst is characterized by the *specific surface area s*_{Pt}, which describes the Pt surface area per mass (unit: m^2/g). The specific surface area is often referred to as *electrochemically active surface area* (ECSA). Owing to the fact that the HOR has a much higher exchange current density compared to the ORR in an acidic electrolyte (cf. Chapter V),

the loading *L* of catalyst is typically lower on the anode, e.g. $0.05 \text{ mg}_{Pt}/\text{cm}^2$, than on the cathode, e.g. $0.3 \text{ mg}_{Pt}/\text{cm}^2$. Therefore the anode catalyst layer is thinner than the cathode catalyst layer (**Figure 7-7b**). The catalyst surface area per geometric area of the electrode is the roughness factor *r* (cf. Chapters I and V), which can be obtained as follows (unit: cm²_{Pt}/cm²):

$$r = s_{\rm Pt} \cdot L \tag{7-8}$$

For a Pt particle to be electrochemically active, it is required that it is electronically connected to other Pt/C particles and, eventually, the GDL, and in contact with the continuous electrolyte phase. Eq. 7-8 therefore assumes an electrochemical utilization of the catalyst of 100% (meaning: all Pt particles are electrochemically active).

Example:

We estimate the specific surface area of Pt nanoparticles with a diameter of 2 nm, assuming spherical particles. The surface area is $S = 4\pi r^2$, the volume $V = 4\pi/3 r^3$. With the density of platinum, $\rho_{\text{Pt}} = 21.45 \text{ g/cm}^3$, we obtain $s_{\text{Pt}} = S / (V\rho) = 3/(r\rho) = 140 \text{ m}^2/\text{g}$.

2.1.1 Cell components & stacks

A single fuel cell provides a voltage of 0.6-0.9 V during operation, hence for technical applications tens or hundreds of cells are commonly combined in a bipolar configuration (cf. Chapter VI) to obtain a fuel cell *stack*. A single MEA is sandwiched between flow field plates, which contain channels to distribute the reactant gases over the electrode and through which the product water is removed (**Figure 7-8a**). A *bipolar plate* is a graphite or metal component that separates two neighboring cells from each other and comprises flow channels for fuel on one side and flow channels for air on the other side. Often, bipolar plates are made of two half-plates glued or welded



Figure 7-8. (a) Exploded view of the components of the repeating unit of a polymer electrolyte fuel cell. (b) Fuel cell stack with cells connected in series. Bipolar plates separate the anode compartment of one cell from the cathode compartment of the neighboring cell. H₂, O₂ (air) and cooling fluid are supplied to the cells in parallel configuration via manifolds. (Source: PSI)

together, with a coolant flow path between them to allow the removal of waste heat during operation. Repeating units, consisting of MEA, bipolar plate and sealing components, are added one after the other, electrically connected in series, to build the fuel cell stack (**Figure 7-8b**). Current collector and end plates are located on either end of the stack, and the whole arrangement is held together and compressed using tie rods, sometimes steel ribbons. Reactants and coolant are supplied via media ports in endplates and then distributed along the stack in manifolds to the individual cells. After flowing through the cells, media are collected again in outlet manifolds and removed from the stack¹.

2.1.2 Overpotentials & electrocatalysis

The electrochemical reactions of the PEFC using a PEM are taking place under acidic conditions. These conditions are challenging from a corrosion point of view and only noble metal catalysts display the necessary stability and activity for the half-cell reactions. **Figure 7-9a** shows polarization curves for the hydrogen and oxygen half-cell reaction, respectively, both in anodic and cathodic direction. The polarization curve of the HOR / HER (hydrogen evolution reaction) is very steep and quasi-linear owing to the high exchange current density (cf. Chapter V). The Pt electrode in acid is a quasi-ideal non-polarizable electrode. The overpotential for the HOR η_{HOR} is therefore very small.



Figure 7-9. (a) Sketched polarization curves for H₂ (HOR = hydrogen oxidation reaction, HER = hydrogen evolution reaction) and O₂ (ORR = oxygen reduction reaction, OER = oxygen evolution reaction) reactions in acidic electrolyte. In the fuel cell, using Pt based electrocatalyst, the anode overpotential, η_{HOR} , is much lower compared to the cathode overpotential, η_{ORR} . The cell voltage U_{cell} (iR-free) is indicated. (b) Typical polarization curve of a polymer electrolyte fuel cell (PEFC) with indicated loss contribution caused by different overpotentials. The measured open circuit voltage (OCV) U_0 is typically around 1 V, whereas the reversible cell voltage U_{rev} is 1.18 V at 80°C under standard conditions. The difference is caused by a mixed potential on the cathode side (cf. text).

¹ The hydrogen is often recirculated to minimize fuel loss.

By contrast, the overpotential of the ORR η_{ORR} is typically in the range of a few hundred millivolts at practical current densities, owing to the much lower exchange current density.¹ The same applies to the OER (oxygen evolution reaction). The HOR and the ORR are taking place at the same geometric current density *i* in the PEFC, and the resulting cell voltage U_{cell} is lower than the reversible cell voltage U_{rev} . For the reverse reaction, the electrolysis of water, the HER is combined with the OER, and the resulting cell voltage is larger in magnitude than U_{rev}^2 .

A polarization curve of a single PEFC is plotted in **Figure 7-9b**, broken down to the different overpotentials. In addition to the anode and cathode activation losses η_{HOR} and η_{ORR} , the cell experiences ohmic losses η_{Ω} and concentration overpotential η_{conc} . The ohmic overpotential is dominated by the ionic resistance of the membrane. The resistance of the different electronically conducting components (GDL, bipolar plate, etc.) is much lower, yet the contact resistance between GDL and the flow field plate causes some degree of ohmic loss (around 25 m $\Omega \cdot \text{cm}^2$). The concentration overpotential is a result of mass transport limitations of O₂ to the catalyst layer on the cathode side in case of the use or air as oxidant. Mass transport losses on the anode side can be neglected if pure H₂ is used as fuel, but may need to be considered in case of the use of reformate fuel, where the H₂ content of the gas may be only 50% or less.



Figure 7-10. Mechanism of the oxygen reduction reaction (ORR) on Pt in acidic medium. The standard potentials E° at 25°C are indicated. (adapted from: Tarasevich, Sadkowski, Yeager, Oxygen Electrochemistry, in: Comprehensive Treatise of Electrochemistry, Springer, 1983, p354)

The measured *open circuit voltage* (OCV) U_0 of a PEFC, i.e. the cell voltage in the absence of current (i = 0), is ~1 V at atmospheric reactant gas pressures. This is significantly lower than the reversible voltage U_{rev} of the cell, which is 1.18 V at 80°C and standard pressure. This is the result of the formation of a *mixed potential* on the fuel cell cathode, for which several side reactions have

¹ The ORR overpotential is negative, as indicated in **Figure 7-9a**, because it is a cathodic reaction, yet we will use it as a positive number for convenience in this Chapter.

² Recall that, to be thermodynamically consistent, U_{rev} of an electrolytic reaction is negative (cf. Chapter II). Again, the use of the positive value is for convenience.

been put forward as an explanation. First of all, the 4-electron reduction reaction of oxygen to water¹ is but one ORR mechanism. An alternative ORR mechanism proceeds via a 2-electron reduction reaction to hydrogen peroxide, H₂O₂, followed by another 2-electron reduction step to water (Figure 7-10). The H_2O_2 is a relatively stable intermediate and can desorb from the catalyst surface. Also, it can disproportionate to O_2 and H_2O . The prevalent ORR mechanism strongly depends on solution properties, e.g. pH, the type of electrocatalyst used, and the electrode potential. The ORR on Pt happens to proceed mainly according to the 4-electron mechanism. Nevertheless, small amounts of H_2O_2 are formed. Since the 2-electron reaction steps via H_2O_2 as intermediate have a different reversible potential compared to the 4-electron step, the various reactions taking place simultaneously yield a mixed electrode potential that is lower than the reversible potential of the 4electron reaction. Furthermore, Pt undergoes surface and near-surface oxidation reactions in the potential range where the PEFC cathode operates (0.7-0.95 V). As a result, various oxidized Pt species form, such as Pt(OH)₂, PtO and PtO₂. The involved electrochemical reactions contribute to the mixed cathode potential. Moreover, owing to the very low exchange current density of the ORR of $i_0 = 10^{-9}$ A/cm² at 25°C (cf. Table 7-2, Chapter V), the oxygen electrode is sensitive to oxidizable impurities, such as trace organic compounds supplied with the air to the cathode. This then yields a mixed potential formed between the cathodic reduction of O_2 and an anodic reaction of the impurities. Last but not least, hydrogen diffusing through the membrane from the anode to the cathode leads to a lowering of the cathode potential. This effect is more pronounced for thinner membranes, which show a higher hydrogen permeability. The latter two mechanisms are explained in more detail in Appendix A.

Whereas the ORR is a complex reaction involving several intermediates, reaction pathways and side reactions, the HOR in acid is a fairly simple mechanism involving only one type of intermediate, namely adsorbed hydrogen atoms, H_{ads} . The HOR mechanism consists of a hydrogen adsorption and charge transfer sequence. Following reaction steps have been identified:

Tafel:	H_2	与	2 H _{ad}	(T)
Volmer:	H_{ad}	₽	$H^+ + e^-$	(V)
Heyrovsky:	H_2	₽	$H_{ad} + H^+ + e^-$	(H)

We generally distinguish between two HOR mechanisms, the *Tafel-Volmer* (TV) and the *Tafel-Heyrovski* (TH) mechanism. The *Tafel* reaction is the dissociative adsorption of H_2 to yield H_{ads} , which can also be written as Pt-H. The *Volmer* reaction is the oxidation reaction of H_{ads} , yielding

¹ Evidently, the reaction does not involve the transfer of 4 electrons at the same time, even the simultaneous transfer of two electrons is very unlikely. The reduction reaction proceeds via several intermediates, such as (OOH)_{ads} and (OH)_{ads}.

the final product H⁺ (and e⁻). The *Heyrovski* reaction is a mixed adsorption and charge transfer step. The predominant reaction mechanism depends on the type of electrocatalyst. On platinum, the TV mechanism is prevalent.

As mentioned above in connection with **Table 7-3**, Pt is easily poisoned by carbon monoxide at the operating temperature of the PEFC. Even ppm levels of CO lead to a high coverage θ_{CO} of CO on the Pt surface of close to 100%. The layer of adsorbed CO blocks the access of H₂ to the catalyst surface, the effective exchange current density of the HOR is therefore reduced by a factor of $(1-\theta_{CO})^x$. $1-\theta_{CO}$ is the fraction of the catalyst surface not covered by CO and hence available for hydrogen adsorption. Since 2 adjacent catalyst sites are required for the Tafel reaction, the exponent *x* equals 2 for the TV mechanism and 1 for the TH mechanism. In addition, owing to the limited availability of Pt surface sites, the hydrogen adsorption step can become rate limiting. In case of the TV mechanism, the limiting current density of the HOR is given by the rate of the dissociative adsorption of H₂, the Tafel reaction.



Figure 7-11. Volcano curves for (a) the hydrogen evolution reaction (HER) (Source: J Electroanal Chem 39, 1972, 163), and (b) the oxygen reduction reaction (ORR) (Source: Nature Chem 1, 2009, 552). The x-axes show the binding strength of intermediates on the catalyst surface, the y-axes the electrocatalytic activity, characterized for example by the exchange current density.

In general, a good electrocatalyst, in analogy to a gas phase catalyst, provides a reaction pathway for a given reaction with a low activation energy ΔG^{\ddagger} (cf. Chapter V). The bond strength of the intermediate with the catalyst is an important descriptor of electrocatalyst activity. We consider the hydrogen reaction, HOR or HER, to start with. It is found that the highest electrocatalytic activity, characterized for example by the exchange current density j_0 , is obtained at an intermediate Pt-H bond strength (**Figure 7-11a**). The electrocatalytic properties of various metals M form a so-called 'volcano' curve, where the 'best' electrocatalysts, such as Pt, are found near the top. The M-H bond is here of intermediate strength, which yields a maximum in activity. If the M-H strength is too low, there is a small driving force for the formation of the intermediate. In case of a high M-H bond strength, the intermediate is too stable and further reaction to H^+ and e^- is disfavored. This is known as the *Sabatier principle*, which states that the interaction between catalyst and the intermediate should be 'just right', i.e., not too high and not too low. From the volcano curve of the HER/HOR in acid we notice that, if a catalyst could be found that has a slightly lower M-H bond strength than Pt-H, its activity would be expected to be higher than that of Pt.

The same principle can be applied to the ORR (**Figure 7-11b**). Here we find that Pt is not the best electrocatalyst, as the oxygen adsorption energy is somewhat weak. A number of Pt-alloys, such as PtNi and PtCo, show improved catalytic activity towards the ORR compared to Pt. It has to be pointed out, though, that also stability properties have to be considered. Most alloying components of Pt, such as Ni or Co, tend to be leached out over time under the acidic conditions of the cell. Nevertheless, Pt-alloy catalyst are typically used today as ORR electrocatalyst in the PEFC.



Figure 7-12. Left: illustration of the cathode catalyst layer of the PEFC, which forms a three-phase region, and the adjoining microporous layer (MPL) and proton exchange membrane (PEM). The porous composite structure consists of catalyst particles (carbon supported noble metal nanoparticles) and H⁺ conducting ionomer, which also acts as a binder. For the reaction to proceed continuously on the catalyst it has be accessible to reactant via pores in the structure and be connected to the continuous ionomer as well as the electronically conducting phase. Right: illustration of the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) proceeding via adsorbed hydrogen atoms and oxygen intermediates. The gases need to diffuse through a thin ionomer layer to get to the catalyst.

As the half-cell reactions of the PEFC indicate, gas (H_2 , O_2), electrons and protons are involved in the electrode processes. Therefore, the active catalyst site must be accessible by electrons, protons, and gas, and the formed water on the cathode side must be removed. The catalyst layer is a cocontinuous three-phase region, composed of carbon supported catalyst, ionomer, and open porosity. The network of catalyst particles provides electronic conductivity, the ionomer proton conductivity, and gas access and the removal of water is allowed by the porous structure (**Figure 7-12**). Only when those 3 phases are present a continuous electrochemical reaction is possible. Essentially, the structure of the anode catalyst layer is similar. In fact, as confirmed by transmission electron microscopy (TEM) images, the catalyst particles are covered by a thin ionomer layer of nanometer thickness, through which the reactants and product have to diffuse to / from the catalyst surface. The optimization of the catalyst layer structure and morphology is essential to maximize catalyst utilization, minimize ohmic losses in the electronic and ionic phase and mass transport limitations with a view to maximize fuel cell performance by minimizing overpotentials. A hydrophobic microporous layer (MPL), consisting of carbon black and PTFE as binder, is deposited between the GDL (cf. **Figure 7-7a**) and the catalyst layer for improved electrical and thermal contact. The MPL also helps to improve the water management by preventing water pooling at the catalyst layer / GDL interface.

2.1.3 Performance analysis & metrics, overpotential breakdown

Understanding of performance limitations of a PEFC operating on H₂ and air requires us to analyze and quantify the magnitude of the different overpotentials as a function of current density. In general terms, we can describe the cell voltage U in the polarization curve as the reversible cell voltage U_{rev} minus the loss term ΔU_{loss} , the sum of all overpotentials (cf. Chapter V):

$$U = U_{\text{rev}}(T, p) - \Delta U_{\text{loss}} = U_{\text{rev}}(T, p) - (\eta_{\text{ORR}} + \eta_{\text{HOR}} + iR + \eta_{\text{conc}})$$
(7-9)

where we recall that all the overpotentials are taken as positive values. If pure H₂ is used as fuel, the concentration overpotential η_{conc} is governed by the mass transport limitation of oxygen in air on the cathode side. Therefore, if we use pure O₂ as oxidant, we can largely ignore mass transport limitations and assume $\eta_{\text{conc}} \approx 0$. The ohmic resistance R_{Ω} can be determined by measuring the AC impedance of the cell at high frequency. The ohmic drop $\eta_{\Omega} = iR$ can thus be calculated. If we furthermore neglect η_{HOR} , then the only overpotential left is η_{ORR} . We can calculate the so-called *iR*-free cell voltage $U_{\text{iR-free}}$ by correcting the cell voltage U by the ohmic loss *iR*:

$$U_{iR-\text{free}} = U + iR \approx U_{\text{rev}}(T, p) - \eta_{\text{ORR}}$$
(7-10)

The equation shows that the choice of operating conditions (H₂/O₂), correction for *iR*-losses and assumption of negligible η_{HOR} allows us to quantify η_{ORR} . For the description of the ORR overpotential we assume a Tafel relationship according to $\eta_{ORR} = b \cdot \log(i/i_0)$, where *b* is the Tafel slope (unit: V per decade of current density, V/decade) and i_0 the exchange current density with respect to the geometric surface area of the cell. A plot of the *iR*-free cell voltage $U_{iR-free}$ vs. the base-10 logarithm of the current density should now yield a straight line. This is indeed the case, as shown

in **Figure 7-13a** for MEAs with different cathode catalyst loading. The relation of i_0 to the catalyst specific exchange current density j_0 (unit: A/cm²(Pt)) is given by the roughness factor r according to $i_0 = r \cdot j_0$., where j_0 is a function of temperature and the partial pressure of the reactant, oxygen. We recall from Chapter V that the partial pressure dependence of the exchange current density is described by the reaction order γ . Therefore, the relation of the ORR overpotential η_{ORR} to the catalyst unique parameters is given by:

$$\eta_{\text{ORR}} = b \log(\frac{i}{i_0(p,T)}) = b \log(\frac{i}{rj_0(p,T)}) = b \log(\frac{i}{s_{\text{Pt}}L_c j_0^*(T)(\frac{p_{\text{O}_2}}{p_0})^{\gamma}})$$
(7-11)

where $j_0^*(T)$ is the catalyst specific exchange current density at the standard pressure p_0 at a given temperature *T*. We have expressed the roughness factor as a function of the specific catalyst surface area s_{Pt} and the cathode catalyst loading L_c (Eq. 7-8). This suggests that for MEAs with different L_c , the polarization curves should have a constant voltage offset, which is indeed what is observed in the experiment (**Figure 7-13a**).



