Chapter 1

Basic Concepts of Electrochemistry used in Electrical Engineering

1.1. Introduction

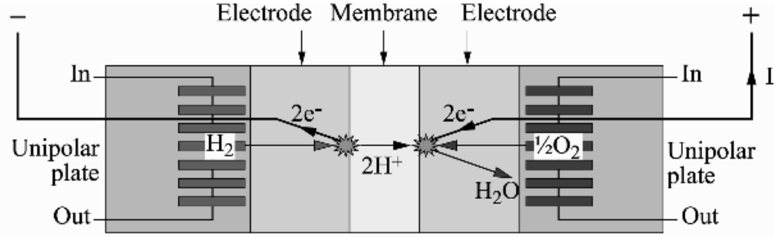
The aim of this chapter is to lay down some basic concepts of electrochemistry which are necessary in order to understand the behavior of the electrochemical components described in this book. For a detailed presentation, the reader could be helped by referring to specialized books such as [DIA 96; LEF 09].

1.2. Brief description and principles of operation of electrochemical components

1.2.1. *Principle of operation [TUR 08]*

Every electrochemical component is made up of a positive electrode and a negative electrode, separated by an electrolyte which may be either liquid or solid (see Figure 1.1). Conventionally, with generators, it is the positive electrode from which the current originates when functioning in generator mode.

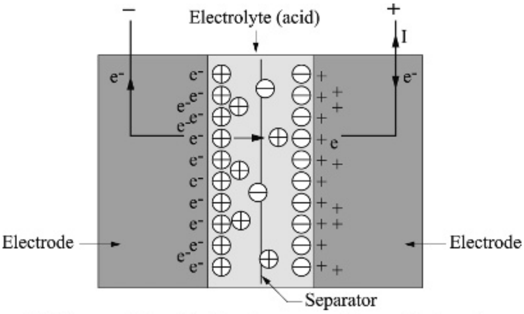
Generally speaking, an electrochemical component can operate as an electric generator or an electric load, or both if it has reversible function.



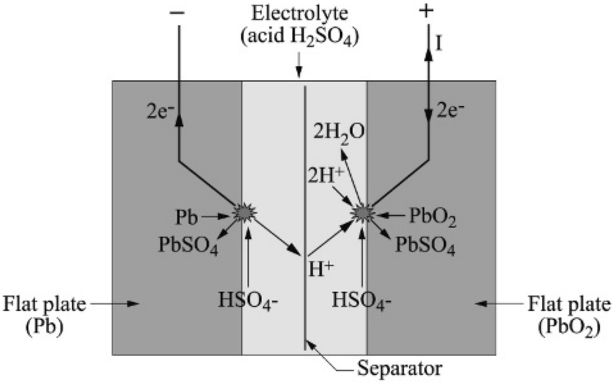
– electrode: $H_2 \leftrightarrow 2H^+ + 2e^-$; + electrode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \leftrightarrow H_2O$

Global reaction: $H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$

a) Diagram of the principle of a proton exchange membrane (PEM) fuel cell (or a PEM water electrolyzer, if the direction of all the arrows is reversed)



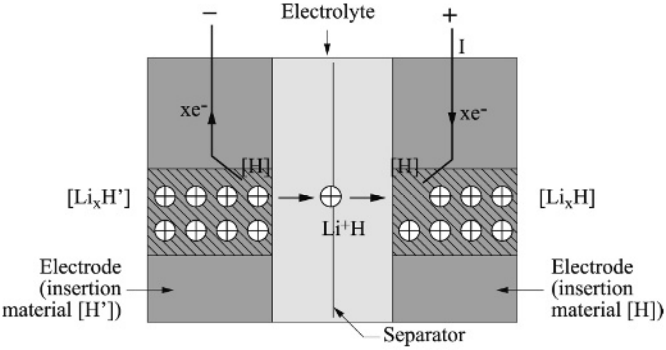
b) Diagram of the principle of a supercondenser (discharge)



