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The Electrode Reaction – The Core of Electrochemistry

In this chapter, we will compare electrochemical reactions with other chemical reactions in order to work out their special features. We will become familiar with basic terminology. This is followed by a discussion of the relationship between the amount of charge transferred in a process and the amount of product formed. We will identify the importance of agreed-upon conventions for the first time in this book. Conventions cannot be derived from experiments or basic principles of nature, but need to be agreed upon in a sensible way. There are cases of different committees reaching different agreements at different times and in different locations, which then led to ineffective communication, as we will see in the development of electrochemistry. The history of electrochemistry is very interesting and, in many ways, exemplary of the history of science. For reasons of brevity, we cannot unfold all aspects of the subject. We will, however, provide biographical footnotes when names have become part of technical terms, which will enable the reader to see the historical context.

Further Reading. A concise description of the conventions in electrochemistry, the set of algebraic symbols, and SI units is provided in a book by the International Union of Pure and Applied Electrochemistry (IUPAC, available also via internet) [1, 2]. The historical aspects of electrochemistry have been covered in some seminal books and articles [3–6]. A current reference source [7], a textbook [8], and Wikipedia [9] frequently provide further historical and biographical accounts of major scientific discoveries.

1.1 Electrical Current and Chemical Conversion in Electrochemical Cells

1.1.1 Charge, Current, and Voltage

Charge (or more precisely electrical charge) Q (coulomb [C][1]) is a property that describes how objects experience a force in an electromagnetic field. Charge (very much like mass) is one of the fundamental properties of subatomic particles such as electrons or protons. The charge of an electron is negative (by convention), and the charge of a proton is positive. Each electron and each proton have the same charge regardless of which state they are (e.g., bound in an atom or free). The charge of a neutron is zero; it is neither positively nor negatively charged but neutral, thus the name “neutron”.

The charge of larger objects is calculated as the charge of all its protons minus the charge of all its electrons. The charge of a proton is constant, called the elementary

[1] Charles Augustin de Coulomb, 1736–1806, French physicist, founded the area of electrostatics.

charge $e \approx +1.602 \times 10^{-19}$ C; the charge of the electron is opposite $e^- \approx -1.602 \times 10^{-19}$ C. Thus, the charge of any body composed of N protons and M electrons must be an integral multiple of the elementary charge e, exactly $(N - M)e$. We see that the charge of an object can only assume certain discrete values. For instance, a charge of $^3/_4\, e$ is impossible. Such quantities are called quantized.

Charge is a conserved quantity, which means the charge of an isolated system cannot change. In another phrasing, the charge of a system can only change if charge is transferred across the system boundary. How this transfer happens is one of the central questions in electrochemistry.

Objects with positive and negative overall charge attract each other and objects with charges of equal sign (either both positive or both negative) repel each other. The force resulting from this interaction is called the coulombic[1] force.

We can see from the consideration above that charge cannot exist apart from material objects. We can also say some objects "carry a charge". This phrasing is the origin of the term "charge carrier" frequently used in this book. Of course, electrons and protons are charge carriers, but this term also includes more complex objects that we frequently encounter in chemistry and physics, such as positive and negative ions (Na^+, Cl^-) including complex molecular ions (SO_4^{2-}, acetate CH_3COO^-) or so-called quasi-particles. Quasi-particles are a common concept in physics that ascribes single particle properties (such a mass and charge) to states of matter that are much more complex than a physical particle. A typical example is a "hole" in a semiconductor. In the context of this book this refers to a semiconductor, which has one electron less than it has protons. In the ground state, this electron deficiency is localized in a binding orbital of one atom. However, it is possible that an electron from a similar orbital of a neighboring atoms moves to this initially vacant state. Thus, the vacant state, with it the electron deficiency, has moved to the neighboring atom. Instead of thinking of a deficiency that changes place, it is efficient to consider the deficient state as a mobile particle of the charge $+e$ in the semiconductor. We will make extensive use of this concept in Chapter 10.

An electric field is formed around electrically charged objects. If a charged object, for example, charge carriers move, they cause a flow of charge, called **(electric) current** (symbol I, unit ampere[2] [A]). Moving charges produce a magnetic field.

In addition to charge and current, we will use another quantity called **voltage** U [V]. It is the difference between two electrical potentials at location $\mathbf{r}_1$ and location $\mathbf{r}_2$. [In this book, bold upright symbols stand for a vector quantity. Here it is the location $\mathbf{r} = \vec{r} = \{x, y, z\}$.] This potential difference is related to the work per charge W/Q to move a small probe charge Q in the electric field between the locations $\mathbf{r}_1$ and $\mathbf{r}_2$.

Hydraulic models are sometimes used to illustrate the relation between the electrical quantities by means of a strongly simplified analogy that is more accessible to visual experience (Figure 1.1). The electric charge is represented by the liquid volume in the hydraulic model. With this definition, the electric current corresponds to the volume flow rate (Table 1.1). The voltage is a "tension" under which the charge is stored with respect to a second reservoir. The mechanical equivalent is the hydrostatic pressure difference of two reservoirs. After defining the relations in this way, further a relation can be derived for the stored energy W and the released power P of an ideal turbine and an ideal motor.

[2] André-Marie Ampère, 1775–1836, French physicist and mathematician, founder of electrodynamics, clarified the meaning of voltage and current.

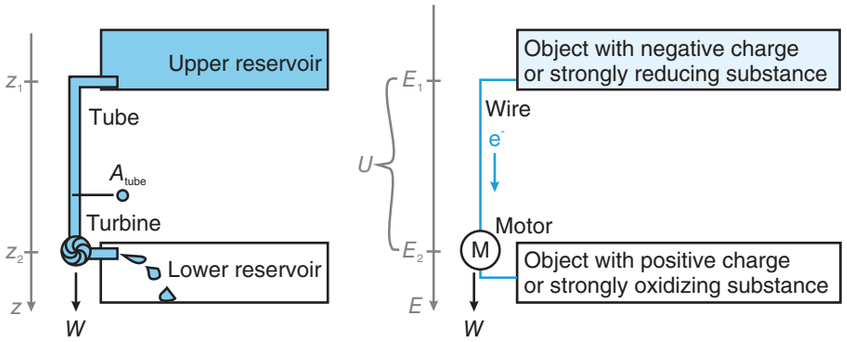

Figure 1.1 Analogy between mechanical energy stored in a water reservoir (left) and electrical energy obtained by moving charge between reservoirs of different electric potentials (right).

Table 1.1 Equation describing equivalent quantities in a hydropower station and an electrochemical cell. The equations are given with absolute values to avoid complication with sign definitions.