Figure 7-13. (a) PEFC polarization curves with 3 different cathode catalyst loadings: *iR*-free cell voltage U + iR vs. geometric current density *i* (Tafel representation), using H₂ and O₂ as reactants. Anode loading: 0.40 mgp_t/cm². Cell temperature: 80°C. Anode and cathode pressure: 2.7 bar_a. (b) Replotted curves with the current density *i* converted to the Pt mass specific current density *j*_m through dividing by the cathode Pt loading *L*_c. The secondary x-axis shows the catalyst specific current density, assuming a specific Pt surface area of *s*_{Pt} = 50 m²/g. (Source: J Power Sources 127, 2004, 162).

Therefore, if we normalize the current density *i* to the catalyst loading L_c , we obtain the catalyst *mass specific current density* $j_m = i / L_c$ (unit: A/mg(Pt)) on the horizontal axis. Alternatively, we can calculate the *catalyst specific current density j* according to j = i / r. For the case of constant

catalyst utilization, i.e. if the effective ECSA does not change as a function of current density, the polarization curves for different cathode catalyst loadings L_c will collapse onto one 'master curve' (**Figure 7-13b**), which describes the unique properties of the used ORR catalyst in terms of the Tafel slope *b* and the exchange current density j_0 . The latter can be obtained by extrapolation of the Tafel line to $U = U_{rev}$, which, however, is commonly associated with considerable uncertainty, because we have to extrapolate over several orders of magnitude of the current density.

2.2 The solid oxide fuel cell (SOFC)

The SOFC is based on the use of crystalline ceramic materials for electrolyte and electrodes. The electrolyte is an oxygen ion conducting solid, such as yttria stabilized zirconia (YSZ). The doping of $Zr(IV)O_2$ with Y(III)₂O₃ leads to the formation of vacancies in the oxygen sublattice (cf. Chapter IV). These vacancies can move within the lattice in a thermally activated process (diffusion, migration, cf. Chapter V), which corresponds to the movement of oxygen ions in the opposite direction. The electrodes are porous to allow the access of fuel and oxidant to the reactive sites. At the high operating temperature of the SOFC hydrogen as well as carbon monoxide can undergo direct electrochemical oxidation. The electrode reactions in the SOFC are:

anada (avidation)	$H_2 + \{O^{2-}\}$	\rightarrow	$H_2O + 2 e^-$	(1a)
anode (oxidation)	$CO + {O^{2-}}$	\rightarrow	CO ₂ + 2 e ⁻	(1b)
cathode (reduction)	O ₂ + 4 e ⁻	\rightarrow	$2 \{O^{2-}\}$	(2)
overall	$H_2,CO + \frac{1}{2}O_2$	↑	H ₂ O,CO ₂	$(1) + \frac{1}{2}(2)$

where $\{O^{2-}\}\$ is an oxygen ion in the lattice of the ceramic. Oxygen is incorporated as O^{2-} into the oxygen sublattice on the cathode side, moves to the anode and reacts there with the fuel to produce steam or carbon dioxide (**Figure 7-14a**).



Figure 7-14. (a) Operating principle of a solid oxide fuel cell (SOFC) operated on a mixture of H_2 and CO. Oxygen ions, O^{2-} are transported through the oxide electrolyte, the reaction products (steam, carbon dioxide) are formed on the anode side. (b) Representation of the components of a single cell. YSZ = yttria stabilized zirconia, Ni-cermet = mixture of nickel particles and YSZ, LSM = lanthanum strontium manganite (Source: J Power Sources 326, 2016, 331).

The anode is a ceramic-metal ('cermet') composite of nickel catalyst and YSZ (**Figure 7-14b**). The nickel provides the electronic conductivity, the YSZ the ionic conductivity. Together with the open porosity, the electrode layer therefore provides the reaction zone for the anodic reaction. The cathode material is usually an electronically conducting perovskite, such as lanthanum strontium manganite, LSM, with the formula $La_{1-x}Sr_xO_3$. Unfortunately, LSM is a poor oxygen ion conductor, hence the electrochemical activity is limited to the *triple-phase boundary* (TPB) where the electrolyte, air and electrode meet (**Figure 7-15a**, mechanism I). The TPB is line-shaped, essentially limiting the electrochemical reaction to a very small region. Alternative cathode materials with mixed ionic-electronic conductivity provide improved performance, because in this case the reaction zone can be extended to the entire surface area of the electrode (**Figure 7-15a**, mechanism II). An example of such a material is lanthanum strontium cobalt ferrite, LSCF, with the general formula $La_xSr_1-xCo_yFe_1-yO_{3-\delta}$.



Figure 7-15. (a) Reaction mechanism of the ORR at the cathode of an SOFC: I Adsorbed oxygen diffuses on the surface of the electrode to the interface with the electrolyte, the triple-phase boundary (TPB), where it reacts to oxygen ions, O^{2-} , which are incorporated into the lattice. II Charge transfer reaction at the electrode surface, in case the electrode material is also an oxygen-ion conductor. (b) Polarization curves of an SOFC at different temperatures with 15 µm thick Ce_{0.8}Sm_{0.2}O_{1.9} electrolyte, using H₂ with ~3 % H₂O and air at ambient pressure at reactants. (adapted from: J. Mater. Chem. A 5, 2017, 12873)

Besides YSZ, gadolinia doped ceria (CGO) is used as electrolyte in SOFCs. Owing to its higher ionic conductivity compared to YSZ (**Figure 7-6**), it allows a lower operating temperature of <700°C in intermediate-temperature (IT-) SOFCs. The partial reduction of Ce(IV) to Ce(III) at low oxygen partial pressures, however, leads to n-type electronic conductivity of the material (cf. Chapter IV). This can cause direct passage of electrons from anode to cathode via the electrolyte and, thus, some degree of internal shorting of the cell. Proton conducting SOFCs, which are under development, offer the prospect of even lower operating temperatures below 600°C in low temperature (LT-) SOFCs.

The equivalent of a bipolar plate in the SOFC is the *interconnect*. As it is exposed to both the oxidizing and reducing side of the cell, it must be extremely stable. Furthermore, the material needs to have a suitable thermal expansion coefficient to be thermally compatible with the other cell components to minimize mechanical damage upon thermal cycling. For this reason, ceramic materials, such as acceptor-doped lanthanum chromite, have been used for reasons of thermal and chemical stability. Operating temperatures below 800°C enable the use of nickel and steel-based interconnects, which allows for a considerable reduction of cost.

The polarization behavior of an SOFC is notably different from that of a PEFC (**Figure 7-15b**). The *Ui*-curve of an SOFC shows no feature at low current density related to activation overpotential, owing to the high operating temperature. Instead, a pronounced linear region is observed, whose slope is strongly temperature dependent. This indicates that the polarization behavior is dominated by ohmic effects, governed mainly by the ionic conductivity of the electrolyte. Furthermore, we see that the OCV changes with temperature, which is related to the temperature dependence of U_{rev} according to $\partial U_{rev}/\partial T = \Delta_r S / zF$ (cf. Chapter II). Since $\Delta_r S < 0$ for a fuel cell with H₂ fuel (also with CO), the OCV decreases with temperature. On the anode side, we have a chemical equilibrium between H₂, O₂ and H₂O(g) with, consequently, a very low oxygen partial pressure of $p(O_2) = 10^{-18}$ bar or lower. We can therefore express U_{rev} or the OCV¹ of an SOFC also in terms of the oxygen partial pressures on the fuel and air electrode:

$$U_{\rm rev} = \frac{RT}{4F} \ln(\frac{p(O_{2,\rm cathode})}{p(O_{2,\rm anode})})$$
(7-12)

This phenomenon is exploited in a lambda probe, an oxygen sensor based on a solid oxide cell, which allows the determination of the oxygen partial pressure, for example in the exhaust of an internal combustion engine, with oxygen in air as the reference (cf. also Chapter VIII).

2.3 Conversion efficiency

The *efficiency* ε of conversion of chemical energy contained within the fuel and the oxidant into electrical energy as the desired output is an important characteristic of a fuel cell. The invested input is the heating value of the fuel, characterized by the enthalpy² $\Delta_r H$ of the fuel cell reaction. The

¹ The oxygen electrode in an SOFC is as 'well-behaved' as the hydrogen electrode in the PEFC, in that its potential is very well defined by the oxygen partial pressure with very little influence of side reactions, unlike the oxygen electrode in the PEFC.

² Fuel cell efficiencies are defined based on the reaction enthalpy $\Delta_r H$ rather than the Gibbs energy $\Delta_r G$. This convention is largely historical to be able to compare the conversion efficiency to the one of thermal engines, where the heat released by the combustion reaction is decisive.

maximum electrical energy that can be obtained in a fuel cell under reversible conditions is given by $-z \cdot F \cdot U_{rev} = \Delta_r G = \Delta_r H - T \cdot \Delta_r S$ (cf. Chapter II). The theoretical efficiency ε_{th} of a fuel cell (or any other galvanic cell) is therefore

$$\varepsilon_{\rm th} = \frac{\Delta_{\rm r}G}{\Delta_{\rm r}H} = 1 - T \frac{\Delta_{\rm r}S}{\Delta_{\rm r}H}$$
(7-13)

Depending on the sign¹ of $\Delta_r S$, ε_{th} can be smaller than 100% (common case), equal or even larger than 100%. For the latter case, the cell absorbs reversible heat from the environment (cf. also Chapter II, Section 1.3).

Example:

For the reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O(1)$ at 25°C we have $\Delta_r H^\circ = -285.8 \text{ kJ/mol}$ and $\Delta_r S^\circ = -163.4 \text{ kJ/(mol}\cdot\text{K})$. Therefore we have $\varepsilon_{th} = 83.0$ %. For the product being water vapor we have $\Delta_r H^\circ = -241.8 \text{ kJ/mol}$ and $\Delta_r S^\circ = -44.5 \text{ kJ/(mol}\cdot\text{K})$ and thus $\varepsilon_{th} = 94.5$ % at 25°C. We see that the efficiency depends on the state of aggregation of the product water.

For comparison, in a thermal engine, e.g. an internal combustion engine, the maximum conversion efficiency from chemical energy to mechanical energy (work) is given by the Carnot efficiency $\eta_{\text{Carnot}} = 1 - T_{\text{cold}}/T_{\text{hot}}$, where T_{cold} and T_{hot} are the temperatures of the cold sink and hot source, respectively.

Under practical fuel cell conditions when the cell is under load, the electrical work supplied per formula unit of reactants consumed is $W_e = -z \cdot F \cdot U$, where U is the cell voltage at the chosen operating point on the polarization curve (**Figure 7-9b**)². The value is lower than the theoretical maximum, because the cell voltage U is lower than the reversible voltage U_{rev} . The practical efficiency of the fuel cell is therefore

$$\varepsilon = -\frac{zFU}{\Delta_{\rm r}H} = \frac{U}{U_{\rm tn}} \tag{7-14}$$

¹ We assume $\Delta_r H < 0$ for a fuel cell reaction, which essentially is a combustion reaction and therefore exothermic, carried out electrochemically ('cold' combustion, cf. Introduction).

² W_{e} actually describes the 'work done on the system', hence, since U > 0 for a fuel cell, W_{e} is negative, which means that the cell is delivering energy (in the form of electric power).

We have introduced the *thermoneutral voltage* $U_{tn} = -\Delta_r H/zF$. It is the cell voltage that corresponds to a conversion efficiency of 100%. It is a hypothetical value for the H₂/O₂ fuel cell, because $\Delta_r S < 0$ and thus $U_{tn} > U_{rev}$.

The efficiency defined in Eq. 7-14 is the voltage efficiency of the cell. Practically, the faradaic efficiency $\varepsilon_{\rm F}$ (cf. Chapter I), i.e. the utilization of the fuel, also has to be taken into account. For example, fuel can be lost by diffusion of H₂ through the membrane of a PEFC or by parasitic consumption in an SOFC with finite electronic conductivity of the electrolyte.

The electrical power (unit: W) that a fuel cell produces is given by $P = U \cdot I$ (cf. Introduction) and, consequently, the *power density* (unit: W/cm²) is $p = U \cdot i$. For the thermal management of a fuel cell it is of interest to quantify the production of waste heat. The fraction of the enthalpy $\Delta_r H$ contained in the reactants converted into heat is $1 - \varepsilon$. Therefore the rate of waste heat production is $P_{\text{heat}} = \dot{Q} = (U_{\text{tn}} - U_{\text{cell}}) \cdot I$. This means that for a fuel cell reaction with $\Delta_r S < 0$ (such as the H₂/O₂ reaction) even if the cell is (theoretically) maintained at the reversible potential U_{rev} the cell is producing the waste heat $Q_{\text{rev}} = -T \cdot \Delta_r S$ per formula unit¹.

The output of a fuel cell is electrical energy and heat. In case of stationary systems, the waste heat can often be used as well, for example for heating or cooling purposes. In this case, in addition to the electrical efficiency, the total efficiency of the fuel cell system, including electrical and thermal energy, is quoted. It is not unusual that values up to 90% total efficiency are attained.

¹ The reaction would obviously be infinitely slow at the equilibrium.

Appendix A: The Mixed Potential on the PEFC Cathode

The lower OCV measured in the PEFC of ~ 1.0 V compared to the reversible voltage, which in the range of 1.2 V, has been explained by the formation of a mixed potential on the cathode. Two mechanisms are explained here in more detail.

Organic impurities, RH, present in the cathode feed (mostly air) are oxidized on the surface of the cathode catalyst: $RH \rightarrow R + H^+ + e^-$. The electrons are consumed by the ORR taking place on the same electrode. Figure 7-A1a shows a sketch of the polarization curves of the impurity oxidation reaction and the fuel cell ORR. The transfer of electrons between RH and oxygen within the fuel cell cathode¹ requires that the current densities of the oxidation and reduction reaction are identical. This leads to the formation of a mixed cathode potential, which corresponds to the open circuit potential E_0 of the cathode. Since the open circuit potential of the anode is very close to the reversible potential of the H⁺/H₂ couple, the OCV of the fuel cell U_0 is close in value to the cathode potential E_0 .



Figure 7-A1. Schematic polarization curves of anodic side reactions and the ORR taking place on the fuel cell cathode, which leads to the formation of a mixed cathode potential E_0 of ~1 V, whereas the reversible potential of the ORR is $E_{rev}(ORR) = +1.18$ V at 80°C and standard pressure. (a) Oxidation of organic impurities RH present in the cathode, with a reversible potential of $E_{rev}(RH) = +0.9$ V. (adapted from: Bockris, Khan, Surface Electrochemistry, 1993, p322) (b) Oxidation of H₂ diffusing through the membrane from the fuel cell anode to the cathode.

Hydrogen from the fuel cell anode diffuses through the membrane to the fuel cell cathode, where it is oxidized: $\frac{1}{2}$ H₂ \rightarrow H⁺ + e⁻. The mixed potential E_0 that is formed on the cathode is determined by the rate of H₂ crossover. Therefore, the rate of the HOR on the fuel cell cathode is diffusion limited at a crossover current density i_x (Figure 7-A1b). The higher the crossover, the lower the cathode

¹ The air electrode is called 'fuel cell cathode' here in quotation marks, because in the used configuration it is both an anode (for the oxidation reaction) and a cathode (for the ORR).

potential E_0 . The effect is particularly pronounced for very thin membranes of 5 to 10 µm thickness used in automotive fuel cells. Oxygen crossover from the cathode to the anode also takes place in the PEFC, yet the effect on the open circuit potential of the anode is negligible, owing to the high exchange current density of the HOR. The hydrogen electrode consisting of (carbon supported) Pt in acid is not easily polarizable.

Chapter VIII

Analytical Methods & Sensors

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In the study of electrochemical reactions, in analogy to chemical reactions, one is interested in understanding mechanisms, rates, influential parameters, concentration dependencies, temperature effects, etc., in qualitative and quantitative manner. This evidently involves the measurement of current in an electrochemical cell and potential of electrodes or cell voltages. Often, the focus of an investigation is on a particular half-cell reaction. Therefore, the typical experimental setup consists of a 3-electrode cell, comprising a working, counter and reference electrode (cf. Chapter III). This may also be in a non-aqueous electrolyte. Moreover, configurations similar to the target application are used. For example, in the study of lithium-ion battery materials, lithium metal is commonly used as combined counter and reference electrode. In this Chapter, we will be looking at an example of electrode characterization in a polymer electrolyte fuel cell (Section 2.3).

Electrochemical phenomena and processes are furthermore useful for the detection and analysis of chemical compounds in liquids and gases. The high accuracy of electroanalytical methods derives from the fact that they are based on exact laws (e.g., those of Nernst and Faraday). Thus, electrochemical sensing is used in a wide range of applications, including environmental monitoring, industrial quality control, or biomedical analysis.

In this Chapter, after a general introduction into electroanalytical methods, we will study the principles of selected methods used for sensor applications that are of high technical relevance. Cyclic voltammetry (CV) and the rotating disk electrode (RDE) are of particular interest to characterize half-cell reactions qualitatively and quantitatively. These methods represent a whole class of electroanalytical electrochemistry, and we could easily dedicate an entire course to this and related topics. Therefore, the content discussed here has to be regarded merely as an overview and introduction into an extensive family of methods.

1 Electroanalytical Methods

The distinction between the different electroanalytical techniques reflects the type of electrical signal that is controlled and the type of signal that is measured. The key quantities are current and potential. Often, measurements are performed with the time as parameter. Current integrated over time yields charge. **Figure 8-1** shows a selection of electroanalytical methods and their categorization. This is but a very basic description of the suite of techniques that is used. In particular, the electrochemical measurements can be combined with other methods, such as various types of spectroscopy (e.g., UV-Vis, IR, X-ray) for chemical analysis, scattering and diffraction methods for structural characterization, microscopic techniques for visualization, and so forth.

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Figure 8-1. Overview of selected electroanalytical methods.