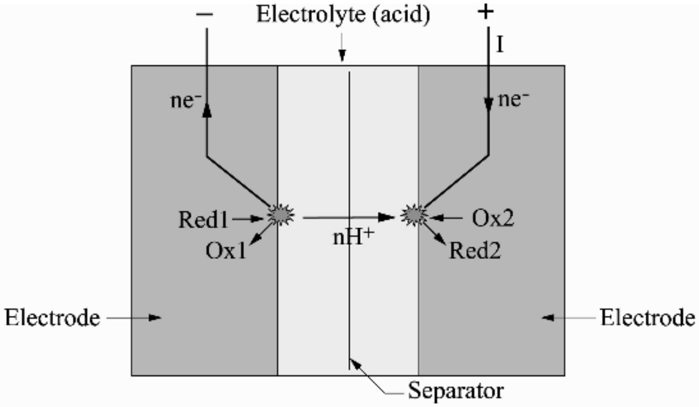
- *electrode*: $Pb + HSO_4^- = PbSO_4 + H^+ + 2e^-$
+*electrode*: $PbO_2 + HSO_4^- + 3H^+ + 2e^- = PbSO_4 + 2H_2O$
Global reaction: $Pb + PbO_2 + 2HSO_4^- + 2H^+ = 2PbSO_4 + 2H_2O$

c) Diagram of the principle of an acid/lead accumulator (discharge)

Figure 1.1. *Principle of operation of electrochemical components [TUR 08]*



d) Diagram of the principle of a lithium-ion accumulator (discharge)



Red1/Ox1 and Red2/Ox2 pairs
(hypothesis: acid medium; the electrolyte is not involved in the reaction):

– electrode: $a_1(\mathrm{Re}d1) + nH_2O \leftrightarrow c_1(Ox1) + ne^- + nH_3O^+$

+ electrode: $c_2(Ox2) + ne^- + nH_3O^+ \leftrightarrow a_2(\mathrm{Re}d2) + nH_2O$

Global reaction: $a_1(\mathrm{Re}d1) + c_2(Ox2) \leftrightarrow c_1(Ox1) + a_2(\mathrm{Re}d2)$

e) Diagram of the principle of an elementary cell in an electrochemical generator (discharge)

Figure 1.1. *(Continued) Principle of operation of electrochemical components [TUR 08]*

In short, the component is the site of an oxidation/reduction reaction which involves two “redox” pairs. More specifically, each electrode is the site of oxidation (loss of electrons) or reduction (gain of electrons) depending on the direction of the current flowing through the component (Figure 1.1e). The *n* electrons released by the oxidation reaction occurring in an electrode circulate from that electrode to the other via the external electrical circuit. Simultaneously to this circulation of electrons, and in the same direction, the *n* ions from the electrode being oxidized circulate toward the other electrode through the electrolyte. Thus, the reduction reaction is able to take place on the other electrode.

The electrodes need to be good electrical conductors. The electrolyte has to be a good ion conductor and a good electron insulator, in order to avoid any short-circuits between the two electrodes. In the case of a liquid electrolyte, a separator is usually used to electrically insulate the two electrodes. The reactions consume reactants and form products, which have to be respectively brought to and evacuated from the reaction area.

In addition, in any electrochemical component, at every interface between an electrode and the electrolyte, there is a spontaneous phenomenon of accumulation of opposite charges on both sides of that interface, which then constitutes a condenser, in the electrostatic sense of the term (Figure 1.2a). This phenomenon is referred to as a "double electrochemical layer". As local electrical polarization occurs over a depth ranging from a few dozen to a few hundred nanometers around that interface, the equivalent condensers may have very large values if the electrodes have a very large surface per volume (they are therefore dubbed supercapacitors). This phenomenon plays an important role in the dynamic behavior of the component.

Finally, the phenomena described above are accompanied by heat exchanges; the performances and lifetimes of the components are very sensitive to temperature. Hence, thermal aspects are of crucial importance for their implementation in electrical systems.