Quantity	Hydrostatic model	Electrochemical cell
Stored energy (or work required to fill the storage device) [W s] = [Nm]	$\lvert W_{mech} \rvert = mg \lvert \Delta z \rvert = V\rho g \lvert \Delta z \rvert$ $= Vp$ $= Pt$	$\lvert W_{el} \rvert = Pt$ $= UQ$ $= UIt$
Power [W]	$P = \mathrm{d}W/\mathrm{d}t$ $= \rho g \Delta z \frac{\mathrm{d}V}{\mathrm{d}t} = \rho g \Delta z \dot{V}$ $= p\dot{V}$	$P = \mathrm{d}W/\mathrm{d}t$ $= U\frac{\mathrm{d}Q}{\mathrm{d}t}$ $= UI$
"Tension" [Pa] or [V]	Hydrostatic pressure $p = F/A$ $= \frac{mg}{A_{tube}} = \frac{A_{tube}\rho g z}{A_{tube}}$ $= \rho g z$ Pressure difference $\Delta p = p_2 - p_1$ $= \rho g (z_2 - z_1)$ $= \rho g \Delta z$	Electric potential Voltage (potential difference) $U = \frac{\int_{r_1}^{r_2} F(Q)\mathrm{d}r}{Q} = E_2 - E_1$
Balanced quantity	Volume V	Charge Q
Current	Volume flow rate $\dot{V} = \mathrm{d}V/\mathrm{d}t$	Electric current ("charge flow rate") $I = \dot{Q} = \mathrm{d}Q/\mathrm{d}t$

Symbols: W – work/energy [W s] = [J] = [Nm], P – power [W], m – mass [kg], V – volume of the liquid [m^3], $\dot{V} = \mathrm{d}V/\mathrm{d}t$ – volume flow rate [$m^3\ s^{-1}$], ρ – density of the liquid, g – local gravitational field of Earth [9.81 $m^2\ s^{-1}$], p – pressure [Pa] = [N m^{-2}], $\Delta z = z_2 - z_1$ height difference between the reservoirs [m], Q – charge [C] = [A s], t = time [s], U – voltage [V].

1.1.2 Electrochemical Cells Convert Charge and Substances

Let us imagine the following experimental setup: a beaker contains two metal sheets of an inert metal, for instance, platinum (Figure 1.2). The metal sheets are connected to a direct current (DC) voltage source via a voltage divider that allows applying a fraction of the maximum output voltage (e.g., 50 V) to the two metal sheets. A current measuring instrument (called ampere meter) displays the resulting current. This could be a

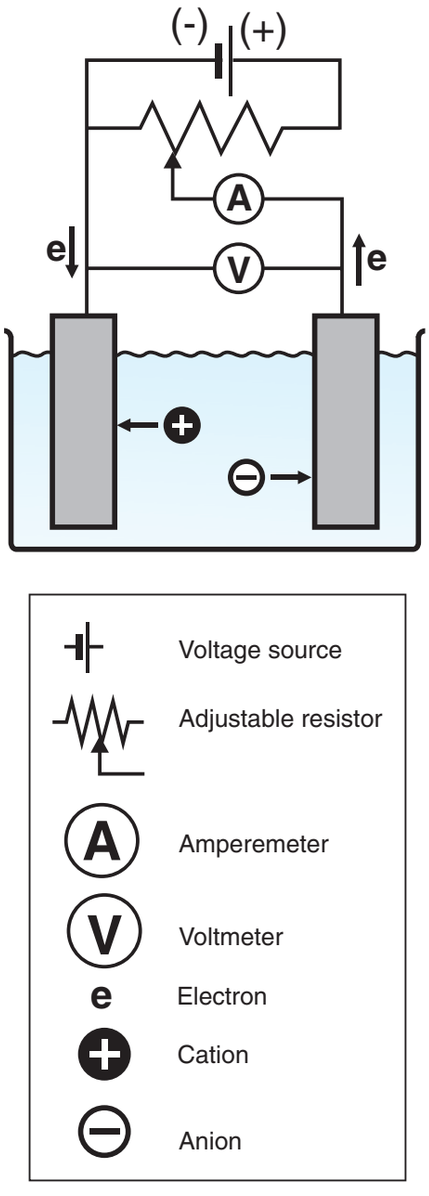

Figure 1.2 Basic experimental setup for an electrolysis cell.

multimeter or an electric light bulb connected in series. The metal sheets are immersed in different materials such as solids or liquids that we add into the beaker. We observe the current and at the same time the generation of chemical products at the interfaces of the metal sheets and the surrounding materials.

We call the experimental setup with two metal sheets connected via an ion-conductor an **electrochemical cell**.

If we manipulate the metal sheets to touch a dry crystal of NaCl at both ends, we will not observe a current (a flow of charge). A similar observation is made when pouring clean water (e.g., deionized or doubly distilled water) into the beaker. However, if we dissolve the solid crystalline NaCl into the water, a current is observed as electrons start flowing in the wire. At the same time, gas bubbles rise from the two metal sheets to the surface of the liquid. Hydrogen gas is formed at the sheet connected to the negative pole of the voltage source. We could trap the gas in a test tube for analysis. At the other metal sheet, mainly chlorine gas is formed, revealed by its characteristic smell. *Caution, this electrolysis should be carried out for a very short time only because chlorine is toxic and hydrogen forms explosive gas mixtures with oxygen from air and with chlorine.*

Conceptually, this type of experimentation can be expanded by placing molten NaCl within a special crucible, employing diluted hydrochloric acid (HCl), or using aqueous sodium sulfate solution (Na_2SO_4). Electrochemical reactions in molten salts (Section 11.4.1) are often performed in salt mixtures in order to lower the melting temperature. Carbon rods are employed as current feeder electrodes because they are relatively stable against corrosion and show little passivation. Table 1.2 summarizes some of the observations made for the different experiments.

From this simple sequence of experiments, we can derive the following condition for a current in an electrochemical cell:

1) Current occurs only if there is a sufficient number of mobile charge carriers between the metal sheets to generate a measurable flow of charge. The aqueous solution of NaCl contains mobile Na^+ and Cl^- ions. It is therefore an ion-conductor. This is not the case for solid NaCl or pure H_2O.
2) A DC current is always coupled to chemical conversions at *both* metal sheets because the medium between the sheets is chemically converted. This process is called **electrolysis** (decomposition by electrical current).

   Let us consider these chemical conversions in more detail: Cl_2 is formed by oxidation of Cl^-, and H_2 is formed by reduction of H^+ in experiments (3) and (5) in Table 1.2.