The name of the analytical method indicates the sensed quantity: in *potentiometry*, it is the potential, in *amperometry* the current, and in *coulometry* the charge passed over a certain time. The odd one out is *voltammetry*, where actually the current is measured as the potential is varied. A key classification is based on whether the method is static (see Section 1.1), where no current is passed, or dynamic, which involves the passage of current. Dynamic techniques are more diverse, and it is the current or the potential that is controlled (*galvanostatic* or *potentiostatic* method). The measurement of a diffusion limited current can be used to determine the concentration of an analyte undergoing a reaction (Section 1.2). Voltammetry is an entire sub-class of methods, and only selected aspects will be discussed in this text (Section 2). The *rotating disk electrode* (RDE) is used in hydrodynamic voltammetry to create a specific flow distribution in the electrolyte and thus a defined limiting current depending on the rotation rate (Section 3).

1.1 Potentiometry

Potentiometry in the absence of a current exploits the phenomenon of an electrochemical equilibrium establishing on a suitably designed interface between two phases, which may be an electrode-electrolyte interface or an interface between two ionically conducting phases. According
to the Nernst equation the Galvani potential difference across an interface depends on the activity of the potential-determining species (cf. Chapter III). The method can therefore be used to determine the concentration / activity of a compound.¹

A prominent example of a potentiometric method based on half-cell equilibria established on electrodes is the lambda probe used for oxygen concentration sensing. The cell is a high-temperature solid oxide cell using an oxygen ion conducting electrolyte (e.g., yttria stabilized zirconia, cf. Chapter IV) and, typically, Pt electrodes, exposed to a known O₂ partial pressure $p(O_2, I)$ on one side and an unknown O₂ partial pressure $p(O_2, II)$ on the other side. The equilibrium that is established at the two electrodes is $O_2 + 4 e^- \rightleftharpoons 2 O^{2^-}$. The potential difference and measured cell voltage U_{cell} between the two electrodes is then given by $U_{cell} = RT/4F \cdot \ln(p(O_2, I)/p(O_2, II))$, i.e. the Nernst equation (cf. also Chapter VII, Eq. 7-12).

In aqueous solutions, potentiometry is not so much used to measure redox equilibria on metal electrodes in an electrolyte, such as M | $M^{z+}(aq)$ (electrodes of the first kind) or M(inert) | $A^{z+}(aq)$, $A^{(z+1)+}(aq)$ (electrode of the third kind, redox electrode), because such equilibria are very likely to be sensitive to the presence of other substances, pH, O₂, etc., and therefore usually not very selective towards the desired compound. Commonly used potentiometric methods employ an ion-selective electrode (ISE). As the name suggests, such electrodes possess a high degree of selectivity towards a certain target ion, determined by the composition of a membrane. Redox processes involving the analyte, i.e. the substance to be sensed, do not occur in ISEs, instead a Galvani potential difference is established between the two sides of the membrane as a result of either an ion exchange or an ion transport process occurring in the membrane and the two interfaces between membrane and solution. Reference electrodes are placed in the two solutions separated by the membrane. In one solution containing the indicator electrode the activity of the analyte is unknown. The other solution, into which the reference electrode is immersed, contains the analyte with known activity. The potential difference measured between the indicator and the reference electrode is then a function of the concentration of the analyte in the test solution. Essentially, the two electrodes sense the difference of the Galvani potential between the test and reference solution. The measurement setup can best be shown in the following representation, where the reference electrodes in the two solutions have been omitted:

test solution, *a*(unknown) | membrane | reference solution, *a*(fixed)

¹ Of course the measurement involves the passage of a very small current owing to the electric circuitry used in the measurement device.

The working principle of an ISE is best explained using an example, such as the well-known pH glass electrode. It is perhaps the most successful and ubiquitous electrochemical sensor. We recall the identity $pH = -log(a(H^+))$, hence we wish to measure the proton activity in a test solution. The used glass, which is rich in Na₂O, when immersed in water exchanges cations with protons in a thin water-swollen surface or gel layer, called the Haber-Haugaard Layer (HHL), which has a thickness in the range of 5 to 500 nm. The bulk of the glass membrane remains unaltered and cations, mostly Na⁺, provide a (weakly) ion conducting path between the two surface layers. The defining feature of the HHL is its exceptionally high selectivity towards H^+ , which thus becomes the species determining the potential difference between solution and HHL according to the equilibrium $H^+(s) \rightleftharpoons H^+(m)$, where 's' stands for solution and 'm' the HHL layer of the glass membrane. The swollen glass laver is therefore a very selective ion exchange phase for H^+ . Since at equilibrium the electrochemical potential of protons has to be the same in the solution and the HHL, a Galvani potential difference, i.e. a Donnan potential, forms between solution and membrane (cf. Chapter IV). Such a Donnan potential forms on both sides of the glass membrane, the side in contact with the test solution with unknown pH and the side in contact with the reference solution with known pH (Figure 8-2a). We recall from Chapter IV that the membrane potential, i.e. the difference in the Galvani potential between the two solutions that an ion-exchange membrane is separating, is composed of the two Donnan potentials plus a diffusion potential. The latter is formed between the two surfaces of the glass membrane, owing to the different cation concentration in the two glass surface layers. We also recall that, if the fixed ion concentration in the membrane is very high, the membrane potential is dominated by the two Donnan potentials. In this case, the Galvani potential difference $\Delta \varphi_{\alpha-\beta}$ between the two solutions α and β is given by the following expression:

$$\Delta \varphi_{\alpha-\beta} = \varphi_{\beta} - \varphi_{\alpha} = -\frac{RT}{F} \ln(\frac{a_{\mathrm{H}^{+}}}{a_{\mathrm{H}^{+}}^{a}})$$
(8-1)

The corresponding distribution of the Galvani potential φ from solution α across the glass membrane to solution β is sketched in **Figure 8-2a**. Since we can neglect the diffusion potential, the potential may be considered constant in the glass¹. In order to measure the potential difference $\Delta \varphi_{\alpha-\beta}$ reference electrodes that are not pH dependent, such as calomel or silver-silver chloride electrodes, are placed in solutions α and β . A typical pH probe is a combination electrode, which is a device that comprises the glass membrane and both reference electrodes. (**Figure 8-2b**). It consists

¹ In fact, there are another two potential differences between the gel layers and the bulk glass, because those phases have a different composition. However, since we can assume that H⁺ activity in the two gel layers is very similar, there would be essentially the same additional $\Delta \varphi$ on both sides, and the potential difference $\Delta \varphi_{\alpha,\beta}$ would therefore not be affected by this.

of the following sequence of components. The internal reference electrode is immersed in the internal solution, usually a buffered pH 7 solution in 0.1 M KCl, which is separated from the test solution with unknown pH by the glass membrane. The compartment of the combination electrode containing the external reference electrode is ionically connected to the test solution via a porous frit. The fill solution is commonly 3 M or saturated KCl to minimize the junction potential between the test solution and the external fill solution. The shorthand representation of the pH measurement cell using a combination electrode is therefore as follows:

Ref'(ext.) | H⁺(aq, unknown) | **glass membrane** | H⁺(aq, fixed), Ref(int.)

The potential difference between the two electrodes can be directly measured as a voltage by a readout device. Taking Eq. 8-1 and considering that $a(H^+)$ in the internal reference solution is constant, the pH of the test solution is obtained from the measured signal as $E_{\text{meas}} = \text{const.} - 59.2 \text{ mV} \cdot \text{pH}$ at 25°C. Const. also contains a possible contribution of a difference in the chemical potential of H⁺ in the inner and outer gel layer (called asymmetry potential) and the influence of the junction potential between the test and external reference solution. In practice, const. is determined through calibration by measurement of the glass electrode potential E_{meas} in different solutions of known, buffered pH.



Figure 8-2. (a) Working principle of the glass electrode: Schematic of a glass membrane (thickness ~0.1 mm) between two solutions of different pH, the test solution (phase α) with unknown pH and the internal solution (phase β) with buffered, known pH. Below, the potential variation through the membrane is shown and the Galvani potential difference between the two solutions $\Delta \varphi_{\alpha,\beta} = \varphi_{\beta} - \varphi_{\alpha}$ is indicated (adapted from: C.H. Hamann, A. Hamnett, W. Vielstich, Electrochemistry, 2nd edition, 2007, p150). (b) Sketch of a combination glass pH electrode, comprising a reference electrode in contact (via a porous frit) with the test solution (adapted from: de.wikipedia.org/wiki/Glaselektrode).

Besides pH glass electrodes there is a number of ISEs for sensing the activity of other types of ions. In analogy to pH the measured activity of ions $X^{z+/-}$ can be represented as $pX = -\log(a(X^{z+/-}))$, such as pNa for Na⁺ or pF for F⁻. The selectivity for the ion of interest is thereby obtained through the use of different membrane materials, which may also be a polymer. **Table 8-1** gives an overview of selected ISEs.

Table 8-1. Selected list of ions, whose concentration is measured using an ion selective electrode (ISE). The influence of interfering ions is given by the respective selectivity coefficient $K_{kl.}$ (Source: B.W. Woodget, Analytical Science, The University of Hull, United Kingdom, hydra.hull.ac.uk/resources/hull:2477, accessed 29-12-2021, p42; J. Wang, Analytical Electrochemistry, 3rd Edition, Wiley, 2006, p175)

Ion k	Membrane	Conc. range	Optimum	Interfering	Selectivity		
		(M)	pН	ions <i>l</i>	K_{kl}		
H^+	glass	$\sim 1 - 10^{-11}$	0.5 - 11	Na^+	10-10		
Na ⁺	glass	$1 - 10^{-5}$	>7	H^{+}	100		
	-			Cs ⁺ , Li ⁺	0.002		
				K^+	0.001		
Br⁻	solid-state	$1 - 5 \cdot 10^{-6}$	2 - 12	S ²⁻ , I ⁻ , CN ⁻	~10 ⁶		
Cl-	solid-state	$1 - 5 \cdot 10^{-5}$	2 - 11	I-, CN-	~10 ⁶		
				S ²⁻	$\sim 10^{6}$		
				Br-	$\sim 10^{5}$		
F-	solid-state	$1 - 10^{-6}$	5 - 8	OH-	~104		
Ca^{2+}	PVC-gel	$1 - 5 \cdot 10^{-7}$	6-8	Zn ²⁺	3.2		
	-			Pb^{2+}	0.063		
				Mg^{2+}	0.014		
NO ₃ -	PVC-gel	$1 - 7 \cdot 10^{-6}$	3 - 10	ClO ₄ -	~10 ⁶		
	-			I-	20		
				Br-	0.1		
				NO ₂ -	0.04		
				Cl-	0.004		
CO ₂	gas-sensing ^a	$10^{-2} - 10^{-4}$		volatile, weak acids interfere			
NH ₃	gas-sensing ^a	$1 - 10^{-6}$		volatile amines interfere			

^a gases cause a change in the pH of the electrolyte

Ion-selective electrodes are selective but not specific. They will respond to other ions in solution. The presence of interfering ions may affect the measurement. Taking the pH electrode as an example, at high pH an alkali error of the glass electrode is experienced (which can be alleviated by using a special type of glass), caused by the high concentration of other cations, notably Na⁺. The competition between Na⁺ and H⁺ to exchange into the gel layer of the glass is described by the equilibrium H⁺(m) + Na⁺(s) \rightleftharpoons H⁺(s) + Na⁺(m). The equilibrium constant of this ion-exchange reaction is very low, yet at high Na⁺ activity and high pH / low H⁺ activity, significant amounts of Na⁺ will be found in the HHL. The ability of the electrode to sense *a*(H⁺) accurately therefore breaks down. The selectivity of an ISE towards a target ion *k* with different interfering ions *l* is described by the *Nicolsky-Eisenman equation*:

$$E_{\text{meas}} = const. + \frac{RT}{z_k F} \ln(a_k + \sum_l K_{kl} a_l^{z_k/z_l})$$
(8-2)

The lower the selectivity coefficient K_{kl} , the higher the selectivity of the ISE towards ion k. It contains the equilibrium constant of the ion-exchange process between k and l ions, yet in addition

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also contains the ionic mobilities of k and l in the membrane (For a derivation of Eq. 8-2 the reader is referred to A.J. Bard, L.R. Faulkner, Electrohchemical Methods, 2^{nd} edition, Wiley, 2001, pp74). In **Table 8-1** we see, for example, that the ISE used to measure Cl⁻ activity is heavily influenced by the presence of the other halides Br⁻ and I⁻. Therefore, when measuring with an ISE one has to be aware of the validity range of the measurement.

1.2 Amperometry

In amperometric sensors the measured current I is used to determine the concentration of a compound of interest. The principle of the method is based on Faraday's law $I = zF\dot{n}$ (cf. Chapter I), where \dot{n} is the rate of reaction of the species (unit: mol/s). The sensor is designed such that access of the reacting entity is limited by diffusion, and the measured current is a diffusion limited current. This means that the sensing reaction must take place at sufficiently high overpotential to ensure that it is in the diffusion limited regime. We recall from Chapter V that for a flat electrode in a semi-infinite electrolyte the maximum obtainable reaction rate is given by the limiting current density i_{lim} , which is proportional to the reactant concentration c and its diffusion coefficient D in the electrolyte, and inversely proportional to the Nernst diffusion layer thickness δ_{N} :

$$i_{\rm lim} = \frac{zFD}{\delta_{\rm N}} \cdot c \tag{5-36}$$

If the solution is stirred, a constant, steady-state value of δ_N is established, which will yield a stable sensing current i_{lim} . In a sensor, the compound of interest is undergoing a reaction at the sensing electrode. The flux of the reactant to this electrode is mass transport limited by the sensor design. Often, a membrane is used to create a diffusion layer with defined thickness. Alternatively, access



Figure 8-3. Schematic of an amperometric gas sensor. The access of the target gas to the sensing electrode is mass transport limited, which allows the measurement of the diffusion-limited current. (Source: online.fliphtml5.com/qyji/uznj, accessed 01-01-2022)

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of the reactant is controlled using a diffusion barrier, such as openings of defined geometry for the sensing of gases (cf. **Figure 8-3**). A hydrophobic membrane separates the gas head-space from the electrolyte and prevents the latter from leaking from the cell. In addition, the cell contains the expected components of an electrochemical cell, i.e. a counter and reference electrode. The measurement principle is therefore based on the diffusion limited access of the compound to the membrane in contact with the electrolyte. The reactant diffuses through the membrane, dissolves in the electrolyte and thus reaches the sensing electrode. In such a configuration, δ_N is an effective diffusion layer thickness, comprised of the contribution of several components. Practically, the sensor is calibrated in gases with defined concentration, such that a linear relationship between measured current *I* and partial pressure of the gas *p* is obtained¹.

Depending on the nature of the compound, the reaction it undergoes at the sensing electrode may be an anodic or a cathodic reaction. **Table 8-2** shows a selection of different sensing reactions, anodic as well as cathodic ones.

Anodic sensing reactions ^a				
carbon monoxide:	$CO + H_2O \rightarrow CO_2 + 2 H^+ + 2 e^-$			
hydrogen disulfide:	$H_2S + 4 H_2O \rightarrow H_2SO_4 + 8 H^+ + 8 e^-$			
hydrogen:	$H_2 \rightarrow 2 H^+ + 2 e^-$			
nitrous oxide:	$NO + 2 H_2O \rightarrow HNO_3 + 3 H^+ + 3 e^-$			
Cathodic sensing r	eactions ^b			
nitrogen dioxide:	$NO_2 + 2 H^+ + 2 e^- \rightarrow NO + H_2O$			
chlorine:	$Cl_2 + 2 H^+ + 2 e^- \rightarrow 2 HCl$			
ozone:	$O_3 + 2 H^+ + 2 e^- \rightarrow O_2 + 2 H_2O$			

 Table 8-2.
 Selection of sensing reactions. (Source: online.fliphtml5.com/qyji/uznj, accessed 01-01-2022)

^a cathode: ORR, i.e. requires the presence of oxygen ^b anode: OER

Note that in all cases, a suitable reaction at the counter electrode has to take place for the establishment of a continuous current, which should, however, not influence the sensing reaction. Often, the counter electrode reaction is the oxygen reduction reaction (ORR) if the sensor is used in air, or the oxygen evolution reaction (OER) from the aqueous electrolyte used. As an example, we look at the working principle of another well-known sensor: the *Clark* electrode is used to measure the dissolved oxygen content in an aqueous solution. One design is based on a circular and a ring-type electrode (**Figure 8-4**). Oxygen is reduced on the platinum sense electrode (cathode): $O_2 + 2 H_2O + 2 e^- \rightarrow 2 OH^-$ (ORR). A membrane on the electrode tip creates a defined diffusion pathway length for oxygen. The anodic reaction on the silver counter electrode (anode) is $Ag + CI^- \rightarrow AgCI + e^-$ in KCl electrolyte. The voltage of the cell is maintained in the range of 0.6 to 0.7 V in order to obtain a mass transport limited reaction of O_2 .

¹ We have to be aware of the fact that the diffusivity of the compound depends on the composition of the gas it is in. For example, the diffusivity of H_2S in air is different from the one in argon, or helium, etc.



Figure 8-4. Operating principle of a Clark electrode for dissolved oxygen. O_2 is reduced at the cathode in a reaction limited by diffusion across a membrane. Silver is used as a counter electrode, which is in contact with KCl(aq).

2 Voltammetry

Voltammetry is predominantly used in the context of the qualitative and quantitative investigation of electrochemical reactions in the laboratory, mostly using a liquid electrolyte and a 3-electrode configuration (cf. Chapter III). As we will see below, the technique can also be used with polymer electrolytes. In most cases voltammetry involves a linear variation of the electrode potential¹, either as a single sweep or a repeated forward and backward sweep with rate v (unit: V/s) describing the change in electrode potential *E* per time: v = dE/dt. Sweep rates are typically in the range between 1 mV/s and 1 V/s, yet one can also find cases with very high sweep rates of hundreds of V/s. The current response depends very much on the type of system under investigation. The most important configurations will be discussed in the following sub-sections.