1.2.2. ***Brief description of groups of components***

There is a wide variety of electrochemical components for the production and storage of electricity [TUR 08], some of which will be the subject of a more in-depth description later on in this book. Amongst other things, it is possible to distinguish the following "families" of electrochemical components:

– accumulators (Chapter 5);

– supercapacitors (Chapter 4);

– fuel cells (Chapter 3);

– metal air batteries;

– electrolyzers (Chapter 2);

– reversible fuel cells (or electrolyzers);

– redox flow accumulators.

In the case of an accumulator (lead–acid, nickel–cadmium etc.), the electrical energy supplied as it discharges comes from the transformation of the free energy (this term will be clearly defined in section 1.4) from a redox reaction involving reagents already present in the accumulator at each electrode (Figures 1.1c and 1.1e). There is consumption or production of species at the electrodes and transport of charges from one electrode to the other via the electrolyte on the one hand, and via the external electrical circuit on the other. The electrolyte itself may be involved in the reaction (Figure 1.1c). This causes a structural alteration of the materials which make up the accumulator, which should ideally be reversible and allow numerous cycles of charge and discharge. Unfortunately, this is not the case in practice, which leads to an alteration of the electrode's internal structure and limits the number of cycles to a few hundred or thousand. The Li-ion accumulator is a special case, in that the lithium is "simply" introduced into the insertion materials (Figure 1.1c), passing from one electrode to the other, assuming different equivalent degrees of oxidation, and sources of chemical and electrical potentials. There is no significant macroscopic structural alteration of the electrodes, which *a priori* ensures better stability of the properties over time and a greater mass power [RAN 98; ROB 04].

In supercapacitors, the energy storage makes optimum use of the phenomenon of the double electrochemical layer, by using very large surface area to volume ratios at the two interfaces between the electrodes and the electrolyte (Figure 1.1b). There is very little structural alteration of the materials or transport of species, which means we are able to obtain power performances far superior to those of accumulators, and achieve a very high number of cycles (> 100,000). Conversely, the mass energy is smaller, and only part of the energy stored is usable, because it is difficult to recover energy ($1/2CV^2$) at low voltage levels [CON 99].

For this reason, in certain supercapacitors, Faradaic reactions are also exploited, yielding a hybrid component (supercapacitor–accumulator), providing a compromise between energy and power, which may be advantageous for certain applications and which enables us to exploit all the energy stored in the double electrochemical layer of the "internal supercapacitor" using the voltage from the "internal accumulator". This type of hybrid component therefore offers interesting avenues for dedicated design in a system approach, but the technology has not yet reached maturity.

In the components discussed above, accumulators and supercapacitors, the energy is stored in the electrochemical component itself. Thus, it is notably characterized by its specific power and specific energy [CHR 00].

In addition, apart from the primary accumulators (which are, by definition, non-rechargeable), all these components instantly facilitate reversible functions in terms of power (charge or discharge) which, unfortunately, are often not symmetrical. This property is of crucial importance for their use in electrical systems.

The situation is entirely different with fuel cells. A fuel cell does indeed experience a redox reaction which converts chemical energy into electrical energy, but the reagents are stored in tanks outside of the cell (Figure 1.1a). It is only truly characterized by its mass and volume powers. The energy that it is capable of supplying depends on the volume of the reservoirs and the nature of the fuel. Thus, there is no direct relation between the stored energy and the power supplied. In addition, theoretically, the fuel cell experiences no structural modification by the principle of its operation (there is no transport of species from one electrode to the other). Nevertheless, it is the site of various degradation phenomena, influenced by the conditions in which it operates, which limit its lifetime [LAR 00; STE 00].