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \quad \text{(oxidation)} \tag{1.1}$$

$$2\,H^+ + 2\,e^- \rightarrow H_2 \quad \text{(reduction)} \tag{1.2}$$

Table 1.2 Reaction products for electrolysis in different electrolytes.

No.	Substance between metal sheets	Current?	Product at (+)	Product at (−)
1	H_2O pure	No	—	—
2	NaCl (solid)	No	—	—
3	NaCl in solution	Yes	Cl_2	H_2
4	NaCl melt	Yes	Cl_2	Na
5	HCl in solution	Yes	Cl_2	H_2
6	Na_2SO_4 in solution	Yes	O_2	H_2

Chlorine Cl_2 is formed by oxidation, and Na metal is formed by reduction in experiment (4).

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \quad \text{(oxidation)} \tag{1.3}$$

$$2\,Na^+ + 2\,e^- \rightarrow 2\,Na \quad \text{(reduction)} \tag{1.4}$$

In experiment (6), the formation of O_2 (by oxidation) and of H_2 (by reduction) is observed.

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \quad \text{(oxidation)} \tag{1.5}$$

$$4\,H_2O + 4\,e^- \rightarrow 2\,H_2 + 4\,OH^- \quad \text{(reduktion)} \tag{1.6}$$

3) Electrochemical cell reactions always comprise an **oxidation** reaction and a **reduction** reaction that occur at the *same time*, but in *different locations*.

The reaction that occurs on one of the current feeders (e.g., the Pt sheets) is called an **electrode reaction**.

We recognize that the mobile ionic species within the solution between the two metal sheets may be directly involved in the electrode reaction (example 4), but that this is not always the case (example 6). From these conditions for current flow through an electrochemical cell, two central questions for electrochemistry arise:

1) How does the **charge transport** proceed in detail in the ion-conducting medium (solution, membrane, ion-conducting solid)? (*ionics*)
2) How does the **charge transfer** occur across the interface between the metal sheet and the ion-conducting medium? (*electrodicss*)

1.2 Electrodes and Ions

In the nineteenth century, Faraday[3] realized that the interface between the current feeder and the electrolyte solution is the location at which the oxidation and reduction reactions proceed. He suggested calling this special interface the "electrode" and to use this terminology instead of the older term "pole". A contemporary phrasing of this principle reads:

An **electrode** is a phase boundary between *two electrically conductive phases* of different structure, at which electrochemical equilibria are attained or approached by *chemical conversions*. At least *one phase must be an ion-conductor*.

At least two electrodes are required to form an **electrochemical cell**. There are many different types of both electrodes and cells. Faraday was far ahead of his time. He identified the interfacial reaction as the unifying principle of all electrodes. This is all the more astonishing as several more decades had to pass until elemental particles and ions were finally discovered. Therefore, it is perhaps not so surprising that a colloquial meaning of the word "electrode" is still in use in addition to the exact scientific definition. If you ask your fellow students during the preparation of an experiment, according to Figure 1.2: "Could you please hand me the Pt electrode", she or he will give you the Pt sheet with an attached wire and a possibly existing casing of glass without any hesitation (Figure 1.3). The situation is indeed even more complicated

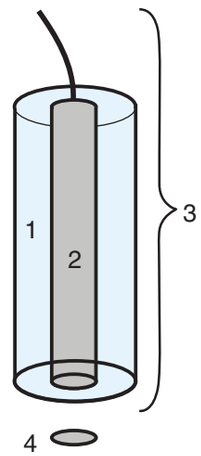

Figure 1.3 Colloquial and scientific meaning of the term "electrode". (1) Sheath or insulating casing, (2) metallic conductor, (3) colloquial meaning of the term electrode, and (4) electrochemical meaning of the term electrode according to Faraday (electrode area).

[3] Michael Faraday, 1791–1867, English physicist and chemist, made decisive discoveries in the fields of electricity and electromagnetism and discovered Faraday's laws named after him.

because one and the same scientific text may contain the term "electrode" in the meaning of Faraday's definition as well as in its colloquial understanding. For distinguishing those different nuances in the meaning of this central concept, further auxiliary terms are frequently used in electrochemical texts such as "electrode surface", "interface electrode-electrolyte", "electrode body", etc. There are many more terminology problems in electrochemistry. This results from the interdisciplinary nature of electrochemistry with different scientific disciplines providing important contributions in different historical periods together with their scientific terminology (chemistry with different subdisciplines, physics, electronics). As a result, a multitude of synonyms and terms with very similar but not completely identical meaning is in use, which makes the study of the electrochemical literature hard. This historical background is authoritatively explained in [6].

Q: What is the meaning of the term "phase" or "phase boundary" in Faraday's concept of an electrode?

A: In thermodynamics, "phase" refers to a compound or a mixture with spatially uniform properties. Phase boundaries are those interfaces at which properties change discontinuously. Examples: zinc powder (one phase), zinc chips suspended in water (two phases), zinc nitrate dissolved in water (one mixed phase), and water on a hotplate (70 °C at the bottom, 40 °C at the water–air boundary, but without a discontinuous change in properties, thus one phase).

Q: Are all electrochemical cells composed of exactly two electrodes?

A: No, electrochemical cells can contain more than two electrodes. We will discuss examples in Chapter 5.

According to Faraday, we call the electrode at which the **reduction** occurs ("electrons flow out of the electrode into the solution") the **cathode**. The **anode** is the electrode at which the oxidation happens ("electrons transfer from the solution into the electrode).

The liquid or the solid between the two electrodes in Figure 1.2 must be an ion-conductor. Liquids in which ions can move freely are obtained either by melting a salt or by dissolving ionizable salts, bases, or acids in a suitable solvent such as water. These compounds dissociate into positively and negatively charged species called **ions**. A negatively charged ion is called an **anion** because it migrates toward the anode during electrolysis ["(+) pole"]. A **cation** is a positively charged ion. It is attracted by the cathode [the "(−) pole" during an electrolysis]. An electrolyte is a material that contains mobile ions. It is not necessarily an aqueous solution. Electrolytes can also be formed with hydrophobic ions in organic solvents, ionic liquids, gel-like polymers, and some ionic solids, which become ion-conducting at elevated temperatures (solid electrolytes, see Chapter 11).

Q: Where do the expressions anode and cathode come from?

A: Faraday derived these terms (using expressions from the Greek language) from consideration of current direction, orientation of the magnetic field of the Earth, and the definition of current induction [6].