2.1 Capacitive currents

The simplest experimental configuration consists of an inert electrode immersed in an electrolyte, say an aqueous solution containing ions, without electroactive species. Thus we do not have faradaic currents², and we have thus an ideal polarizable electrode (cf. Chapter V). An electrochemical double layer forms at the electrode-electrolyte interface (cf. Chapter III), and the only currents that the system allows are capacitive currents. It can be approximately described with an equivalent circuit consisting of a resistor *R* in series with a capacitor *C*, i.e. an RC-circuit³. We now perform cyclic voltammetry on this system, where we sweep the electrode potential from the lower potential limit E_L in positive, i.e. forward or anodic, direction⁴ with a certain sweep rate v to an upper potential

¹ There is also pulse, square-wave, staircase voltammetry, etc.

² Also, the potential does not exceed the electrochemical stability window of water.

³ Evidently, we know from Chapter III that the double layer does not behave like an ideal capacitor, we are looking at an idealized case here.

⁴ The initial charge on the capacitor may be arbitrary, the experiment does not have to start with a fully discharged capacitor.

limit E_U . Then the sweep direction is reversed in the negative, i.e. backward or cathodic, direction with a sweep rate -v of equal magnitude back to the lower potential limit E_L (Figure 8-5a). The current response of an RC-circuit can be determined analytically (cf. Appendix A). Initially, in the forward as well as the backward sweep, there is an exponential rise of the current to a steady state value. This steady state current is the double layer charging / discharging current

$$i_{\rm DI} = c_{\rm DI} \, V \tag{8-3}$$

where c_{DL} is the area specific double layer capacitance (unit: F/cm²), which is taken to be the constant capacitance *C* of the RC-circuit here (**Figure 8-5b**) divided by the electrode area. This means that we can determine the double layer capacitance c_{DL} according to Eq. 8-3 from a measurement of the steady-state current i_{DL} . For an electrode-electrolyte interface with given c_{DL} we notice that the double layer current i_{DL} is proportional to the sweep rate ν .



Figure 8-5. Cyclic voltammetry of an ideal RC-circuit. (a) Triangular potential wave with sweep rate $\pm v$ (unit: V/s) between lower potential limit E_L and upper potential limit E_U . (b) Current response, reaching a steady-state value of $\pm i_{DL} = \pm c_{DL} \cdot v$, where DL stands for 'double layer' and c_{DL} is the area specific capacitance (unit: F/cm²) of the electrode. (Source: A.J. Bard, L.R. Faulkner, Electrochemical Methods, 2nd Edition, Wiley, 2001, p18)

The time constant τ of the exponential rise is the time constant of the RC-circuit given by $\tau = R \cdot C$. For a low resistance *R* and / or capacitance *C*, this transient would be very short and we would essentially observe a nearly rectangular, 'blocky' type cyclic voltammogram. It is also noted that at the upper and lower inflection points, the current momentarily drops to zero before changing direction.

2.2 Redox couple in solution

We can now move on to somewhat more interesting systems that involve electrochemical reactions and, therefore, faradaic current. In the first case, we take the situation of a redox couple Ox/Red in

aqueous solution that can undergo an oxidation and reduction reaction according to $Ox + e^- \rightleftharpoons Red$. Examples are Fe³⁺/Fe²⁺ or [Ru(NH₃)₆]³⁺/[Ru(NH₃)₆]²⁺.¹ We now assume that initially only the reduced species Red is present in the solution. The cyclic voltammetric experiment is then started by sweeping the potential in forward (anodic) direction, resulting in Red being oxidized to Ox. Initially, the current is small, but it increases approximately exponentially with potential (or time). The reaction leads to a decrease in the concentration of the reactant, Red, at the electrode surface. Since the electrolyte is unstirred, the Nernst diffusion layer thickness δ_N increases with time according to the expression $\delta_N = \sqrt{\pi Dt}$ (cf. Chapter V), causing the current to peak and then to decrease again (Figure 8-6a). Upon reversal of the sweep direction, initially Red continues to be oxidized, owing to the high positive electrode potential. Eventually, the current drops to zero and then becomes negative (cathodic), where the Ox species, formed during the forward sweep, are reduced back to Red. A peak current (density) is also observed in the cathodic direction of the sweep. Eventually, the current drops to zero as Ox is consumed. The magnitude of the anodic peak is larger than the one of the cathodic peak, because the Ox species formed in the forward sweep is diffusing into the bulk of the solution, thus its availability for the reaction during the backward sweep is limited. See Appendix B for the concentration profiles of Ox and Red during the experiment and more detailed discussion of the shape of the voltammogram.



Figure 8-6. (a) Cyclic voltammogram of a redox couple Ox/Red (z = 1) in solution with fast (reversible) kinetics at different sweep rates v of 0.05 V/s, 0.2 V/s, and 0.8 V/s. The formal potential $E^{\circ'}$ of the redox couple is indicated. The arrows indicate the sweep direction of the potential. Initially only Red is present. (b) Cyclic voltammograms at v = 0.1 V/s of a redox couple in solution, showing the influence of the reaction kinetics. Reversible reaction: $k_0 \gtrsim 0.1$ cm/s, quasi-reversible: $k_0 = 2 \cdot 10^{-4}$ cm/s, irreversible: $k_0 = 10^{-5}$ cm/s (Calculated using the DigiElch software; parameters: $T = 25^{\circ}$ C, c_{red} (bulk) = 5 mM, c_{ox} (bulk) = 0, $D = 10^{-6}$ cm²/s; capacitive currents are neglected).

¹ We recall from Chapter V that such experiments are commonly performed with a concentration of the redox couple being studied in the range of mM and a supporting electrolyte, say KNO₃(aq), with concentration in the 1 M range.

In the case where further cycling is performed, the sweep direction is reversed again at the lower potential limit, and another anodic sweeps starts. After a number of cycles, a steady-state cyclic voltammogram is obtained, which shows the same shape in further consecutive cycles.

The derivation of the mathematical description of a cyclic voltammogram is rather complex and cumbersome, and thus beyond the scope of this text. The reader is referred to the textbook by Bard and Faulkner for a comprehensive treatment. We are primarily concerned with a qualitative description of the obtained features. First and foremost, the measurement allows us to determine the potential around which the cyclic voltammogram is 'centered'. This is the formal potential $E^{\circ\prime}$, i.e., the potential at which the concentration of oxidized and reduced species at the electrode surface are equal, i.e. $c_{Ox} = c_{Red}$ (cf. Chapter II).

For the analysis of the peak current and peak potential, different cases are distinguished, based on how the rate constant of the electrochemical reaction k_0 (cf. Chapter V) compares to the rate of mass transfer k_d (unit: cm/s, same as that of k_0) given by

$$k_{\rm d} = \frac{D}{\delta_{\rm N}} = \sqrt{D \, \frac{F}{RT} \, \nu} \tag{8-4}$$

which we see depends on the sweep rate v. For fast reactions and / or low sweep rates v_i^1 i.e. $k_0 \gg k_d$, the peak current density i_p of the forward scan for a species A (in our case here: Red) undergoing reaction in an experiment as indicated in **Figure 8-6a** is calculated according to:

$$i_{\rm p} = (2.69 \cdot 10^5 \,\frac{\rm As}{\rm mol}\sqrt{\rm V}) \, z^{3/2} \, D_{\rm A}^{1/2} \, c_{\rm A} \, v^{1/2} \tag{8-5}$$

where c_A is the concentration of A in the bulk. This is the *Randles-Ševčík* equation, the numerical value corresponds to a temperature of 25°C. We notice that the peak current i_p scales with the square root of the sweep rate v. In fact, this proportionality holds for the (faradaic) current i_F at any potential, thus we have : $i_F \propto \sqrt{v}$. This is in contrast to the capacitive current i_{DL} , which, as we recall from above, is proportional to the sweep rate: $i_{DL} \propto v$. In general, we measure a combination of capacitive and faradaic currents in our system $i = i_F + i_{DL}$. If we plot the peak potential i_p as a function of \sqrt{v} we should get a linear relationship. If not, this is a hint that capacitive current i_{DL} is

¹ Practically, we cannot make the sweep rate ν arbitrarily low to maintain a certain instrumental precision for current measurement.

dominating. With a 'blank' measurement in the absence of the redox couple the capacitance of the electrode used can be determined.

We see in **Figure 8-6a** that there is a potential difference ΔE separating the anodic and cathodic peak. For a fast reaction, the position (potential) of the peak does not depend on the sweep rate, and the separation is $\Delta E \cong 57 \text{ mV}$ at room temperature. An electrochemical reaction with $k_0 \gg k_d$ is called a *reversible* reaction. It is characterized in that the concentrations of Ox and Red on the electrode surface, $c_{\text{Ox}}(x=0)$ and $c_{\text{Red}}(x=0)$, are always at the equilibrium given by the Nernst equation for the potential E that is experimentally controlled. In other words, the activation overpotential is negligible. The term 'reversibility', as it is used in this context, therefore refers to the reaction kinetics and has to be distinguished from the concept of invertibility (cf. Chapter III), which characterizes whether a reaction can proceed in principle in forward as well as in backward direction.¹ If the electrochemical reaction is sluggish, i.e. $k_0 \ll k_d$, we speak of an *irreversible* reaction. In this case the separation between anodic and cathodic peak is much more pronounced (Figure 8-6b) and also dependent on the sweep rate. There is a sizeable activation overpotential for such a reaction, and the surface concentrations of Ox and Red therefore deviate from the Nernstian values. The peak current is lower than for the reversible case and the Randles-Ševčík equation no longer applies to the anodic peak current. For the intermediate case with $k_0 \approx k_d$, we speak of a nearreversible or quasi-reversible reaction. We furthermore see that the cathodic peak decreases more strongly than the anodic peak for decreasing k_0 . This is a result of less Ox species being formed in the anodic sweep, owing to the significant activation overpotential. Therefore, there is less Ox available to be reduced in the following cathodic sweep. The more pronounced decrease of the current in the cathodic direction compared to the anodic direction is the background of calling these reactions 'irreversible'. In any case, if we continue to cycle, independent of the reversibility of the electrochemical reaction, we eventually obtain a steady-state voltammogram (see Appendix C for examples using an equimolar concentration of Ox and Red).

In summary, the qualitative analysis of a cyclic voltammogram can provide us with information on the kinetics of the electrochemical reaction under study. From the increase of the peak separation ΔE with the sweep rate v the extent of irreversibility can be judged and, with the proper quantitative analysis, the rate constant k_0 can be obtained (for details see textbook by Bard and Faulkner).

¹ The literature rarely distinguishes between *reversibility* and *invertibility* of electrochemical reactions (except Bagotsky, see for example V.S. Bagotsky, Fundamentals of Electrochemistry, 2nd Edition, Wiley, 2006, p13). Invertibility describes whether a reaction can take place in both forward and backward direction, regardless of its electrochemical kinetics. Reversibility of a reaction, on the other hand, describes the electrochemical kinetics and characterizes the extent of departure of the reaction from the thermodynamic equilibrium.

Cyclic voltammograms can be arbitrarily complex, with side reactions occurring, parasitic reactions involving the solvent, multi-electron transfer reactions – some slow, some fast, coupled chemical reactions, which either precede or follow the electrochemical reaction, or both, and so forth. The corresponding features can become difficult to analyze and, therefore, complementary techniques, such as various types of spectroscopy, may have to be used to provide additional puzzle pieces to understand the reaction system.



Figure 8-7. Selected more complex cyclic voltammograms (parameters: z = 1, $T = 25^{\circ}$ C, $c_A(\text{bulk}) = 5$ mM, $c_B(\text{bulk}) = c_C(\text{bulk}) = 0$, $D = 10^{-6}$ cm²/s, v = 0.1 V/s). Left: electrochemical-chemical (EC) reaction, consisting of an invertible electrochemical reaction A \rightleftharpoons B (reversible kinetics, i.e. $k_0 \rightarrow \infty$) and a (non-invertible) chemical reaction B \rightarrow C (rate constant k_c). Influence of the rate constant of the chemical reaction k_c on the shape of the voltammetric response is shown. Right: Reaction system with two invertible electrochemical reactions A \rightleftharpoons B and B \rightleftharpoons C with formal potentials $E_1^{\circ'}$ and $E_2^{\circ'}$, respectively (reversible kinetics). (Calculated using the using the DigiElch software)

In the framework of this text, we will limit ourselves in the following to the qualitative description of two educationally valuable examples (**Figure 8-7**). In dealing with electrochemical reactions coupled with chemical reactions, according to a common notational method, a heterogeneous electron transfer step is denoted as an 'E' step and a homogeneous chemical reaction is termed a 'C' step. The example on the left side of **Figure 8-7** shows an EC reaction, i.e. an invertible electrochemical reaction A \rightleftharpoons B followed by a non-invertible chemical reaction B \rightarrow C. The shape of the obtained cyclic voltammogram depends on the ratio of the kinetic rate constants of the E and C step. If the chemical reaction with rate constant k_c is slow compared to the electrochemical one, the cyclic voltammogram essentially shows the oxidation and reduction wave of the reaction A \rightleftharpoons B, as the reaction B \rightarrow C is negligible. With increasing k_c , the cathodic peak decreases in magnitude, as an increasing fraction of B reacts to C and is therefore not available anymore to the reaction B \rightarrow A. The EC reaction system is, therefore, moving from an invertible reaction to a non-invertible one. The extent of invertibility also depends on the potential sweep rate: a lower sweep rate 'leaves more time' for the chemical reaction $B \rightarrow C$ to take place. We furthermore notice that the anodic wave of the reaction $A \rightarrow B$ shifts cathodically, i.e. it becomes easier to oxidize A as the rate constant k_c increases. This can be understood by recalling the Nernst equation, which, for a fast reaction near equilibrium, describes the relationship between the electrode potential and the concentration ratio of species A and B. The chemical reaction $B \rightarrow C$ removes B and therefore perturbs the surface equilibrium between A and B. In order to re-establish the equilibrium at the electrode surface, the electrochemical reaction $A \rightarrow B$ is driven to the right side, producing more B. This replenishes some B lost by the chemical reaction $B \rightarrow C$ and causes a cathodic shift of the oxidation wave of A.

The second example shows the voltammogram of an electrochemical reaction with the transfer of two electrons in two consecutive, reversible one-electron transfer steps $A \rightarrow B$ and $B \rightarrow C$ and their respective reverse reaction $C \rightarrow B$ and $B \rightarrow A$ (without any side reactions). If the formal potentials $E_1^{\circ'}$ and $E_2^{\circ'}$ of the two reactions $A \rightleftharpoons B$ and $B \rightleftharpoons C$ are sufficiently far apart, two well-separated oxidation and reduction waves can be observed.

2.3 Adsorbed species

In the second class of voltammetric experiments to be discussed here we consider the reaction of species adsorbed on the electrode surface. If the formation of an adsorbate or a reaction it undergoes is associated with electron transfer from the electrode, we can measure this as a current. If the adsorbate forms a layer with a defined coverage θ on the electrode, we can use the reaction of the adsorbate as a method, using Faraday's laws, to determine ('titrate') the microscopic surface area of the electrode and thus obtain its roughness factor *r*.

As a 'classical' example to study as a model case, we choose a platinum electrode immersed in an aqueous sulfuric acid electrolyte (**Figure 8-8a**). The electrolyte does not contain any redox couple, hence the observed features of the cyclic voltammogram must be related to the properties of the Pt-electrolyte interface. The potential of the electrode is maintained within the stability window of water during the experiment to prevent hydrogen or oxygen evolution. It is furthermore important to purge the measurement cell with an inert gas, such as nitrogen, as the presence of oxygen would lead to it being reduced at potentials below ~1 V (remember that the standard equilibrium potential $E^{\circ}(O_2/H_2O)$ is +1.23 V at 25°C and pH 0). The potential range below ~0.4 V is called the *hydrogen underpotential deposition* (H-UPD) region. The observed current response is related to the desorption (a) and adsorption (b) of hydrogen on the Pt surface according to:

$$Pt + H^+ + e^- \rightleftharpoons Pt - H_{ad}$$
(8-6)

The protons originate from the acid. In the cathodic scan (b) they react with electrons to produce Pt surface adsorbed hydrogen species Pt-H_{ad}. The required electrons are measured as a cathodic current. The different peaks correspond to hydrogen adsorbing on different crystallographic locations of the exposed Pt surface. In the corresponding anodic scan (a) the reverse process takes place as Pt-H_{ad} is oxidized and protons are released into the solution. UPD is a phenomenon of electrodeposition of a species, here protons, but it is originally known from metal cations depositing on an electrode material at a potential less negative than the equilibrium potential (hence 'underpotential deposition') for the reduction of this species. In our case, bulk hydrogen evolution sets in below ~0 V,¹ and H-UPD takes place in the potential region above the equilibrium potential.

Region (c) is called the *double layer region*, as here the Pt surface displays only capacitive behavior. From the current in this region the double layer capacitance can be calculated according to Eq. 8-3. At potentials above ~ 0.6 V in the anodic sweep (d) platinum oxidation sets in, which produces Pthydroxides and Pt-oxides at the surface and in the surface-near region, which are reduced again to metallic Pt in the cathodic sweep (e):



Figure 8-8. (a) Cyclic voltammogram of smooth polycrystalline platinum in N₂ purged 0.5 M H₂SO₄, $\nu = 50$ mV/s, $T = 20^{\circ}$ C. The arrows indicate the sweep direction (anodic, cathodic, the letters indicate a-e characteristic regions, and the horizontal blue lines the capacitive current, HER and OER the potential region where hydrogen and oxygen evolution, respectively, is expected to occur (adapted from: C.H. Hamann, A. Hamnett, W. Vielstich, Electrochemistry, 2nd edition, 2007, p263). (b) CO-stripping followed by cyclic voltammogram of a Pt/C electrode in a polymer electrolyte fuel cell. Pt loading L = 0.6 mg/cm², $\nu = 10$ mV/s, $T = 80^{\circ}$ C. $Q_{\rm H}$ and $Q_{\rm CO}$ indicate the charge associated with the hydrogen underpotential (H-UPD) and the CO electrooxidation process, respectively. The horizontal blue lines indicate the capacitive current $i_{\rm DL}$ associated with double layer charging / discharging (source: PSI, 2003).