Certain fuel cells can carry their fuel along with them, and therefore are halfway between a fuel cell as defined above and an accumulator. Such is the case, in particular, for metal–air batteries, which directly consume the metal fuel (zinc, aluminum, etc.) that their negative electrode is made of, by reaction with oxygen (contained in the air or purified), which transforms it into metal oxide stored in the battery. The consequence of this is that as it discharges, the component may become heavier and be deformed by the fixation of oxygen. In order to prevent this situation, which could render the component unusable, the metal oxide formed by the reaction must be regularly evacuated by circulation of the liquid electrolyte before it precipitates. To recharge the component, we have to replace its negative electrode when it is consumed. Note that it is possible to recycle the metal oxide recovered by electrolyzing it to re-create the metal to make the negative electrode. For very low-power applications, the metal–air battery is equivalent to a very long-lasting primary accumulator (very slow discharge when protected from oxygen) and with quasi-instantaneous recharge. This type of battery, which is less common, will not be discussed in Chapter 3.

Electrolyzers can be viewed as the dual components of the corresponding fuel cells (Figure 1.1a). This is true, in particular, of water electrolyzers and metal oxide electrolyzers. They employ the reverse redox reactions to those involved in the corresponding fuel cells, and function as receivers of electrical energy and thermal energy. The reagent for the positive electrode must be regularly supplied, and the by-products evacuated and stored (which is not often the case with the oxygen that is produced). Thus, the electrolyzers can refill the reservoirs that are emptied by the fuel cells – this property might be particularly advantageous in an electrical system. The electrolyzers are really components for storage of electric energy in the form of synthesized chemical compounds (gases, metals, etc.) – granted, with lesser efficiencies than accumulators but with good potentials for mass storage [MIL 07].

In general, fuel cells and electrolyzers cannot offer power-reversible function. As they are designed to be electricity generators and receivers, respectively, operating them respectively as receivers and generators – even temporarily – can accelerate their aging and breakdown. Indeed, the redox reactions, which are in principle reversible, are generally not symmetrical, and optimal use of them – particularly in catalytic terms – may be very different depending on whether the cell is charging or discharging. This remark is particularly accurate in the context of fuel cells and electrolyzers, but can be extended to accumulators, where the conditions of charging and discharging are not at all symmetrical. Nevertheless, reversible fuel cells (or electrolyzers) are the subject of research, because they could present a particularly promising potential.

Finally, there are redox flow batteries which result from the hybridization of the functions of an accumulator and a fuel cell. Two reservoirs contain the liquid reagents at different levels of oxidation, which are brought in to react in a reversible fuel cell core. In these power-reversible devices, which represent a viable solution for heavy-duty storage of high-energy, high-power electricity, the energy stored and the power are unrelated, and there is no structural alteration of the component. In the principle of its operation, the device is comparable to reversible pumping/turbining groups exploiting two dams, as is the combination of an electrolyzer, storage of reagents and a fuel cell.

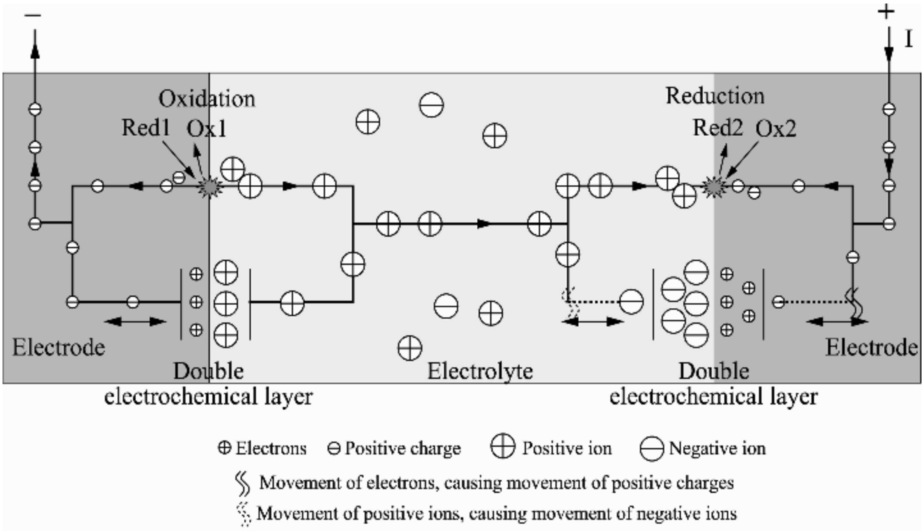
There is a wide variety of redox pairs and technologies within these broad categories, which means we have a very wide range of solutions to choose from, depending on the constraints of the technical specifications and of the system.