Practically, there is a large number of different types of electrodes, but we can distinguish two key classes: ion electrodes (Figure 1.4a) and redox electrodes (Figure 1.4b). In **ion electrodes**, it is an ion that transfers the charge across the phase boundary. If an electron crosses the phase boundary during the electrode reaction, the electrode is called a **redox electrode**.

Within both classes, there are further subgroups. For a compact description of the electrode, a short-hand notation is used, in which chemical symbols describe the composition of the interacting phases. The boundary between two adjacent phases (e.g., solid|liquid) is indicated with a vertical bar. The description of the phase composition can be supplemented by providing the concentration or activity of the electrolyte solutions (1 mol L^{-1} KNO_3). The physical state is given in brackets (Figure 1.5a–d), where *s* stands for solid, *l* for liquid, *g* for gaseous, *aq* for an aqueous solution, and *sol* for a nonspecified solution. The abbreviation *sa* stands for a saturated solution.

Example Calculation 1.1 Provide the short notation of a silver wire immersed in a 0.1 mol L^{-1} $AgNO_3$ solution.

$$Ag(s) \,|\, 0.1 \text{ mol } L^{-1} \, AgNO_3(aq)$$

Example Calculation 1.2 Provide the short notation of a silver wire covered by a layer of solid silver chloride and immersed in a 1 mol L^{-1} solution of NaCl.

$$Ag(s) \,|\, AgCl(s) \,|\, 1 \text{ mol } L^{-1} \, NaCl(aq)$$

We should reflect for a moment and contrast heterogeneous electrochemical reaction with homogeneous charge transfer reactions in chemistry. Such reactions always require two reaction partners. In a homogeneous reaction, electrons or ions are transferred directly from a donating species to an accepting species. The reaction rate of such a transfer depends strongly on the distance and usually happens only over a few hundred picometers, that is, the length of a few chemical bonds. In an electrochemical reaction, one of the reaction partners is the electrode. Thus, the charge transfer step becomes a step in which an electron or an ion crosses the phase boundary (Section 3.1.1). The strong distance dependence of such a reaction step remains. Therefore, the reactants must be transported to the interface and often require very close contact with the electrode surface (Chapter 4).

The coupling of charge transfer processes and transport processes, such as the movement of an ion or molecule from one place to another, is a key feature of electrochemical reactions.

There are various types of ion electrodes (Figure 1.5e–j). If a metal is in contact with a solution of one of its salts, it is called an electrode of the first kind.

$$Ag \rightleftharpoons Ag^+ + e^- \tag{1.7}$$

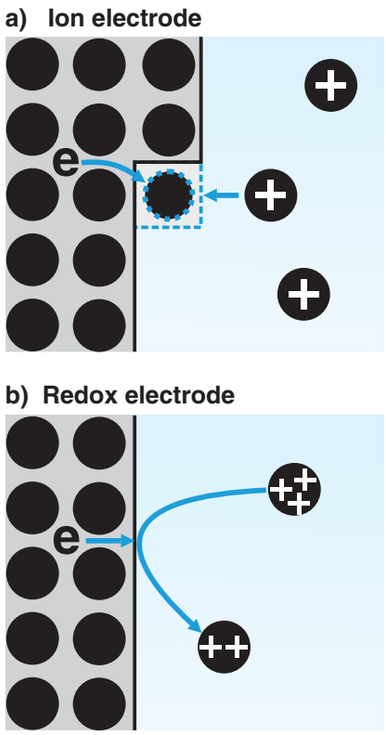

Figure 1.4 Distinction between a) an ion electrode (e.g., galvanic deposition of a metal) and b) a redox electrode (example reduction of Fe^{3+} to Fe^{2+} ions).

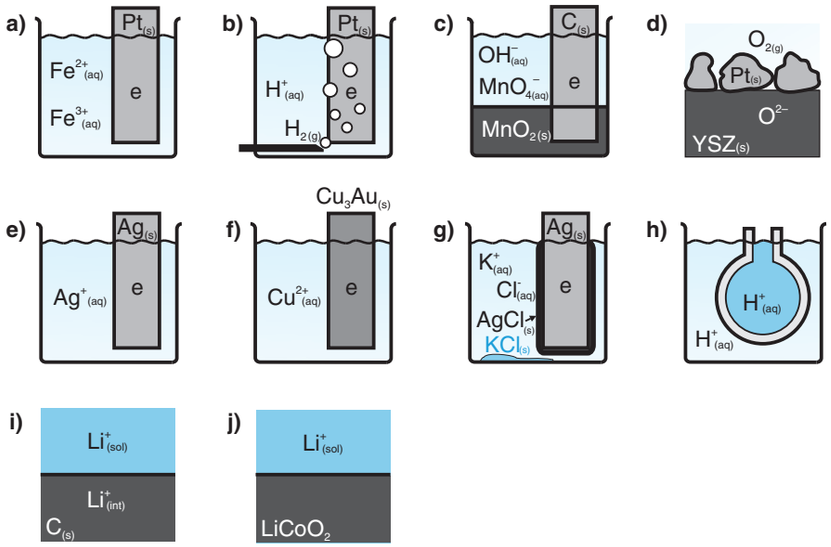

Figure 1.5 Examples of redox electrodes:

a) $Pt(s) \mid Fe^{2+}(aq), Fe^{3+}(aq)$;
b) gas electrode $Pt(s) \mid H_2(g), H^+(aq)$;
c) $C(s) \mid MnO_2(s), MnO_4^-(aq), OH^-(aq)$;
d) $Pt(s) \mid O_2(g), O^{2-}(s)$ (ionic conduction in the oxide lattice of yttria-stabilized zirconia, YSZ, see Excursion 11-1).

Examples of ion electrodes:

e) electrode of the 1st kind: $Ag(s) \mid Ag^+(aq)$;
f) alloy electrode of the 1st kind: $Cu_3Au(s) \mid Cu^{2+}(aq)$;
g) electrode of the 2nd kind: $Ag(s) \mid AgCl(s) \mid KCl(aq, sa)$;
h) glass electrode (Section 5.2.3);
i) graphite intercalation electrode: $[(C_6)_n][Li^+]\ (s) \mid Li^+(sol)$ (Section 15.6); and
j) metal oxide intercalation electrode: $Li_xCoO_2\ (s) \mid Li^+(sol)$ (Section 15.6).