¹ The exact value of the equilibrium potential $E(H^+, H_2)$ obviously depends on the solution pH and partial pressure of H₂. Furthermore, we know from Chapter V that this reaction has a high exchange current density on Pt, and hydrogen evolution, the cathodic reaction, also takes place, albeit at small rate, at electrode potentials positive of the equilibrium value.

$$Pt + H_2O \rightleftharpoons Pt - OH + H^+ + e^-$$
(8-7)

$$Pt-OH \rightleftharpoons Pt-O + H^+ + e^-$$
(8-8)

A similar voltammogram of platinum can be observed in alkaline solution or in case of the use of a hydrated ionomer, for example NafionTM (cf. Chapter IV), as electrolyte. This is relevant for the characterization of electrocatalysts in the polymer electrolyte fuel cell (PEFC) (cf. Chapter VII). **Figure 8-8b** shows the cyclic voltammogram of a PEFC catalyst layer containing a carbon supported platinum catalyst (see **Appendix D** for a detailed description of the experimental setup). The H-UPD region can be used to determine the microscopic surface area of the platinum catalyst, which is also referred to as *electrochemically active surface area* (ECSA), because only the Pt that is connected to the continuous electronic phase in contact with a continuous ionomer phase is probed in the experiment (cf. Chapter VII). The Pt-H_{ad} species form a well-defined monolayer, with one hydrogen atom adsorbed per Pt atom. This corresponds to a surface coverage of $\theta_{\rm H} = 1$. From the measured current *I* in the H-UPD region, either in anodic or cathodic direction, corrected for the double layer current *I*_{DL}, we can calculate the charge $Q_{\rm H}$ associated with the area under the H-UPD region according to $\int (I - I_{\rm DL})/\nu dE$, where ν is the sweep rate. The example in **Figure 8-8b** yields $Q_{\rm H} = 1.18$ As. Using current densities *i* and $i_{\rm DL}$, the roughness factor of the electrode can then be calculated from

$$r = \frac{1}{v} \frac{1}{zF\Gamma_{\rm Pt}} \int (i - i_{\rm DL}) dE$$
(8-9)

where Γ_{Pt} is the adsorption site density on the platinum surface (unit: mol/cm²). For polycrystalline Pt the value is $\Gamma_{Pt} = 2.18 \text{ nmol/cm}^2$. For Pt-H_{ad} we have z = 1. We recognize that for the case of adsorbed species, the current response in the cyclic voltammogram scales linearly with the sweep rate, $i \propto v$, unlike for reactants dissolved in the electrolyte (see above).

The H-UPD region may be difficult to analyze since it is next to the HER region, which may disturb the measurement. The Pt-(hydr)oxide region cannot be used for quantitative analysis of the Pt surface, because the oxidized Pt species do not form a defined coverage. Therefore, CO stripping voltammetry has often been used for Pt surface area quantification, as carbon monoxide strongly adsorbs on Pt and forms a next-to-complete CO-monolayer with high coverage of $\theta_{CO} \approx 1$ at temperatures below 100°C. CO therefore effectively 'poisons' the Pt surface (cf. Chapter VII). The experimental procedure of CO-stripping voltammetry first involves the adsorption of CO at a defined electrode potential, commonly between 0.1 and 0.3 V, from the gas phase, e.g. by flushing the cell with 1 % CO in N₂. Then, the cell is again purged with inert gas to remove CO in the gas phase. Subsequently, the anodic sweep is started. At an electrode potential of around 0.5 V, CO electrooxidation kicks in according to the following reaction equation:

$$Pt-CO + Pt-OH \rightarrow 2Pt + CO_2 + H^+ + e^-$$
(8-10)

The current peaks and then drops again, as all the adsorbed CO gets oxidized to CO₂ (**Figure 8-8b**). Subsequent cycles then produce a regular cyclic voltammogram of Pt. It is important to realize that the oxidation of CO on platinum requires Pt-OH species, i.e. Pt-surface hydroxides, which form according to Eq. 8-7. Overall, therefore, 2 electrons are required for the oxidation of CO to CO₂ (as also the change in the oxidation number of carbon indicates). Pt-CO occupies the same adsorption sites on platinum as Pt-H, thus the same value of Γ_{Pt} is used to calculate the roughness factor *r* of the electrode using Eq. 8-9, yet for Pt-CO we have *z* = 2. Therefore, the charge associated with the CO-electrooxidation peak $Q_{CO} = 2.39$ As is about twice that obtained for the H-UPD region Q_{H} . The content of the released CO₂ can be quantified, for example, with mass spectrometry, and the result obtained has been shown to correlate very well with the charge associated with the oxidation of adsorbed CO.

Example:

We analyze the ECSA of the Pt in a fuel cell cathode catalyst layer from **Figure 8-8b** based on the H-UPD region and the CO-stripping peak. The area under the H-UPD peak is $\int_{\rm H} (I - I_{\rm DL}) dE = 11.8$ V·mA, the one under the CO-oxidation peak $\int_{\rm CO} (I - I_{\rm DL}) dE = 23.9$ V·mA. Dividing by the sweep rate v = 0.01 V/s we obtain $Q_{\rm H} = 1.18$ As and $Q_{\rm CO} = 2.39$ As. With the geometric electrode area of A = 29.2 cm² and the adsorption site density on Pt of $\Gamma_{\rm Pt} = 2.18$ nmol/cm², a roughness factor r of 188 cm²(Pt)/cm² (H-UPD) and 190 cm²(Pt)/cm² (CO-stripping), respectively, is obtained, where z = 1 for H-UPD and z = 2 for CO oxidation. With the catalyst loading of L = 0.6 mg(Pt)/cm² we calculate a specific Pt surface area of $s_{\rm Pt} = r/L = 31-32$ m²/g (see also Chapter VII). In addition, from the current in the double layer region of $2 \cdot I_{\rm DL} = 56.4$ mA, a capacitance of the electrode of $C = I_{\rm DL} / v = 2.69$ F and thus an area specific capacitance of c = 92 mF/cm² is obtained.

In addition to platinum, voltammetric methods to determine the microscopic surface area also works for some other noble metals, such as palladium, because they typically have a 'clean' and welldefined surface. In alkaline electrolyte, metals like silver, copper or nickel will also give a reasonable votammetric response. Metal dissolution and/or irreversible oxide formation should be minimal. The roughness factor can be quantified based on oxide reduction charge, provided surface reactions are associated with a defined oxide coverage, or metal-UPD reactions (e.g., Pb-upd has been extensively used for Cu or Ag), which is generally less sensitive to the electrolyte pH.

3 Rotating Disk Electrode (RDE)

The voltammetric methods discussed in the previous section are non-steady state techniques, as the applied potential is time-dependent and the solution is stagnant (unstirred), which results in constantly changing concentration profiles of reactants and products. Often, however, one is interested in measuring a steady-state response in terms of potential and current of an electrochemical system. To achieve a better control of effects related to mass transport, the solution may be stirred or otherwise mixed to homogenize the electrolyte solution. This will lead to a situation with some sort of steady, but not necessarily uniform diffusion layer thickness at the electrode. Alternatively, instead of agitating the solution, the electrode itself may be moved with respect to the solution. In the method of the rotating disk electrode (RDE) a circular, flat electrode imbedded in a rod of insulating material (e.g. Kel-F, Teflon) is immersed into the electrolyte and rotated at a defined rate, characterized by the angular velocity $\omega = 2\pi f$, where f is the rotation rate in 1/s or 1/min (revolutions per minute, RPM). The rotation of the electrode leads to a well-defined flow pattern. The RDE is therefore a hydrodynamic method. It allows for measurements at a steady state. A corollary of this is that double-layer charging effects are absent, as capacitive currents only arise when the electrode potential is varied (see Eq. 8-3). It might appear that the time variable is lost in a steady-state convective method, yet this is not so, as it enters the experiment as the rotation rate of the electrode or, more precisely, the solution velocity with respect to the electrode. The spinning body pulls the solution towards it and then flings it outward sideways from the center in



Figure 8-9. (a) Sketch of a rotating disk electrode (RDE) rotating at an angular velocity ω and corresponding electrolyte flow pattern. (b) Flow functions to calculate the electrolyte flow velocity $\mathbf{u}(u_t, u_{\theta}, u_z)$ as a function of the dimensionless distance γ from the center of the disk. $Z_{\rm H} = \sqrt{\nu/\omega}$ is the hydrodynamic length, where ν is the kinematic viscosity of the electrolyte (unit: cm²/s). Radial velocity $u_r = \omega r F(\gamma)$, azimuthal velocity $u_{\theta} = \omega r G(\gamma)$, axial velocity $u_z = -\sqrt{\omega \nu} H(\gamma)$. (Adapted from: D. Pletcher, F. Walsh, Electrochemical Processes and Fuel Cell Technology, Johnson Matthey Technology Centre, Sonning Common, Reading, United Kingdom, September 10-12, 2002).

radial direction (**Figure 8-9a**). The steady velocity profile of the fluid near the electrode can be obtained, provided that the flow is laminar, by solving the hydrodynamic problem (Navier-Stokes equations) for steady-state conditions. The velocity profile is described in terms of the axial velocity u_z , which is perpendicular to the planar electrode, the radial velocity u_r , and the azimuthal velocity u_{θ} , which are given as a function of the distance from the center of the electrode with the help of flow functions for the 3 velocity components (**Figure 8-9b**). The flow in axial direction is directed towards the electrode ($u_z < 0$), characterized by the flow function $H(\gamma)$, and increases in magnitude with the distance from the electrode and converges towards a value of $u_0 = \lim_{z\to\infty} u_z = -0.884 \sqrt{\omega v}$ far away from the electrode. At the electrode surface (z = 0) the velocity is zero, owing to the non-slip boundary conditions imposed by the finite viscosity of the electrolyte and the laminar flow conditions.

Mass transport to the electrode surface takes place by a combination of convection and diffusion. The steady velocity profile leads to a defined Nernst diffusion layer thickness δ_N (cf. Chapter V), which can be calculated by solving the convection-diffusion equation¹. The analysis shows that δ_N is independent of the radial coordinate *r*, thus it is uniform across the electrode and given by

$$\delta_{\rm N} \cong 1.61 \, D^{1/3} v^{1/6} \omega^{-1/2} \tag{8-11}$$

where *D* is the diffusion coefficient of the reactant and ν is the kinematic viscosity of the solution. Since convective diffusion takes place uniformly over the disk surface, there is a constant diffusion limited current density i_{lim} everywhere on the electrode, given by

$$i_{\rm lim} = \frac{zFD}{\delta_{\rm N}} c_{\infty} \cong 0.62 \ zFD^{2/3} v^{-1/6} \omega^{1/2} c_{\infty}$$
(8-12)

This is the *Levich* equation. We can therefore adjust the diffusion limited current i_{lim} conveniently via the rotation rate ω of the electrode. For a reaction in the diffusion limited regime, i.e. at sufficiently high (anodic) or low (cathodic) overpotential, a plot of i_{lim} as a function of $\sqrt{\omega}$ yields a straight line through the origin, which is called *Levich plot*.

¹ Convection-diffusion equation: $\dot{c} = D \cdot \nabla^2 c - \mathbf{u} \cdot \nabla c$, where $c = c(r, \theta, z)$ is the concentration of the species of interest in solution, *D* its diffusivity, and $\mathbf{u} = \mathbf{u}(r, \theta, z)$ the velocity profile of the solution. For the steady state we have $\dot{c} = 0$. We have implicitly assumed that migration effects can be neglected, because electrochemical experiments are commonly performed using a supporting electrolyte (cf. also Chapter V).

Example:

For the study of the oxidation of ferrocyanide in aqueous solution using the RDE at 25°C, we calculate the Nernst diffusion layer thickness δ_N and the limiting current density i_{lim} . The electrode is rotated at 1'500 RPM. The concentration of K₄[Fe(CN)₆] is 5 mM, KCl solution of 1 M is used as supporting electrolyte. The diffusion coefficient of ferrocyanide is $D = 6.7 \cdot 10^{-6} \text{ cm}^2/\text{s}$, the kinematic viscosity of water is $v = 8.9 \cdot 10^{-3} \text{ cm}^2/\text{s}$. With Eq. 8-11 we obtain $\delta_N = 11.0 \,\mu\text{m}$, where we have converted the rotation rate of 1'500 1/min to the angular velocity $\omega = 2\pi f = 157 \, 1/\text{s}$. With the Levich equation (Eq. 8-12) a value of $i_{lim} = 2.93 \, \text{mA/cm}^2$ is calculated.

Having established the situation under the conditions of limiting mass transfer of the reactant to the electrode surface, we can next discuss the general polarization behavior of an RDE, involving effects of charge transfer kinetics and diffusion limitations. We consider an oxidation reaction and study the polarization behavior of the electrode, i.e. the change in current density *i* with increasing overpotential η . If mass transport effects are neglected, the reaction may be typically assumed to follow Butler-Volmer behavior. The corresponding kinetic current density *i*_{kin} increases exponentially at sufficiently high overpotential ($\eta \ge b$). However, the finite diffusive flux of the reactant will lead to a gradual decrease of the reactant concentration at the electrode surface. From Chapter V we recall that this leads to a concentration overpotential η_{conc} , which is related to the diffusion limited current density *i*_{diff} according to:

$$i_{\text{diff}} = i_{\text{lim}} \cdot \exp(-\frac{zF}{RT}\eta_{\text{conc}})$$
(8-13)

For our sample oxidation reaction, the current density in case of pure activation control i_{kin} and pure diffusion control i_{diff} is plotted in **Figure 8-10a** as a function of the overpotential η . The measured current density i_{meas} at a given overpotential η for the combined effects under mixed activation-diffusion control is obtained as follows:

$$\frac{1}{i_{\text{meas}}} = \frac{1}{i_{\text{kin}}} + \frac{1}{i_{\text{diff}}} = \frac{1}{i_{\text{kin}}} + \frac{A}{\sqrt{\omega}}$$
(8-14)

The diffusion-limited current i_{diff} is proportional to the limiting current density i_{lim} , which itself is proportional to $\sqrt{\omega}$ (Levich equation). This means that from a measurement series of polarization curves at different rotation rates ω , we can plot the inverse of the measured current density $1/i_{\text{meas}}$ versus $1/\sqrt{\omega}$ to obtain a linear relationship with slope A and intercept $1/i_{\text{kin}}$. This is the *Koutecký-Levich* plot (**Figure 8-10b**), which allows us to obtain the kinetic current density i_{kin} through extrapolation to $1/\sqrt{\omega} \rightarrow 0$. At high overpotential $\eta \rightarrow \infty$, we reach the limiting current density i_{lim} and in this regime the Levich equation, Eq. 8-12, holds.



Figure 8-10. Model RDE experiment calculated using: $k_0 = 0.002$ cm/s, b = 59.1 mV/decade, c = 5 mM, z = 1, $T = 25^{\circ}$ C, $v = 8.92 \cdot 10^{-3}$ cm²/s, $D = 7 \cdot 10^{-6}$ cm²/s. (a) Polarization curves at different rotation rates. The orange lines represent the measured current i_{meas} , the solid and dotted black line, respectively, the theoretical kinetic current i_{kin} and diffusion limited current i_{diff} . (b) Koutecký–Levich plot, based on values of i_{meas} extracted from (a) at different overpotentials η (vertical gray lines). The dashed line represents the Levich equation (Eq. 8-12). Linear regression analysis according to Eq. 8-14 yields i_{kin} as intercept.

The RDE is used to study the electrochemical kinetics of solution species qualitatively and quantitatively. The electrode is typically made of an inert material, such as gold, glassy carbon or platinum. Also, the electrochemical activity of catalysts for electrochemical conversion reactions are often studied using the RDE. In this case, the electrocatalyst or supported electrocatalyst is deposited as a thin layer on the electrode (and fixed with a thin layer of ionomer, e.g. NafionTM, to prevent it from being washed away during the experiment). In **Figure 8-11** an example of an RDE study of different carbon supported catalysts for the oxygen reduction reaction (ORR) is shown (This is a cathodic reaction, hence the negative current density values). The rotation rate is constant at 1'600 RPM, which entails the same limiting current density of around -6 mA/cm² for the different catalysts. In the kinetic and mixed regime, say at 0.9 V, we observe the highest current density for the Mo-PtNi/C catalyst, which therefore shows the highest activity towards the ORR out of the three catalysts. If we were to extract measured current values at different potentials and arrange the data in a Koutecký-Levich plot, we could extract the kinetic current densities.



Figure 8-11. (a) Carbon supported noble-metal catalyst particles deposited on a glassy carbon electrode for the characterization of their electrocatalytic activity. Often, Nafion[™] is used as binder or top-coat to avoid washing away in the liquid electrolyte. (b) Characterization of the different catalysts towards the oxygen reduction reaction (ORR) in an RDE setup. Electrolyte: O₂ saturated 0.1 M HClO₄, room temperature, sweep rate: 20 mV/s, rotation rate: 1'600 rpm. (Source: Nano Lett 18, 2018, 798)

Appendix A: Response of an RC-Circuit in Cyclic Voltammetry

A cyclic voltammetry experiment is performed on an RC-circuit (Figure 8-A1), which represents the characteristics of an ideal polarizable electrode in an electrolyte solution. We account for the double layer capacitance C of the electrode and the ohmic resistance R of the system.



Figure 8-A1. RC-element with capacitance C and resistance R, to which a potential E(t) is applied.

During the experiment, we apply a potential E(t) to the electrode, starting at the lower potential limit $E_{\rm L}$ and increasing the potential linearly with sweep rate ν , so we have $E(t) = E_{\rm L} + \nu t$. The potential difference across the capacitance $E_{\rm C}$ and across the resistor $E_{\rm R}$ add up to E(t):

$$E(t) = E_{\rm C}(t) + E_{\rm R}(t) = E_{\rm L} + v \cdot t$$
(8-A1)

For the charge on the capacitor we write $Q(t) = C \cdot E_C(t)$. From Ohm's law we have $E_R(t) = I(t) \cdot R$, where $I(t) = \dot{Q}(t)$. After inserting in Eq. 8-A1 and differentiating with respect to time we obtain the following differential equation:

$$\frac{1}{C}I(t) + R\frac{d}{dt}I(t) = v$$
(8-A2)

This is a first-order nonhomogeneous linear ordinary differential equation with constant coefficients, the solution for which is the sum of the solution of the homogeneous equation and a particular solution of the nonhomogeneous equation. The solution of the homogeneous equation is $I_h(t) = A \cdot \exp(-t/\tau)$, where $\tau = RC$ is the characteristic time constant of the RC-circuit. A particular solution of the nonhomogeneous equation is a constant, which is the double layer charging current $I_{DL} = C \cdot v$. The general solution of Eq. 8-A2 is therefore, considering the initial condition I(t=0) = 0:

$$I(t) = Cv(1 - \exp(-\frac{t}{RC}))$$
(8-A3)

We see that the current increases with a characteristic time to the steady state I_{DL} in the forward (anodic) scan. An analogous expression is obtained for the reverse (cathodic) scan.

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Appendix B: Concentration Profile in a Cyclic Voltammetric Experiment

A cyclic voltammetric experiment using a flat electrode is carried out in quiescent solution, thus effects of diffusion affect and, in certain regimes, dominate the measured current over time. We are considering a reaction $Ox + e^- \rightleftharpoons$ Red with fast, i.e. reversible, kinetics, such that the concentrations of Red, c_{Red} , and Ox, c_{Ox} , at the electrode surface (x = 0) are always given by the Nernst equation (such a system is therefore also called 'Nerstian'). When the experiment is started, there is only Red present, $c_{\text{Red}}(x, t=0) = c_0$ and $c_{Ox}(x, t=0) = 0$. The concentration of Ox and Red is therefore the same everywhere for t = 0. The experiment starts with the forward (anodic) sweep up to the upper potential limit, then the potential is swept in cathodic direction as explained in the main text. In the resulting cyclic voltammogram (**Figure 8-B1a**), we choose 8 points for which we plot the concentration profile of Red as a function of Ox and Red, which is what we are assuming here, the concentration of Ox is complementary to that of Red, given by $c_{Ox}(x,t) = c_0 - c_{\text{Red}}(x,t)$.



Figure 8-B1. (a) Cyclic voltammogram of a reaction $Ox + e^- \rightleftharpoons Red (z = 1)$ with reversible kinetics, initially with $c_{Red} = 5 \text{ mM}$ and $c_{Ox} = 0$ (parameters: $T = 25^{\circ}C$, $D = 10^{-6} \text{ cm}^2/\text{s}$, $\nu = \pm 0.1 \text{ V/s}$). (b) Concentration profile of Red as a function from the distance x from the electrode surface, corresponding to points 1 to 8 in the cyclic voltammogram. (Calculated using the DigiElch software)

We see that the gradual depletion of Red in the forward scan, especially after the anodic peak current (point 2), leads to a decrease in the current. We recall from Chapter V that the current is proportional to the concentration gradient at the electrode surface (x = 0), specifically $i = zFD(dc/dx)|_{x=0}$ (here: z = 1). Indeed, we see that the slope of c_{Red} at x = 0 decreases from point 2 to point 4, owing to the increase of the Nernst diffusion layer δ_N and thus the flattening of the concentration profile. There is near-Cottrellian behavior here with $i \propto t^{-0.5}$. After the reversal of the scan direction the current remains anodic for a while (point 5). At point 6 the direction of the current changes from anodic to cathodic, which is in agreement with the slope of c_{Red} at x = 0 changing from positive to negative.

At point 7 the maximum cathodic current is reached. Then its value decreases, again due to depletion of the reactant, in this case Ox. If we were to continue cycling, we would see concentration waves of Ox and Red propagating into the solution, slowly dissipating according to Fick's second law of diffusion, $\dot{c}(x,t) = D \cdot \nabla^2 c(x,t)$ (cf. Chapter V).



Figure 8-B2. If the cyclic voltammetry experiment shown in **Figure 8-B1** were to be stopped at point 4 where $E - E^{\circ'} = 0.3$ V by disconneting the working electrode from the potentiostat, the concentrations of Ox and Red at the electrode surface (*x*=0) would relax over time as indicated in (a). Since we are considering an ideally reversible (= Nernstian) process, the electrode potential would drop as indicated in (b). For the cyclic voltammetry experiment with potential sweep in cathodic direction after reaching the upper potential limit of 0.3 V, the potential needs to follow the dotted line (linear decrease with v = -0.1 V/s), which requires an anodic current up to ~3 s after the reversal of the scan direction. (Calculated by numerically solving the non-stationary diffusion equation using a finite difference method to obtain $c_{Ox}(x,t)$ and $c_{Red}(x,t)$. The first few calculated points in (b) are shown with symbols.)

The situation after the reversal of the scan direction at the upper potential limit of $E_{\rm U} = 0.3$ V deserves a bit more attention. Why does the current remain anodic for a while before flipping to cathodic current? To understand this behavior, we consider a second experiment, which we stop when the potential reaches $E_{\rm U}$ by interrupting the current flow. How will the potential of the electrode react and develop? When the electrode potential $E - E^{\circ'}$ reaches $E_{\rm U} = 0.3$ V, the concentration of Red and Ox at the surface of the electrode (x=0) is given by

$$E - E^{\circ'} = \frac{RT}{zF} \ln(\frac{c_{\text{Ox}}}{c_{\text{Red}}})$$
(8-B1)

since we are considering a Nernstian process. With $c_{Ox} + c_{Red} = c_0 = 5$ mM we obtain $c_{Red} = 4.2 \cdot 10^{-8}$ M and $c_{Ox} \approx c_0 = 5 \cdot 10^{-3}$ M. Also, there is a pronounced concentration gradient of both species, illustrated in **Figure 8-B1b** for Red at point 4. Consequently, now that the current flow is stopped, the concentration profile will relax quickly as Red is going to diffuse back from the bulk and Ox is going to diffuse into the bulk (remember that in the bulk $c_{Red} = c_0$ and $c_{Ox} = 0$). Therefore the concentrations of Ox and Red at the electrode surface (*x*=0) are going to change with time as

illustrated in **Figure 8-B2a**. As a result, the electrode potential $E - E^{\circ}$ is going to change according to Eq. 8-B1, showing a steep initial drop and then a more gradual change (**Figure 8-B2b**). In case of our cyclic voltammetry experiment, the potential, after reversal of the scan direction at 0.3 V, will have to follow the dotted curve, corresponding to a (cathodic) scan rate of v = -0.1 V/s. Therefore, in order to follow this potential course, the potentiostat needs to drive an anodic current for ~3 s to maintain the concentrations of Ox and Red such that they conform with Eq. 8-B1. After ~3 s, a cathodic current is required for the potential to follow the linear sweep towards more negative potentials. The electrode potential is around 0.025 V when the two curves cross in **Figure 8-B2b**. This corresponds the point in the cyclic voltammogram of **Figure 8-B1a** when the current passes through zero.

Appendix C: Steady-State Cyclic Voltammograms

The cyclic voltammograms in **Figure 8-6** essentially only show the first anodic and cathodic scan (1 cycle) with an asymmetric concentration of Ox and Red in the bulk, namely $c_{red} = 5$ mM and $c_{ox} = 0$. In cyclic voltammetry, cycling is typically repeated until a steady-state voltammogram is obtained, which may take 10 cycles or so. Steady-state voltammograms obviously look different than the one obtained in the first cycle. For illustration, **Figure 8-C1** shows steady-state voltammograms for a reversible, quasi-reversible, and irreversible process with equimolar concentration of Ox and Red. The voltammograms are therefore symmetric with regard to the formal potential $E^{\circ'}$. As above, we see the separation of the peaks increasing and the peak current decreasing with increasing irreversibility.



Figure 8-C1. Steady-state cyclic voltammograms of a redox couple $Ox + e^- \rightleftharpoons Red$ in solution. Reversible reaction: $k_0 \gtrsim 0.1 \text{ cm/s}$, quasi-reversible: $k_0 = 2 \cdot 10^{-4} \text{ cm/s}$, irreversible: $k_0 = 10^{-5} \text{ cm/s}$ (Calculated using the DigiElch software; parameters: $T = 25^{\circ}\text{C}$, $c_{red}(\text{bulk}) = c_{ox}(\text{bulk}) = 2.5 \text{ mM}$, $D = 10^{-6} \text{ cm}^2/\text{s}$, $\nu = 0.1 \text{ V/s}$; capacitive currents are neglected, steady state reached after ~5 cycles).

Appendix D: Electrode Characterization in the Polymer Electrolyte Fuel Cell

The main components of the polymer electrolyte fuel cell (PEFC) are the ion conducting membrane and the two gas diffusion electrodes, where at the interface between membrane and electrodes the catalysts layers are deposited, which contain the electrocatalyst and ionomer, and which are porous to allow the access of fuel and oxidant (cf. Chapter VII). To study the properties of the two electrodes independently, for example by performing cyclic voltammetry, a reference electrode should be used. It is, however, not straightforward - but not impossible - to introduce a reference electrode into a PEFC. Therefore, cyclic voltammetry of fuel cell electrodes is commonly performed by purging the compartment of the working electrode (the fuel or air electrode of the fuel cell) with nitrogen to suppress faradaic reactions. The opposite electrode is then purged with hydrogen to act as a combined counter and reference electrode (Figure 8-C1). With a Pt electrocatalyst, the obtained potential is very stable and deviates only by a few millivolts upon the passage of current. With this configuration, cyclic voltammetry or CO-stripping voltammetry can be performed on the working electrode (cf. Figure 8-8b in the main text). If this happens to be the fuel cell cathode (air electrode), the setup can subsequently be flipped to make the fuel cell anode (fuel electrode) the working electrode by flushing it with nitrogen, and the H_2 flushed counter / reference electrode is then the fuel cell cathode.



Figure 8-C1. Experimental setup around the membrane electrode assembly (MEA) of a polymer electrolyte fuel cell to allow the study of the electrochemical characteristics of the catalyst layer. The working electrode (WE) is hereby flushed with nitrogen, the opposite electrode is flushed with hydrogen and serves as a combined counter electrode (CE) and reference electrode (RE).

Chapter IX

Corrosion & Corrosion Protection

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Corrosion is an important problem in many practical uses of materials. Corrosion and its prevention are assoiciated with a sizeable economic footprint. Important artificial structures, such as automobiles, bridges, buildings, machinery, pipelines, ships, etc., are often susceptible to corrosion and therefore appropriate measures need to be taken to increase their service life. Corrosion is not restricted to metals, other materials can also undergo corrosion. For example, 'normal' soda-lime glass readily corrodes when exposed to alkaline solutions, especially at elevated temperatures. Polymers can 'corrode' when exposed to an aggressive environment, yet in most cases the phenomenon is not referred to as 'corrosion' in that context. In this Chapter the phenomenon of metal corrosion will be discussed. Metals not only corrode chemically by direct reaction with oxygen and water from the environment, but also through an electrochemical process, where the anodic reaction, the dissolution of the metal, is spatially separated from the cathodic reaction, for example the reduction of oxygen. Therefore, in contrast to most electrochemical phenomena discussed so far in this course, to reduce corrosion we aim to prevent the electrochemical reaction from happening by minimizing the flow of charge.

1 Corrosion Essentials

Corrosion is the unwanted reaction of a material with its environment causing damage to the component. This may have aesthetic or functional consequences. An example of the former is the development of rust spots on (so-called) stainless steel cutlery. This is not harmful and does not impair the function of fork, knife and spoon, but it is of course an unwanted effect. Damage to engineered structures and components due to corrosion is very common. Almost all steel structures need to be protected against corrosion and often replaced after some time in service.

The primary and most fundamental step in corrosion is the oxidation of the metal to its nearest stable oxidation state through the reaction with oxygen. This leads to the formation of hydroxides, oxides or mixtures thereof. In some cases, such as aluminium and titanium, the corrosion products form dense insulating layers, which slows down the reaction of the underlying metal, thus protecting it from further corrosion. In contrast to this chemical corrosion reaction, in electrochemical corrosion the (anodic) metal dissolution and corresponding cathodic reaction take place in different locations on the metal surface, whereby the two regions are connected electronically via the workpiece and ionically via a moisture film on the metal or an electrolyte, in which the metal is immersed. This is the archetypical corrosion reaction of iron or steel, where normally the (hydr)oxides do not stick well to the metal surface (except under some specific conditions, see below) and thus cannot form a protective layer. Depending on the pH of the solution and the availability of oxygen (water is always needed), the predominant cathodic reaction in corrosion is either the hydrogen evolution

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reaction (HER) (H⁺-type corrosion) or the oxygen reduction reaction (ORR) (O_2 -type corrosion). The reactions occurring during iron and steel corrosion can therefore be written as follows:

anodic metal dissolution	Fe	\rightarrow	$Fe^{2+} + 2 e^{-}$	(9-1)
H ⁺ type corrosion (HER)	$2 H^+ + 2 e^-$	\rightarrow	H ₂	(9-2)
O ₂ type corrosion (ORR)	$O_2 + 2 H_2O + 4 e^-$	\rightarrow	4 OH^-	(9-3)

The thermodynamics and kinetics of metal corrosion will be discussed in detail in forthcoming sections. We start here by qualitatively looking at the reactions occurring during iron / carbon steel¹ corrosion according to O₂-type mechanism. On the metal surface in contact with moisture, iron oxidation (Reaction 9-1) takes place in anodic regions, whereas oxygen is reduced in cathodic regions (**Figure 9-1a**). In the primary reaction, therefore, iron(II) hydroxide, Fe(OH)₂, is formed, which has a low solubility of $1.59 \cdot 10^{-5}$ mol/L at room temperature² and precipitates on the metal surface. As we can see, the electrons for the ORR are supplied from the anodic iron dissolution process via the metal itself. Therefore, the electrochemical corrosion of Fe can also be represented as an electrochemical cell with shorted Fe electrodes (**Figure 9-1b**).



Figure 9-1. (a) Corrosion ('rusting') of an iron or steel component upon exposure to humidity and oxygen (at intermediate pH range). In the primary corrosion reaction, Fe is oxidized to Fe^{2+} in the anodic region of the metal, oxygen is reduced to OH⁻ in cathodic areas where O₂ supply can be sustained, resulting in the precipitation of Fe(OH)₂. The iron gets further oxidized to Fe^{3+} in a secondary, chemical reaction with O₂ to form FeOOH. This and its dehydrated forms is known to us as 'rust'. (b) Schematic of the iron corrosion process, represented as an electrochemical cell with shorted electrodes.

The question is: what makes a region on the metal anodic or cathodic ? For the ORR to occur, access of oxygen is required. Therefore, areas near the boundary of water droplets tend to be cathodic. Areas with poor access of oxygen thus become anodic.

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¹ Carbon steel contains iron and carbon (<2.1 %) with a low content of alloying elements, commonly manganese and silicon with a concentration of less than 1 wt-%.

² source: en.wikipedia.org/wiki/Iron(II) hydroxide

The primary corrosion reaction of iron is therefore an electrochemical process, leading to the formation of $Fe(II)(OH)_2$, which can be further oxidized to Fe(III)OOH in a chemical reaction with O₂. The iron oxide-hydroxide can dehydrate with the end product being Fe_2O_3 . We know these iron (hydr)oxides as 'rust'. Hydrated Fe_2O_3 can also be written as $Fe_2O_3 \bullet xH_2O$, with various degrees of hydration *x*. The overall process of iron corrosion is summarized as follows:

primary reaction (electrochemical)	$Fe + H_2O + \frac{1}{2}O_2$	\rightarrow	Fe(OH) ₂	(9-4)
a a a martine (alternical)	$2 \text{ Fe}(\text{OH})_2 + \frac{1}{2} \text{ O}_2$	\rightarrow	$2 \text{ FeOOH} + \text{H}_2\text{O}$	(9-5)
secondary reactions (chemical)	2 FeOOH	\rightarrow	$Fe_2O_3 + H_2O$	(9-6)

Rust does not act as a stable barrier against further corrosion. As the hydrated iron oxide layer forms, it tends to flake off instead of adhering to the substrate's surface.

The reader might ask: since oxygen has sufficient driving force to oxidize Fe(II) to Fe(III) chemically, why does Fe not get electrochemically oxidized by O_2 all the way to Fe(III) ? To understand the reason, we recall the Frost diagram of iron from Chapter II. Fe²⁺ is thermodynamically much more stable than Fe(s) and Fe³⁺. Therefore, whenever Fe³⁺ forms near metallic Fe, the two species have a strong tendency to comproportionate to Fe²⁺. Fe³⁺ will only be found at some distance from the metal. Once Fe(III) precipitates as Fe₂O₃ (in a certain pH range, see below) it may deposit on the metal. Its reaction with Fe(0) is then strongly kinetically hindered.

Most metals, except some noble metals, undergo corrosion reactions in the presence of water and oxygen or other compounds found in the environment. For illustrative purposes, the prominent behavior of two elements will be described in the following as examples. Copper and copper alloys, such as bronze, form a *patina*, which typically has a green of bluish-green appearance (cf. for example the Statue of Liberty in New York). The copper patina is composed of (hydrated) copper oxides, sometimes also containing sulfates and chlorides (near the sea). It is relatively stable and acts as a protective barrier for the underlying copper or bronze. Silver is a relatively noble metal, but it tends to react with sulfur-containing substances found in the air, thereby becoming *tarnished*. These silver sulfides are black and will make silver cutlery look unsightly.