At an electrode of the second kind, the ion transfer is coupled to a further equilibrium reaction, most often a solubility equilibrium. For instance, a layer of solid AgCl is formed on a Ag wire during anodic dissolution in HCl solution. Two equilibria are attained simultaneously at two phase boundaries.

$$Ag \rightleftharpoons Ag^+ + e^- \tag{1.8}$$

$$Ag^+ + Cl^- \rightleftharpoons AgCl \tag{1.9}$$

The electrode reaction can be summarized as

$$Ag + Cl^- \rightleftharpoons AgCl + e^- \tag{1.10}$$

Very rarely, electrodes of the third kind are encountered. At such electrodes, the charge transfer is coupled to two further equilibria in solution. One example would be a metal ion electrode $M \mid M^{n+}$, at which the released metal ion M^{n+} is complexed by a ligand L. Another metal ion M'^{m+} in the solution competes with M^{n+} for the ligand. In this way, the electrode potential becomes dependent on M'^{m+}.

$$M \rightleftharpoons M^{n+} + ne^- \tag{1.11}$$

$$M^{n+} + L \rightleftharpoons ML^{n+} \tag{1.12}$$

$$M'^{m+} + L \rightleftharpoons M'L^{m+} \tag{1.13}$$

1.3 What Is the Relationship Between Degree of Chemical Conversion and Flow of Charge?

Faraday diligently investigated the relationship between current I and charge Q. For a constant current, the charge is the product of current and time t ($Q = I\,t$). For a current that changes with time (a transient current), we have to integrate the current over t and obtain **Faraday's First Law**.

Q – Charge [C = A s]
t – Time [s]
I – Current [A]

$$Q = \int_{t_1}^{t_2} I(t)\,\mathrm{d}t \tag{1.14}$$

The electrochemical reaction in Eq. (1.2) states that one electron reduces exactly one proton. Consequently, one mole of electrons can reduce one mole of protons. The required charge Q to convert a given amount of a material N, is described by Faraday's Second Law. Q is the sum of elementary charges transferred in the reaction (Section 2.2.4) and directly proportional to the amount N of converted substance. Usually, the symbol "n" is recommended for the amount of substance, but within the field of electrochemistry, the symbol n is strongly preferred for the stoichiometric number of charges transferred across the phase boundary per reaction turnover as written in the reaction equation. This book follows this common practice. For reactions like that in Eq. (1.11), $n = 2$ corresponds to the charges transferred per metal cation, for example, $Cu^{2+} + 2e^- \rightleftharpoons Cu$. However, for the hydrogen evolution reaction in Eq. (1.2) the stoichiometric number of electrons is $n = 2$ and thus different from the charge number $z = 1$ of H^+. The amounts of consumed reagents or formed products must be multiplied by the stoichiometric number of charges, the elementary charge e, and the number of objects in one mole (Avogadro's[4] constant N_A) to obtain the total charge.

$$Q = n \cdot N \cdot e \cdot N_A \tag{1.15}$$

$$Q = n \cdot N \cdot F \tag{1.16}$$

The natural constants e and N_A were not yet known in Faraday's time and could not be determined separately. However, the product $N_A \times e$ could be determined. This quantity is called the **Faraday constant** F. It is the electrical charge of 1 mol electrons expressed in the SI unit of the electric charge (1 C = 1 A s) [Eq. (1.17)].

Q – Charge [C = A s]
N – Converted amount of substance [mol]
n – Stoichiometric number for charges as defined in the reaction equation [dimensionless]
e – Elementary charge = 1.602177×10^{-19} A s
N_A – Avogadro constant = 6.022140×10^{23} mol^{-1}
F – Faraday constant [A s mol^{-1}]

Example Calculation 1.3 Calculation of the Faraday constant.

$$\begin{aligned} F &= e \times N_A \\ &= 1.602177 \times 10^{-19}\ \text{A s} \cdot 6.022140 \times 10^{23}\ \text{mol}^{-1} \\ &= 96485.34\ \text{A s} \cdot \text{mol}^{-1} \approx 100\,000\ \text{C mol}^{-1} \end{aligned} \tag{1.17}$$

1.4 What Is the Relationship Between Electrical Current and Electrochemical Reaction Rate?

A chemical process that occurs at the interface between two phases is called a **heterogeneous reaction**. Electrochemical reactions are important, but not the only examples of heterogeneous reactions. The reactions of gases at the surface of solids are heterogeneous. In contrast, **homogeneous reactions** occur in the bulk of a gas or a solution phase (Figure 1.6).

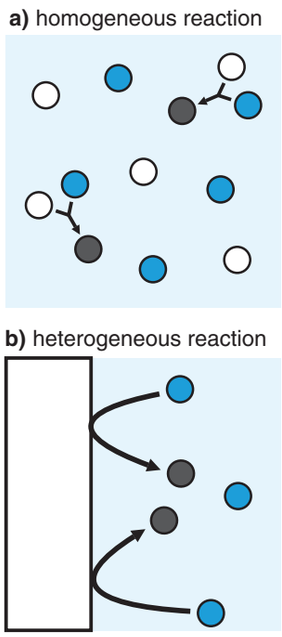

Figure 1.6 Comparison between a) a homogeneous and b) a heterogeneous chemical reaction.

[4] Lorenzo Romano Amedeo Carlo Avogadro, 1776–1856, Italian physicist and chemist, professor of mathematical physics at the University of Torino, lent his name also to the mineral Avogadrite and a crater on the Moon.

The reaction rate r for a homogeneous reaction is defined as the amount of product generated per unit time and per unit of the reaction volume V.

r – Homogeneous reaction rate [mol L^{-1} s^{-1}]
N – Converted amount of substance [mol]
t – Time [s]
V – Volume [L]
c – Concentration (of amount of substance) [mol L^{-1}]

$$r = \frac{1}{V} \cdot \frac{\mathrm{d}N}{\mathrm{d}t} = \frac{\mathrm{d}c}{\mathrm{d}t} \tag{1.18}$$

The reaction rate r for a heterogeneous reaction is obtained by relating the amount of product generated per unit time and per unit area A of the interface at which the reaction occurs.

r – Heterogeneous reaction rate [mol cm^{-2} s^{-1}]
A – Interfacial area [cm^2]

$$r = \frac{1}{A} \cdot \frac{\mathrm{d}N}{\mathrm{d}t} \tag{1.19}$$

From Faraday's First Law (1.14), one obtains for the current $I(t) = \mathrm{d}Q/\mathrm{d}t$. Replacing Q by the right side of Eq. (1.16) and considering n and F constant for a particular reaction yields the expression

Q – Charge [C = A s]
N – Converted amount of substance [mol]
n – Stoichiometric number of charges in the reaction [dimensionless]
F – Faraday constant [96 485 A s mol^{-1}]

$$I(t) = \frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}(N \cdot n \cdot F) = n \cdot F \cdot \frac{\mathrm{d}N}{\mathrm{d}t} \tag{1.20}$$

Rearranging leads to

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{I(t)}{nF} \tag{1.21}$$

Inserting Eq. (1.21) into (1.19) provides an expression for the heterogeneous reaction rate

$$r = \frac{1}{A} \cdot \frac{I(t)}{nF} \tag{1.22}$$

We note as a second characteristic feature of electrochemical reactions, that the current is *proportional to the momentary reaction rate* at any given time. Thus, electrochemical systems offer the unique opportunity to measure reaction rates directly. An interruption of the current ($I = 0$) causes an instantaneous termination of the reaction, which offers a way for reaction control that is not easily available for other types of chemical systems. Reaction rate control via current is employed in electrosynthesis. In order to facilitate comparison between different experiments, the current is often related to the electrode area. This quantity is called the **current density** $j = I / A$. Thus, the reaction rate can be expressed as

r – Heterogeneous reaction rate [mol cm^{-2} s^{-1}]
n – Stoichiometric number of charges for the reaction [dimensionless]
F – Faraday constant = 96 485 A s mol^{-1}
j – Current density [A cm^{-2}]

$$r = \frac{1}{nF} \cdot j \tag{1.23}$$

Note that the choice of area A can be important here when surfaces are rough. Often, there are more than one electrode reaction occurring simultaneously at one electrode. In this case, the charge crossing the interface is distributed among several reaction channels. If there are m different electrode reactions, the current yield $\varepsilon_{\mathrm{F},l}$ describes the ratio between the current for reaction number l and the total current. The same quantity is also called faradaic efficiency or coulombic efficiency in different areas of electrochemistry.

$$\varepsilon_{\mathrm{F},l} = \frac{n_l F N_l}{\int I(t)\mathrm{d}t} = \frac{n_l F N_l}{\sum_{k=1}^{m} n_k F N_k} \tag{1.24}$$

$\varepsilon_{\mathrm{F},l}$ – Current yield or faradaic efficiency for the l^{th} reaction (dimensionless, $0 \leq \varepsilon \leq 1$, speak "epsilon")
N – Number of formula conversions, subscript l is the number of the reaction [mol]
I – Current [A]
t – Time [s]

Q: What is the meaning of the subscripts F and l in $\varepsilon_{\mathrm{F},l}$? Can't we just drop them?

A: The subscript F stands for Michael Faraday, because we calculate the yield with reference to Faraday's Law. The subscript helps us to distinguish this particular yield from other measures of efficiency (Chapter 15; for energy efficiency of a battery, "energy yield" can be defined). The subscript F is printed nonitalicized because it is an abbreviation. In contrast, the symbol F, which you will find frequently in this book, stands for the Faraday constant. This is defined as the product of a number and a unit ($F = 96\,485.3\ \mathrm{A\,s\,mol^{-1}}$). The subscript l refers to the numbering of the reactions at the electrode. It is printed italicized because it is a symbol (and not an abbreviation). One could, of course, drop the subscript if it is clear from the context which quantity is meant. The symbol η (eta) is also frequently used for the current yield. However, this symbol is also used to denote the overpotential or overvoltage (Chapter 3).

Signs are used to indicate the **direction of the current**. There are no clear-cut criteria to assign a specific current direction to the signs "+" or "−". In such a case, one must rely on an agreement (**convention**). Unfortunately, there are opposing or competing conventions in electrochemistry regarding the direction of current and other quantities. Both conventions exist in the contemporary literature in parallel. It is suggested to follow the convention of IUPAC (*International Union of Pure and Applied Chemistry*) [1], but electrochemists have to be aware of the conflicting conventions in the literature and be able to convert intuitively, especially when reading the older literature.

There are opposing sign conventions in electrochemistry.

According to the IUPAC definition, oxidative currents (anodic currents) are positive and reductive currents (cathodic currents) are negative (Figure 1.7). The direction of the current defined in this way corresponds to the physical motion of electrons in the metal wires and of anions in solution. In contrast, the technical current direction is positive toward the (−) pole of the circuit and thus opposite to the IUPAC definition. The American Chemical Society (ACS) and the Electrochemical Society (ECS) have often followed the definition of the technical current direction [2]. However, there are papers in major journals of those learned societies using both conventions even in the same issue! When reflecting about this and other nomenclature problems, one should always ask which rules are derived from experiments and therefore represent an objective fact (i.e., a fact that does not depend on the opinions of the observer) and which are resting on conventions. Conventions have frequently been changed and adapted in the history of science and could be changed again in the future.

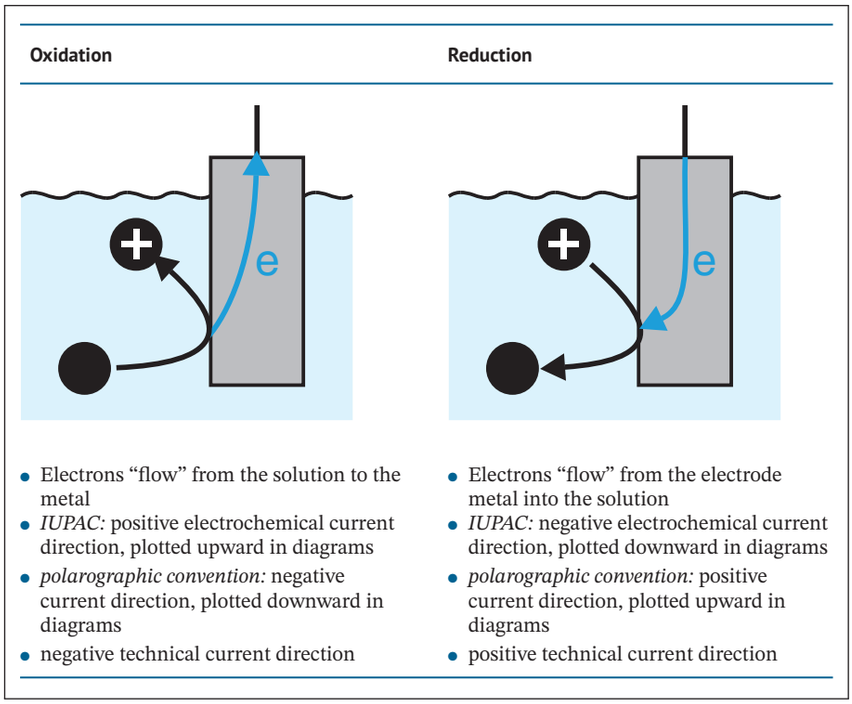

Figure 1.7 Definitions and explanation of the direction of current in electrochemical cells.