1.1 Thermodnamics: Pourbaix diagrams

For the analysis of corrosion problems, we first have to address the question: is the reaction of the material of interest with its environment thermodynamically favorable or not? A widely used representation of the thermodynamic stability region of a metal to acid or oxygen corrosion are potential-pH diagrams, introduced by *Pourbaix*, in which regions of thermodynamic stability of different redox states of an element are identified, most typically in an aqueous environment. They

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are therefore also referred to as predominance area diagrams. We consider a hypothetical metallic element Me as an example to discuss the general features of a Pourbaix diagram (**Figure 9-2a**). We identify three species: metallic Me, the hydrated ion $Me^{z+}(aq)$, and the solid $Me(OH)_z(s)$.



Figure 9-2. (a) Hypothetical Pourbaix diagram of metal Me with three predominant species, drawn with $E^{\circ}(Me^{z+}/Me) = -0.2 \text{ V}$, $\Delta_t G^{\circ}(Me^{z+}/Me(OH)_z) = 85.6 \text{ kJ/mol}$, z = 2, $T = 25^{\circ}\text{C}$. The different lines correspond to different concentrations of Me^{z+} in solution, expressed as pMe = $-\log(a_{Me})$. The slanted lines show the electrochemical stability region of water for $p(H_2) = p(O_2) = 1 \text{ bara}$. (b) Pourbaix diagram of iron at 25°C, with soluble species Fe²⁺, Fe³⁺, and HFeO₂⁻ at a concentration of 1 mM (pFe = 3), the metal Fe, and the (hydr)oxides Fe(OH)₂, Fe₃O₄ and Fe₂O₃ (adapted from: en.wikipedia.org/wiki/Pourbaix diagram, accessed 06-03-2022).

The boundaries separating predominance areas of species from one another represent the equilibrium of a chemical or electrochemical reaction. A vertical line describes an acid-base reaction, in our case here:

$$Me^{z^{+}}(aq) + z H_{2}O \leftrightarrows Me(OH)_{z}(s) + z H^{+}$$
(9-7)

For this acid-base reaction, the following relation between concentrations of H^+ and Me^{z^+} holds (law of mass action):

$$K_{a} = \frac{c(\mathrm{H}^{+})^{z}}{c(\mathrm{Me}^{z^{+}})}, \quad \mathrm{p}K_{a} = z \cdot \mathrm{p}\mathrm{H} - \mathrm{p}\mathrm{Me}$$
(9-8)

where K_a is the acid dissociation constant and $pK_a = -\log(K_a)$. We have used concentrations here instead of activities, because for corrosion problems we expect the concentrations of dissolved species to be low. The compound Me(OH)_z does not appear in the equation, because it is a solid, hence its activity is unity. Also, $a(H_2O) \approx 1$ because we are dealing with a dilute solution. With Eq.

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9-8 the position, i.e. the pH, of the vertical line is obtained from K_a and the concentration of Me^{z^+} in solution, $c(Me^{z^+})$, for which we can also write $pMe = -\log(c(Me^{z^+}))$. For a decrease in $c(Me^{z^+})$ by an order of magnitude, the vertical line shifts right by one *z*-th of a pH unit. Often, in corrosion problems, soluble species are taken to have a concentration of 10^{-6} M. For a reaction in the alkaline region of the pH-scale, we should write the acid-base reaction as

$$\operatorname{Me}^{z+}(\operatorname{aq}) + z \operatorname{OH}^{-} \leftrightarrows \operatorname{Me}(\operatorname{OH})_{z}(s)$$
 (9-9)

Horizontal lines describe an electrochemical reaction, here between the metal Me and the dissolved species Me^{z+} in solution:

$$Me^{z^+}(aq) + z e^- \leftrightarrows Me(s)$$
 (9-10)

The position of the horizontal line is the equilibrium potential of $E(Me^{z+}/Me)$ given by the Nernst equation:

$$E(Me^{z^{+}}/Me) = E^{\circ}(Me^{z^{+}}/Me) + \frac{RT}{zF}\ln(c(Me^{z^{+}}))$$
(9-11)

The value of *E* decreases by 59.2 mV / *z* at room temperature for every drop in $c(Me^{z^+})$ by a factor of 10. A slanted line represents a reaction involving both H⁺ or OH⁻ and electrons. For our sample system here, we have:

$$Me(s) + z H_2O \leftrightarrows Me(OH)_{\varepsilon}(s) + z H^* + z e^-$$
(9-12)

or an equivalent expression balanced with OH⁻. The expression describing the equilibrium is again a Nernst equation, which in this case also includes a pH term, and only a pH term because all other species are solids and, as usual, $a(H_2O) \approx 1$:

$$E(\text{Me(OH)}_{z}/\text{Me}) = E^{\circ}(\text{Me(OH)}_{z}/\text{Me}) - \ln(10)\frac{RT}{F}\text{pH}$$
(9-13)

For each increase in pH by one unit, the equilibrium potential *E* drops by 59.2 mV at $25^{\circ}C^{1}$. This slope is well known to us as the pH dependence of the reversible potential of the reactions 2 H⁺

¹ The slope might be different for another reaction stoichiometry. Essentially, it depends on the ratio of the stoichiometric factors of H^+ and $e^-(z)$.

+ 2 e⁻ \leftrightarrows H₂ and $\frac{1}{2}$ O₂ + 2 H⁺ + 2 e⁻ \leftrightarrows H₂O (cf. Chapter II). The equilibrium lines characterizing these reactions are normally included in Pourbaix diagrams. They are vertically separated by the familiar value of 1.23 V for $p(H_2) = p(O_2) = 1$ bar. In the area below the H⁺/H₂ line, there is a thermodynamic driving force for H⁺-type corrosion to take place, and below the O₂/H₂O line for O₂-type corrosion.

Most metals have more complicated Pourbaix diagrams than the hypotetical one shown in **Figure 9-2a**. The Pourbaix diagram of iron is shown in **Figure 9-2b**. In fact, we can identify qualitatively similar features. The metal Fe is stable at low potential. It is therefore *immune* against corrosion in this region. The two soluble species in acidic solution are Fe^{2+} and Fe^{3+} . Iron readily corrodes in this region. On the more alkaline side of the diagram, iron shows different (hydr)oxides with oxidation state +II, $Fe(OH)_2$, oxidation state +III, Fe_2O_3 , and a compound with mixed oxidation states of Fe(II) and Fe(III), Fe_3O_4 (magnetite). The compounds indicated are the most stable ones under the prevailing conditions, However, as we have seen above, the oxides may also be hydrated, represented for example by FeOOH or $Fe_2O_3 \bullet x H_2O$. In principle, iron forms a passive (hydr)oxide layer under these conditions. However, as discussed earlier, the oxides do not stick well to the metal and cannot protect it from further corrosion. Many other metals, such as aluminium, titanium, niobium or chromium, form stable, dense oxide layers, which render the metal passive, which is an effective mechanism for corrosion protection (see below).

Pourbaix diagrams are usually discussed in the context of metal corrosion, yet it is also a useful tool to map stability regions of non-metals, such as nitrogen, chlorine, sulfur, etc. From Chapter II, we recall that Frost diagrams serve a similar purpose in that they indicate thermodynamic stability features, yet at a given pH. Hence, Frost diagrams correspond to the situation along vertical lines in a Pourbaix diagram.

1.2 Kinetics: corrosion rate

Thermodynamics establish if a reaction *can* happen, whether it *will* happen depends on the kinetics of the process. A corrosion reaction may be very fast. For example, when an iron bar is immersed in an acid of ~1 M concentration, hydrogen evolution takes place readily with bubbles forming visibly. Also, a fresh metallic aluminium surface exposed to air develops an oxide layer of a few nm thickness in much less than a second. Once the dense aluminium oxide layer has formed, further oxidation is strongly hindered. Thus, the aluminium corrosion rate drops to almost zero and the metal structure is very well protected against weathering. In general, the kinetics of corrosion depend on the charge transfer kinetics as well as on mass transport phenomena (cf. Chapter V). The corrosion of iron is discussed in the following in detail, as it is the most relevant corrosion reaction.

Also, since the formed iron (hydr)oxide does not stick well to the metal surface, we can, at least initially, assume that the dissolution of iron is not hindered by the presence of an oxide layer. Fundamentally, the reaction $Fe \rightarrow Fe^{2+} + 2e^-$ follows a mechanism described by Butler-Volmer kinetics. The equilibrium potential for the couple Fe^{2+}/Fe at 25°C and a Fe^{2+} concentration of 1 μ M is $E_{Fe} = E_{Fe}^{\circ} + RT/2F \cdot \ln(c(Fe^{2+})) = -0.44 \text{ V} - 6 \cdot 59.2 \text{ mV} / 2 = -0.62 \text{ V}$. An increase in (anodic) overpotential leads to a strong increase in the rate of iron dissolution (**Figure 9-3a**). The corrosion reaction is assumed to take place according to the O₂-mechanism, hence the cathodic reaction is the ORR. The equilibrium potential E_0 of the O₂/H₂O couple depends on the pH and the partial pressure of O₂. At pH 7 and $p(O_2) = 1$ bar the value is $E_0 = E_0^{\circ} + RT/F \cdot \ln(c(H^+)) = E_0^{\circ} - 59.2 \text{ mV} \cdot \text{pH} =$ $+1.23 \text{ V} - 7 \cdot 59.2 \text{ mV} = +0.82 \text{ V}$. The ORR also follows Butler-Volmer type kinetics at low overpotential. However, owing to the limited access of oxygen to cathodic reaction sites (cf. **Figure 9-1a**), the reaction quickly reaches mass transport limitation, corresponding to a limiting current density of $i_{O2,\text{lim}} = 4F \cdot D(O_2) \cdot c(O_2) / \delta_N$, where δ_N is the Nernst diffusion layer thickness (cf. Chapter V).



Figure 9-3. (a) Polarization diagram for the iron dissolution reaction with equilibrium potential E_{Fe} and the oxygen reduction reaction (ORR) at various pH values, which influences the oxygen equilibrium potential E_0 . The limiting ORR current density $i_{02,\text{lim}}$ is given by the diffusion limitation of O₂ to the electrode. The corrosion potential E_{corr} is the mixed potential that establishes where the anodic reaction rate i_+ is equal to the cathodic reaction rate i_- , which is then the corrosion current density i_{corr} . (b) Evans diagram, showing the polarization curves for iron oxidation and ORR in a Tafel representation. Here, the situation for different concentrations of dissolved oxygen is shown, leading to a variation of E_0 and different limiting ORR current densities.

During iron corrosion the anodic and the cathodic areas of the workpiece are essentially shorted (cf. **Figure 9-1b**), and the potential of the metal is therefore uniform (we assume negligible electronic resistance). The potential that establishes is the so-called *corrosion potential* E_{corr} , which is characterized in that at this potential the anodic reaction rate (= current) is equal to the cathodic reaction rate / current, because the electron transfer takes place within the metal and there is no net

external current. E_{corr} is a *mixed potential*, established by the balance between anodic and cathodic half-cell reactions. This is not an equilibrium potential, but a rest potential. The corresponding current density is the *corrosion current density* i_{corr} . As it is a priori not known which part of a work piece is anodic and which is cathodic, the area is usually taken to be the exposed metal area.

In the literature, different representations of the anodic and cathodic polarization curves describing a corrosion reaction can be found. An often-found representation is the *Evans* diagram (**Figure 9-3b**), a plot of *E* vs. log(|*i*|). The section of the curves showing straight lines therefore represent Tafel behavior of the half-cell reactions. Different concentrations of dissolved oxygen lead to different limiting current densities of the ORR. This has a direct effect on the resulting corrosion potential E_{corr} and corrosion current density i_{corr} . Also, the reader may note that E_0 decreases by 59.2 mV / 4 = 14.8 mV at 25°C and given pH per 10-fold drop in the concentration of dissolved oxygen. This change is small and does not influence the current density in the limiting current regime. We can imagine that this description of reaction kinetics pertains to an experiment under controlled laboratory conditions. In reality, the Nernst diffusion layer in a corrosion system is ill-defined and the concentration of oxygen is expected to vary between different areas of the workpiece. The ORR kinetics can therefore be understood to represent the situation at a given location of a workpiece.

The illustration depicted in **Figure 9-3** describes an O₂-type corrosion process. The situation for H⁺type corrosion is analogous, the cathodic reaction is then the H₂ evolution reaction, and the equilibrium potential $E_{\rm H}$ also varies in well-known manner with pH. Under strongly acidic conditions, protons are abundant and mass transport limitations are unlikely to occur, unlike in mild acid, where a limiting current density $i_{\rm H+,lim}$ may be observed.

Example:

The corrosion rate is often expressed in mm per year, a relevant quantity to estimate the lifetime of a loadbearing structure. Assuming a uniform corrosion rate of steel (\approx iron), what corrosion current density i_{corr} does a corrosion rate of v = 0.05 mm/year correspond to ? First, the corrosion rate \dot{n} of iron in mol/s is calculated: $\dot{n} = v \rho(Fe) / M(Fe)$, where $\rho(Fe) = 7.87$ g/cm³ is the density of iron, and M(Fe) = 55.8 g/mol. Insertion of values yields $\dot{n} = 2.24 \cdot 10^{-11}$ mol/s. Finally, we use Faraday's law to calculate the corresponding corrosion current density $i_{corr} = \dot{n} z F = 4.32 \mu A/cm^2$. For the reaction Fe \rightarrow Fe²⁺ + 2 e⁻ we have z = 2.
2 Corrosion Protection

The protection of metal structures against corrosion requires a major economical effort. Since the main constituent of steel, iron, is inherently susceptible to corrosion under ambient conditions, in particular when exposed to sea water, nearly all steel structures need to be protected against corrosion in one way or another. This applies to many other metals as well, such as copper, but the focus of corrosion protection measures discussed here is mainly directed at steel. There are different conceptual approaches for corrosion protection. Some methods aim at modifying the corrosion potential such that the metal becomes immune against corrosion. In this case, corrosion becomes thermodynamically unfavorable. In other methods the corrosion rate is sought to be minimized in various ways, thus reducing the rate of corrosion.

2.1 Inhibitors

A corrosion inhibitor is a compound that is added to the fluid which the metal part to be protected comes in contact with. It adsorbs on the metal surface and decreases the rate of metal oxidation by decreasing the rate of oxygen (or water) reduction, or by shifting the metal potential into the passive region (cf. below). Inhibitors are used primarily for acidic electrolyte solutions, sometimes also for neutral ones. Various organic compounds with -OH, -SH, $-NH_2$, -COOH, etc., as the functional groups are used as inhibitors, for example hexamine or thiourea. The adsorption of the inhibitor on the metal surface can be characterized by the coverage θ , where $\theta = 1$ corresponds to a monolayer coverage. Typical concentration of inhibitors is in the range of mM. The reduction in metal corrosion rate can be described by a decrease of the exchange current density i_0 according to $i_0 = (1-\theta) i_0^*$, where i_0^* is the exchange current density for the bare metal surface.

A common mechanistic description of the coverage θ_A of a compound A as a function of its concentration c_A in solution (unit: mol/L) is given with the *Langmuir adsorption isotherm*

$$\theta_{\rm A} = \frac{K_{\rm A}c_{\rm A}}{1 + K_{\rm A}c_{\rm A}} \tag{9-14}$$

where K_A is the adsorption constant (unit: L/mol) (cf. **Appendix A** for a derivation of the Langmuir isotherm). At low concentration, $K_Ac_A \ll 1$, the coverage is proportional to c_A , whereas at high concentration, $K_Ac_A \gg 1$, the coverage approaches 1. Therefore, the Langmuir isotherm is limited to a maximum of monolayer coverage.

2.2 Passivation

The formation of a dense oxide layer on the metal can reduce the corrosion rate drastically by minimizing the exposure of the metal to oxygen and humidity. As mentioned above, some metals, especially such with low reduction potentials, e.g. aluminium and titanium, develop dense, insulating oxides. Magnesium also gets easily oxidized, but its oxide layer is porous and does not provide an effective barrier against the corroding medium. The thickness of the oxide layer can be increased artificially by anodizing, which involves passing an anodic current through the workpiece, whereby the metal is oxidized to greater depth. In this way, the oxide layer thickness can be increased to the micrometer level.



Figure 9-4. Polarization diagram for a steel with active, passive and transpassive region, with oxygen reduction as the cathodic reaction. The system transitions to the passive region when the current density exceeds the critical current density i_{crit} . The corrosion current density for a passivated metal i'_{corr} with corrosion potential E'_{corr} is much smaller than that for a metal in the active rection i_{corr} with corrosion potential E_{corr} . The passive layer breaks down in the transpassive region. In electrolytes containing chloride ions, steels can undergo pitting corrosion at relatively low potentials.

Passivation of steels is possible under certain conditions. The polarization behavior of a steel that can be passivated is shown in **Figure 9-4**. Starting from the reversible potential with a clean, pristine surface, metal dissolution increases strongly upon polarization in anodic direction (such an experiment is performed with a potentiostat). This is the *active* region on the potential scale. If the rate of metal dissolution exceeds some critical value, characterized by the critical current density *i*_{crit}, the local concentration of metal ions near the surface may exceed the solubility limit of the metal hydroxide or oxide, which will then deposit as a layer on the metal surface. As a result, the corrosion rate drops precipitously, perhaps by several orders of magnitude, as the (hydr)oxide layer forms a protective film, the *passive layer*. In this *passive* region, only a small residual current is observed, which, in the case of Fe, corresponds to the transport of Fe-ions through the passivating layer to the interface between the (hydr)oxide layer and the electrolyte, where it may contribute to the slow growth of the passive film or simply dissolve into the solution. The current increase in the

transpassive region may be due to a disruption of the passive film and further metal dissolution. Also, the oxygen evolution reaction may set in, if the potential is above the equilibrium potential E_0 . This requires some electronic conductivity of the oxide film, which is the case on iron, chromium, nickel, cobalt or zinc. On metals with very poorly conducting oxide layers, no transpassive region is observed. The passive layer of titanium is semi-conducting, that of aluminium non-conducting. On steels, under certain conditions, there may be a sudden increase in the corrosion rate in the passive region, with is due to a local corrosion phenomenon: *pitting corrosion* (see below).