1.5 Galvanic Cells and Electrolytic Cells

The large variety of types of electrochemical cells can be divided into two main groups: An **electrolysis cell** is a cell in which a current and the associated electrochemical conversion are driven by an external voltage applied to the cell. Water electrolysis, from example 6 of Table 1.2. is a typical example. Electrical energy of the voltage source is converted into chemical energy (H_2 and O_2 contain much more Gibbs energy than H_2O at the same temperature). Electrolysis cells are applied in industry for the synthesis of commodity chemicals (Chapter 17), for the extraction and refinement of metals (Chapter 9), and in some chemical sensors (Sections 5.4 and 18.3.3).

In contrast, processes in electrochemical cells can be spontaneous. Energy-rich oxidants and reductants can be made to react spontaneously in an electrochemical cell. For instance, H_2 and O_2 react at the electrodes in a fuel cell, producing water and energy. The direct (homogeneous) reaction of the two gases occurs with an explosion over a wide range of the composition of the gaseous mixture. However, in a fuel cell, H_2 and O_2 react with each other in a controlled manner (i.e., with a controlled reaction rate). The electrons provided at the H_2 electrode are transmitted to the O_2 electrode via an external electrical circuit to produce electrical work. In such a cell, chemical energy is converted into electrical energy. These cells are called **galvanic cells**.[5] The reaction occurs spontaneously and is not driven. Important examples of galvanic cells are batteries (Section 2.4.4. and Chapter 15), fuel cells (Section 2.4.4 and Chapter 16),

[5] Luigi Galvani, 1737–1798, Italian physician, anatomist and physicist, professor of medicine in Bologna, famous for his work on electrophysiology with frog legs, lent his name to galvanic technology, the Galvani potential, galvanometer, and a crater on the moon.

and some types of chemical sensors (Section 5.1). Rechargeable batteries are galvanic cells during discharge and electrolysis cells during charging.

Of course, there is no *perpetuum mobile* in electrochemistry! For instance, the electrical energy used to drive a water electrolysis can by principle never be regained by bringing the formed H_2 und O_2 to a fuel cell for generating electricity. We will explore the energetics of electrochemical processes in detail in Chapters 2 and 3. We will treat the energy efficiency of electrochemical energy conversion devices in Chapter 15.

Figure 1.8 illustrates the relation between galvanic and electrolysis cells for the example of the Daniell cell.[6] A Cu sheet is immersed in the solution of a copper salt, for example $Cu(NO_3)_2$, in the left beaker. We call such an arrangement a **half-cell**. Electrochemical cells in Figure 1.8 consist of two half-cells each. In the right half-cells, a Zn sheet is placed in a zinc salt solution ($Zn(NO_3)_2$). The Cu and Zn electrodes in Figure 1.8 are immersed in different solutions. To distinguish them, the electrolyte around the anode is also called anolyte and the electrolyte around the cathode is called catholyte. The reactions in both half-cells commence only if the two metal sheets are connected by an electronic conductor (e.g., a metal wire). The electrolyte solutions in both half-cells also have to be connected electrically. A suitable connection could be based on a filter paper soaked in electrolyte solution, a porous glass disk (frit), or an ion-conducting membrane. In the laboratory, a salt bridge is frequently used. It consists of a glass tube terminated at both ends with a porous frit. The frits prevent the solution from leaking out of the tube, but allow ions to move to connect the two electrolyte reservoirs electrically. If the two metal sheets of the cell are connected via a voltmeter, the cell voltage can be determined. This voltage can also drive a small device. While electrical work is provided to the device, Cu is deposited and Zn is dissolved. If one connects a DC voltage source with the right polarity to the cell, a reversal of the reaction can be achieved: The noble Cu is dissolved and the nonnoble Zn is redeposited.

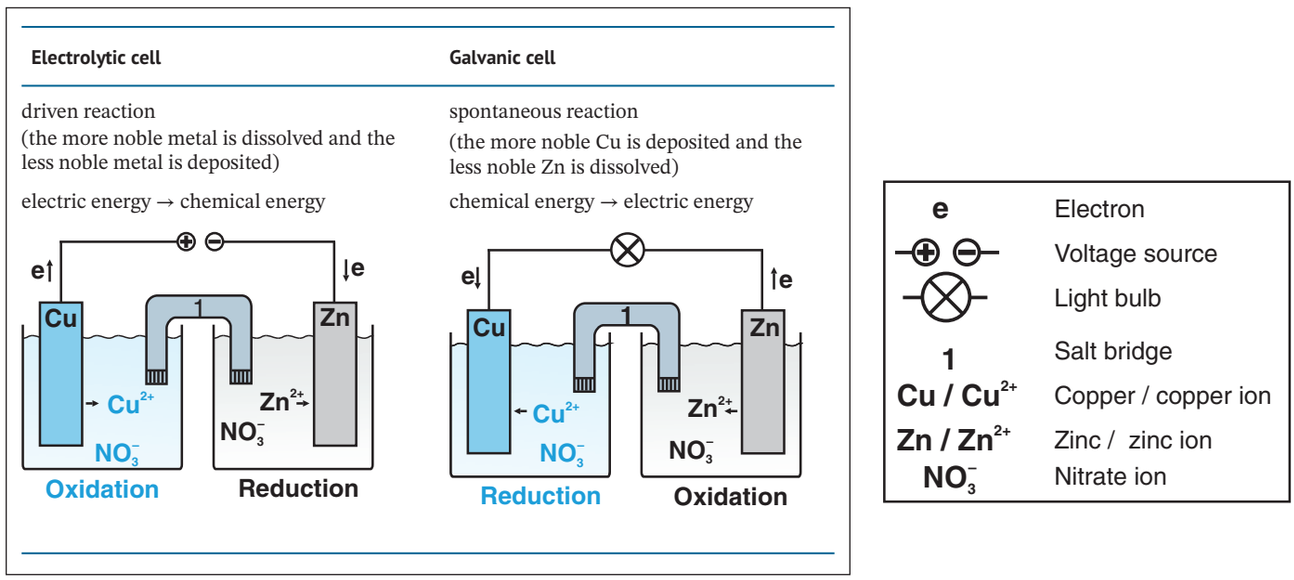

Figure 1.8 Comparison of electrolytic cell (left) and galvanic cell (right).

[6] John Frederic Daniell, 1790–1845, English scientist, professor of chemistry in London, the Daniell cell was widely used during the development of the telegraph system.

Q: It seemed to me that the (+) pole is always the anode and the (–) pole is always the cathode. Isn't this true?