In a corrosion system with a corresponding cathodic reaction, such as the ORR, the corrosion potential of the steel may be in the active region, E_{corr} , for an equal anodic and cathodic reaction rate (**Figure 9-4**). The resulting corrosion current density i_{corr} is high. For a passivated metal, there is a stable corrosion potential at higher value, E'_{corr} , in the passive region where the corrosion current density i'_{corr} is much lower. If the passive layer is damaged, for example in the form of a scratch, the exposed metal can undergo *repassivation* when the corrosion potential of the workpiece remains in the passive region. The corrosion protection is thus re-established. Maintaining the potential of the metal in the passive region can also be accomplished with a power supply. Since the potential is positive of the active region, this method is also referred to as *anodic protection* of the metal.



Figure 9-5. (a) Critical current density for passivation i_{crit} at room temperature for various elements as a function of pH (Source: Lecture Notes, Prof. H. Böhni, ibwk, ETH, ~1993). (b) Mechanism of pitting corrosion, where metal dissolution takes place in the pit and oxygen reduction in the metal area covered by an electronically conducting passive layer.

In practical applications, there are several ways to promote passivation of steels. From the Pourbaix diagram of iron (**Figure 9-2b**) we see that the formation of iron hydroxides and oxides is thermodynamically favored under alkaline conditions. The high concentration of OH^- facilitates passive layer formation. OH^- is formed in the ORR, thus the presence of oxygen and water promotes passivation. This is exploited in concrete with rebar (= reinforcement bar) steel. The concrete creates

a corrosive alkaline environment, which generates a compact and adherent passive film on the steel. The corrosion potential of rebar in concrete at a pH of ~12 is in the range between -0.4 and 0.0 V. The Pourbaix diagram indicates that this lies well within the passive region of iron. Passivation is facilitated under alkaline conditions, evidenced by the decrease of the critical current density *i*_{crit} with increase in pH (**Figure 9-5a**). This is not only true for iron, but even more so for chromium and nickel. At a given pH, *i*_{crit} is much lower for nickel and chromium than for iron. Therefore, *stainless steels* typically contain chromium and nickel, as the presence of these alloying elements greatly facilitates passivation and enables the formation of dense protective oxide layers. A selection of common stainless steels is given in **Table 9-2**. The most widely used stainless steel 1.4301, for example in cutlery and kitchen countertops, contains 18% chromium and 10% nickel. It has been introduced commercially at the beginning of the 20th century.

Table 9-1. Common stainless steels. (Source: Lecture Notes, Prof. H. Böhni, ibwk, ETH, ~1993; dew-stahl.com, accessed 28-03-2022).

EN	AISI /	Composition	Туре	Comment	
number	ASIM	1	vı		
1.4301	304	X5CrNi18-10	austenitic	all-purpose, e.g. food industry	
1.4401	316	X5CrNiMo17-12-2	austenitic	increased resistance to pitting	
1.4404	316L	X2CrNiMo17-12-2	austenitic	low carbon, better weldability	
1.4512	409	X2CrTi12	ferritic	car exhaust	
1.4116	440A	X50CrMoV15	martensitic ^a	kitchen knives	
1.4417	315	X2CrNiMoSi19-5	duplex ^b	high chemical & mechanical resistance	

^a can be hardened and tempered

^b two-phase structure containing a ferritic and austenitic phase in about equal proportions

A particularly challenging environment for steels is sea water, locations with sea water spray, or other chloride containing environments, for example in indoor swimming pools. The presence of Cl⁻ promotes pitting corrosion, a phenomenon where the steel develops local spots with high rates of corrosion. Chloride attacks thin or otherwise weak spots in the oxide layer, for example where there are inclusions, i.e. imperfections in the metal. This leads to the formation of small anodic areas with metal corrosion surrounded by a large cathodic area of passive metal (Figure 9-5b). Once the process starts, corrosion occurs primarily at the anodic sites and a corrosion pit forms and grows. The dissolution of iron and accumulation of Fe²⁺ in the pit leads to a local drop in pH because of the acidic properties of hydrated ferrous iron, $[Fe(H_2O)_6]^{2+} \Rightarrow [Fe(H_2O)_6OH]^+ + H^+$. In addition, owing to the local electric field, Cl⁻ ions migrate into the pit, and the diffusion of oxygen into the pit is diffusion limited. All these phenomena impede re-passivation. The oxide layer is electronically conductive, thus a large surface area of the steel can act as a cathodic reaction site, thereby promoting the pitting of the workpiece. Stainless steels with improved resistance against pitting corrosion contain molybdenum as alloying element (Table 9-2), as it enhances the passive film resistance. In order to account for the influence of chloride ions on the thermodynamics of iron, modified Pourbaix diagrams involving chloride compounds can be constructed. Complexation of metal ions with anions, e.g. chloride, in solution may stabilize the metal ions and prevent the formation of solid, passivating products.

2.3 Protective coatings

Perhaps the most straightforward way to protect steel or another metal against corrosion is the application of a dense protective coating, which acts as a barrier against the corrosive environment. A layer of paint that completely coats the steel structure does not allow or at least minimizes the access of humidity and oxygen, or other corrosive substances. This is a very common method for protecting ships against corrosion, which is more challenging in an environment with sea water and salt spray. The layer of paint has to be defect-free, otherwise the underlying metal is exposed and will readily corrode (**Figure 9-6a**). Another coating type is enamel, which is a glass-type layer on a metal substrate. The protective role of enamel has been used since the 18th century in everyday objects, such as cooking vessels. Coatings with another metal is also common. Chrome plating provides corrosion resistance and is also used for hard as well as decorative coatings. For improved adhesion on steel, nickel is used as an intermediate layer before chromium is plated on top (**Figure 9-6b**).



Figure 9-6. (a) A paint layer can provide effective protection against corrosion of the underlying metal, but only if it is not damaged. (b) Chrome plating provides protection against corrosion of the underlying steel if the layer is dense and intact. A nickel interlayer promotes the adhesion of the chromium layer. (c) Mechanism of corrosion protection in galvanized steel. The less noble Zn provides electrons for the ORR, thereby protecting the iron cathodically. (d) Sn is more noble compared to Fe, hence it promotes corrosion of the steel if the Sn layer is damaged.

A very widely used method to protect (mild) steel from corrosion is by galvanization, which is a process to apply a zinc layer to steel or iron. There are different methods to do this, the most common one being hot-dip galvanization, in which the component is submerged in a bath of hot, molten zinc (at ca. 450°C). Owing to the lower equilibrium potential of zinc, $E^{\circ}(Zn^{2+}/Zn) = -0.76$ V, compared to that of iron, $E^{\circ}(Fe^{2+}/Fe) = -0.44 V$, the zinc layer protects the iron from corrosion even if the zinc layer is damaged, because the zinc preferentially corrodes in lieu of the iron (Figure 9-6c). It is also possible to coat mild steel with a metal that has a higher equilibrium potential, such as tin, $E^{\circ}(\text{Sn}^{2+}/\text{Sn}) = +0.44 \text{ V}$, which corrodes much less easily. This is widely used commercially in tin cans. The tin layer, however, has to be free of any defects, as faults lead to an increased rate of corrosion of the exposed iron, owing to the galvanic coupling between Sn and Fe (Figure 9-6d), where the undamaged layer of tin acts as a cathode. It is helpful to revisit the method of chrome plating at this point. Although the equilibrium potential of chromium, $E^{\circ}(Cr^{3+}/Cr) = -0.74$ V, is lower than that of iron, its corrosion potential in humid air is in the passive region and therefore relatively high, because it forms a dense oxide layer (cf. Figure 9-4). This (mixed) potential is higher than the equilibrium potential of iron, thus the dissolution of iron is promoted. Passivated chromium effectively behaves like a metal with high equilibrium potential, such as tin.

2.4 Cathodic protection

A general feature of the Pourbaix diagram of metals is the immunity region at low potential.¹ If we could make sure, somehow, that the potential of the metal is maintained in this range, there would be no thermodynamic driving force for corrosion. Since this potential may be low, we can at least, for a non-passivated metal, try to move the corrosion potential in cathodic direction, as this would reduce the corrosion current density (cf. **Figure 9-3**). The methods to accomplish this are described as *cathodic protection* measures. In fact, as discussed in the previous section, the zinc layer in galvanized steel is doing exactly this. In the galvanic couple Fe-Zn, zinc serves as an anode and iron as the cathode. The same effect can be achieved if the anode is a proper electrode and spatially separated from, yet electronically connected to the iron structure to be protected. Also, ions need to be able to flow between the two electrodes, such that a continuous cathodic protection current can flow from the anode to the cathode.² This type of cathodic protection is routinely used to protect ships' hulls, oil platforms and other ocean structures, buried pipelines, and storage tanks. The two approaches of cathodic protection using dedicated anodes are either passive (without forced current) or active (with forced current) methods.

¹ Obviously, this potential can be very low for reactive metals, such as the alkali metals, e.g. $E^{\circ}(\text{Li}^+/\text{Li}) = -3.04 \text{ V}!$

² This wording is a bit sloppy: since current describes the flow of (imaginary) positive charges, current actually always flows from cathode to anode, yet electrons are flowing from cathode to anode.

2.4.1 Sacrificial anode

An electrode that is made of a material that will readily corrode when electronically and ionically connected to the main metal object is called a *sacrificial anode*, as it will gradually dissolve over time. Also the zinc layer in galvanized steel can be considered a sacrificial component. Sacrificial anodes are often used on ships' hulls under the water line. The ideal anode material has some passivity so that the rate of self-corrosion is low, but a completely passive anode would impart limited protection. Magnesium is an often used material for sacrificial anodes, as its oxide layer is porous and allows a continuous current. A sketch of a sample application and a description of the corresponding electrochemical processes is given in Figure 9-7. The object to be protected is a buried steel vessel. The sacrificial anode is connected to it electronically with a cable, the surrounding soil forms the electrolyte. In ships, sacrificial anodes are attached directly to the steel hull, whereby electronic contact is established. The electrons for the ORR on the steel vessel are thus provided from the sacrificial anode, which undergoes dissolution, and not from the anodic dissolution of the iron in the steel. If a large structure, such as a pipeline, needs to be protected, sacrificial anodes need to be placed along the pipeline with adequate spacing. The distance between the steel object and the sacrificial anodes and the spacing between anodes needs to be carefully adjusted. If the anode is placed very close to the pipeline, the local current density in the area just opposite of the anode, owing to the low ionic resistance, will be unnecessarily high (cf. Chapter VI, current density distribution) and the anode consumption excessively fast. If the anode is placed too far away, the protection current will be low and thus the cathodic protection weak. The same will happen at positions on the pipeline between two sacrificial anodes if those are spaced too far apart. Sacrificial anodes are passive components, therefore the overall protection current and the local current density is determined by the electrode materials, their geometric arrangement, and the ionic conductivity of the environment they are in (soil, sea water).



Figure 9-7. A sacrificial anode (e.g. of magnesium) has a lower equilibrium potential than the steel structure to be protected against corrosion. If electronically and ionically connected (via the soil or sea water), the sacrificial anode is undergoing oxidation, thereby lowering the potential of the steel structure and providing electrons for the ORR taking place on its surface.

2.4.2 Impressed current cathodic protection (ICCP)

An alternative cathodic protection method involves a DC power supply to provide cathodic current to the structure to be protected (mostly some sort of steel construction). The anode is an external electrode. The technique, called *impressed current cathodic protection* (ICCP), is therefore an active method, because it requires the input of electrical energy. The negative terminal of the ICCP rectifier is connected to the steel, the positive terminal to the anode. As with a sacrificial anode, the two electrodes need to be connected via an ionically conducting medium (Figure 9-8a). Since the current can be tuned, we wish to know the magnitude of the current that needs to be supplied to completely suppress corrosion, i.e. to push the potential of the steel to the range where it is immune. If the current is too small, the iron will still corrode, albeit at a slower rate. If the current is too large, the steel is 'overprotected' and electricity, which is expensive, is wasted. To understand the situation, we draw a polarization curve of the steel and the ORR that is taking place on its surface as the reduction reaction in the corrosion process (Figure 9-8b). In the absence of cathodic protection, the corrosion potential $E_{\rm corr}$ is established, which is characterized by an equal magnitude of the iron dissolution reaction and the ORR. If we apply an external cathodic current, E_{corr} is moved towards more negative potentials, hence the rate of metal dissolution decreases, whereas the ORR rate increases. When the metal potential reaches the equilibrium potential of the steel, metal dissolution stops. The required protection current is then entirely spent on the ORR (the ORR in Figure 9-8b is sketched as an exponential curve, in reality, as shown above, the ORR may also reach limiting current behavior). For cost reasons, it is also conceivable to apply a lower current, and the steel would then not be entirely protected against corrosion, yet the corrosion current would still be lower than in case of the unprotected structure.



Figure 9-1. (a) Corrosion protection of a work piece using impressed current cathodic protection (ICCP), which uses a power supply to lower the potential of the structure to be protected and to provide electrons for the ORR. The anode is often of an inert material on which the oxygen evolution reaction (OER) is taking place. (b) Polarization curves of the metal dissolution reaction and the ORR. In the absence of a protective current, the corrosion potential E_{corr} establishes. The current density required for a complete protection against corrosion is indicated.

A number of different anode types are used in ICCP (**Table 9-2**). Consumable anodes, such as scrap steel electrodes, are cheap, but are used up over time and need to be replaced periodically. Silicon iron and graphite are semiconsumable electrode materials, they are consumed much more slowly and last much longer. Inert electrodes, e.g. platinized or mixed metal oxide (MMO) anodes, have much longer lifetimes and can sustain higher current densities, but at higher capital cost. MMO anodes are similar to the electrodes used in the chlor-alkali process for the chlorine evolution reaction (cf. Chapter VI). Although lead silver electrodes are of lower cost their use has decreased due to environmental concerns. The most common anodic reaction taking place on inert electrodes is the oxygen evolution reaction (OER), $2 H_2O \rightarrow O_2 + 4 H^+ + 4 e^-$. In sea water chlorine may be evolved, $2 Cl^- \rightarrow Cl_2 + 2 e^-$.

Material	Current density range (mA·cm ⁻²)	Consumption rate (kg·A ⁻¹ ·a ⁻¹)
Scrap steel	<0.1	9
Silicon iron	1-3	0.2-0.5
Graphite	1-2	0.3-0.5
Lead silver	20-30	0.1
Platinized anodes	25-200	10-5
Mixed metal oxide	25-60	$0.5 - 4 \cdot 10^{-6}$

 Table 9-2.
 Characteristics of ICCP anodes for seawater applications (source: T.F. Fuller, J.N. Harb, Electrochemical Engineering, Wiley, 2018, Tab. 16.1, p397).

As with sacrificial anodes, the location and spacing of anodes in an ICCP system needs to be carefully chosen. The ohmic resistance of the environment where the structure to be protected and the anodes are embedded in, which acts as electrolyte, is an important design factor. Owing to the potential drop in the electrolyte, regions on the structure far away from the anode will be less effectively protected, and the spacing of anodes needs to be adjusted accordingly.

Compared to sacrificial anodes, an ICCP system is more flexible as it allows the adjustment of the driving force for protection via the current. The operating cost is determined by the electricity use to drive the protection current, yet, at least in the case of inert anodes, they do not need regular replacement. The choice of system eventually depends to a large extent on the overall lifetime cost of the system, including investment, operating, maintenance and recycling cost.

Compared to anodic protection with a power supply (cf. Section 2.2), cathodic protection with an ICCP requires higher currents, as the ORR counter reaction, which can be of considerable rate, needs to be sustained on the metal surface. For an active anodic protection, the current is much smaller and merely needs to be large enough to maintain the structure in the passive region of the steel.

Appendix A: Langmuir Isotherm

The Langmuir isotherm is a simple adsorption model, as it contains only one parameter, the adsorption coefficient K. For the derivation of the Langmuir isotherm, we are considering the following adsorption reaction of compound A:

$$A \leftrightarrows A_{ad}$$
 (9-A1)

A is the species in solution, A_{ad} the adsorbed species. Next, we formulate the rate law for the adsorption and desorption reactions. The rate of adsorption r_a (unit: mol·cm⁻²·s⁻¹) is proportional to the concentration of the species in solution *c* (unit used here: mol/cm³, can also be mol/L) and the fraction of the bare surface (1- θ):

$$r_{\rm a} = \Gamma \frac{d\theta}{dt} = k_{\rm a} c \left(1 - \theta\right) \tag{9-A2}$$

where k_a is the adsorption rate constant (unit: cm/s).¹ This means that A can only adsorb on sites that are not occupied yet by A. So in the Langmuir model the adsorption of A on top of already adsorbed A is not considered. To obtain the change in the surface coverage $d\theta/dt$ (unit: 1/s) the adsorption site density Γ (unit: mol/cm²) on the surface has to be taken into account. The rate of desorption r_d is proportional to the overage θ .

$$r_{\rm d} = -\Gamma \frac{d\theta}{dt} = k_{\rm d} \,\theta \tag{9-A3}$$

with the rate constant k_d (unit: mol·cm⁻²·s⁻¹). The minus sign in the term with $d\theta/dt$ indicates that the coverage decreases when the species desorbs. At equilibrium adsorption and desorption are balanced and $d\theta/dt = 0$, so we set $r_a = r_d$ and solve for the steady-state coverage θ .

$$\theta = \frac{k_{\rm a}c}{k_{\rm a}c + k_{\rm d}} \tag{9-A4}$$

Dividing the nominator and denominator by k_d and introducing the equilibrium constant for adsorption $K = k_a / k_d$ we obtain Eq. 9-14, the Langmuir isotherm.

¹ The unit is the same as the one for an electrochemical reaction (cf. Chapter V), because in both cases the described process is a surface reaction.

It is helpful to keep in mind the underlying assumptions of the Langmuir model. The surface of the solid is assumed to be homogeneous with a constant adsorption site density Γ . Each site can only accommodate one adsorbed species. Furthermore, there are no lateral interactions in the adsorbate layer. In reality, this is often not the case. Also, the adsorption coefficient can be a function of coverage. Such features are accounted for in more elaborate adsorption models, such as the Frumkin and Temkin isotherm.