A: It does not matter whether we consider a galvanic or an electrolysis cell; the anode is always the interface at which the oxidation happens and the cathode is associated with the reduction. This definition implies that the interface $Zn \mid Zn(NO_3)_2$ solution of the galvanic cell in Figure 1.8 is the anode, whereas it is the cathode in the electrolysis cell! It is recommended to avoid the terms (+) and (–) poles. In the context of battery technology, the electrode is called a cathode (anode) when the reduction (oxidation) occurs during the *discharge process*. Because this causes confusion in the context of rechargeable batteries, it is recommended to refer to the positive and the negative electrodes in this case.

By combining the shorthand notation for two electrodes from Figure 1.5 and salt bridge, we obtain

$$Cu \mid Cu(NO_3)_2(aq) \mid KNO_3(aq) \mid Zn(NO_3)_2(aq) \mid Zn \mid Cu'$$

The exact content of the salt bridge is not relevant (as long as no additional voltages are generated), and therefore, the salt bridge is often simplified and presented as a vertical double bar:

$$Cu \mid 1\ mol\ L^{-1}\ Cu(NO_3)_2(aq) \parallel 1\ mol\ L^{-1}\ Zn(NO_3)_2(aq) \mid Zn \mid Cu'$$

If the cell contains sheets of different metals, we have to consider a wire connection based on a uniform material as current feeders. In the example, a Cu wire (Cu and Cu′) is connected to the Cu and Zn sheets. This creates an additional Zn | Cu interface. We will return to this problem in Chapter 2.

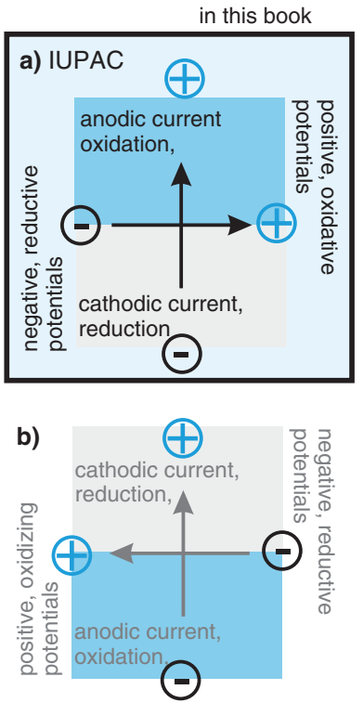

Figure 1.9 Conventions for plotting of currents and electrode potentials a) according to IUPAC and b) according to the polarographic convention. This book follows the convention in a), except for a few original figures taken from the literature.

1.6 Summary

Electrochemical reactions are redox reactions in which the oxidative and reductive partial reactions occur *simultaneously but spatially separated* at two electrodes: The oxidation proceeds at the anode, the reduction at the cathode. *Electrodes are interfaces* between structurally different, electrically conducting phases with at least one phase being an ion-conductor. The charge transmitted via the external electrical circuit equals the charge converted in the anodic and cathodic partial reaction $Q = nFN$. The current $I = \mathrm{d}Q/\mathrm{d}t$ is proportional to the heterogeneous reaction rate $I = nF\ \mathrm{d}N/\mathrm{d}t$ at any time. The current divided by the electrode area is the current density j. The sign of the current indicates the *direction of transport*. Oxidative (anodic) currents are positive and plotted upward according to the recommendation of IUPAC (Figure 1.9a). Positive and oxidizing potentials are plotted to the right. Note that the opposite *polarographic convention* is also common (Figure 1.9b). An *electrolysis cell* is used to drive chemical processes under the consumption of electrical energy (driven reaction). If chemical processes in an electrochemical cell occur spontaneously to generate electrical energy, we call the system a *galvanic cell*.

Test your knowledge

Exercise 1.1: Compile the definitions of scientific terms and physical quantities (with symbols and units) for: electrode, anode, cathode, electrode reaction, current density, Faraday constant, Avogadro constant, elementary charge, electrolysis cell, galvanic cell, half-cell, anodic current, cathodic current, ions, electrolyte, anion, cation. Provide an example and an algebraic formula for each term.

Exercise 1.2: A solution contains 0.4 mol L^{-1} potassium chloride and 0.3 mol L^{-1} magnesium chloride. Calculate the weight in grams of chloride ions contained in 200 mL of this solution.

Exercise 1.3: The electrolytic production of H_2 and O_2 is conducted with a current of 28 kA at electrodes with an area of 16 m^2 each. Calculate the current density and the reaction rate for the formation of molecular hydrogen in mol cm^{-2} s^{-1}.

Exercise 1.4: An electrolytic refinery plant for nickel is operated without interruption 24/7 with a constant current of 15 kA. Raw nickel is dissolved at the anode ($Ni \rightarrow Ni^{2+} + 2e^-$) and redeposited at the cathode ($Ni^{2+} + 2e^- \rightarrow Ni$).

a) How many tons can be purified in 16 days with an assumed faradaic yield of 100%?
b) What would be the length of an edge of a cube containing the amount of Ni purified in 16 days?

Exercise 1.5: For the electrolytic refinery of copper, copper is dissolved at the anode and redeposited at the cathode. In a pilot plant, an anode of 10 cm length, 10 cm width, and 1 cm thickness is used with a constant current of 10 A. The solution is stirred with 1500 revolutions per minute by a mechanical stirrer and kept at 40 °C. The energy for the pilot plant is supplied by a wind turbine with a specified output of 2 MW. The turbine runs under full load during the experiment. How long (hours and minutes) does this electrolysis take if the current yield is 90%.

Exercise 1.6: The chlorine gas obtained via chlorine-caustic electrolysis is filled into a steel cylinder of 100 L volume with a pressure of 100 MPa (at 298 K). One module of a large-scale electrolysis plant operates with 2.0 V cell voltage and at 200 kA current.

a) How long does it take to produce the chlorine for filling one steel cylinder?
b) How long would it take for a wind turbine of 2 MW specified power under full load to generate the electric energy required for the production of one cylinder of chlorine gas, provided that current yield is 100% and there are no energy conversion losses *outside* of the electrolytic cell (no losses in transformation, transmission, and rectification).
c) Discuss the consequences of the numerical results of a) and b) for using fluctuating sources of renewable electric for the described task.

Exercise 1.7: Provide a schematic drawing of the following electrochemical cell

$$Ag \mid AgCl \mid 1\ mol\ L^{-1}\ KCl \parallel 1\ mol\ L^{-1}\ KBr \mid AgBr \mid Ag$$

Exercise 1.8: Provide a shorthand notation of the electrochemical cell in Exercise 1.4 employing chloride as the anion in the electrolyte.

Exercise 1.9: Explain the fundamental differences between galvanic and electrolysis cells.

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