Following this brief overview, the rest of this chapter is given over to the formalization and expression in equation form of the main phenomena described above.

1.3. Redox reaction

As mentioned in section 1.2.1, a redox reaction involves a redox pair whose oxidized (or oxidizing) form is represented as *Ox* and the reduced (or reducing) form denoted as *Red*. These two species exchange electrons in accordance with equation [1.1]. In the oxidation direction, electrons are produced. In the reduction direction, the electrons are consumed. When we write a chemical equation, we do not express the quantity in terms of the number of molecules or ions, but rather the number of moles. Remember that a mole is equal to N, Avogadro's number ($N = 6.02214 \times 10^{23}$). Coefficients a and b are called stoichiometric coefficients: when n moles of electrons are exchanged, a moles of reducing species and b moles of oxidizing species are produced or consumed, depending on the direction of the reaction.

$$a \ \mathrm{Red} \overset{K_{ox}}{\underset{K_{red}}{\leftrightarrow}} b \ \ Ox + ne^{-} \qquad [1.1]$$



a) Redox and double layer phenomena in an electrochemical component

	Electrostatic supercapacitor	Electrochemical supercapacitor	Accumulator FC Electrolyzer
Majority physical phenomena	Double layer *	Double layer * + redox **	Redox **
Minority physical phenomena	Redox		Double layer *

* Electrostatic phenomenon ** Faradaic phenomenon

b) Predominant phenomena in electrochemical components (excluding thermal phenomena)

Figure 1.2. *Coupled electrostatic and Faradaic phenomena in an electrochemical component [TUR 08]*

In an electrochemical component, redox reactions occur at the interface between an electrode (which is an electron-conductive medium) and an electrolyte (which is an ion-conductive medium). Furthermore, in such a component, two electrodes are involved, as a cell is made up of two electrodes and an electrolyte. In addition, the elements described hereafter may relate only to one electrode and to one half of the reaction, or indeed to the whole cell with its two electrodes, the two half reactions at each of the two electrodes and the balance reaction.

1.4. Chemical energy

1.4.1. *Enthalpy, entropy and free energy*

A system is said to be open if it exchanges energy and species with its environment, regardless of its form. The characteristic state function of the system is therefore the enthalpy, notated as *H*. When a chemical reaction occurs in the system at a given pressure and temperature, the enthalpy of the system changes, and that change is notated as $\varDelta H$. It is accompanied by a release or absorption of heat Q_{rev}:

– if the system releases heat, Q_{rev} is positive, and the reaction is said to be exothermic; and

– if the system absorbs heat, Q_{rev} is negative, and the reaction is said to be endothermic.

The heat produced or absorbed is expressed as a variation in the entropy of the system, which is said to be reversible:[1]

$$Q_{rev} = T\varDelta S_{rev} \tag{1.2}$$

Thus, we define the variation in free enthalpy or the variation in the Gibbs free energy ΔG as being the difference between the variation in enthalpy and the heat released or absorbed.

$$\varDelta G = \varDelta H - T\varDelta S_{rev} \tag{1.3}$$

The variation in free energy thus represents the energy released or consumed during the reaction which can be converted – into electrical energy in the case of discharge of an accumulator, for instance, or into chemical energy in the case of recharge.

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[1] The term “reversible” indicates that it is a heat exchange, with heat given to the medium when the reaction is exothermic, and taken away from it in the case of an endothermic reaction. It is not a question of loss, which corresponds to an irreversible phenomenon with heat given to the medium.

1.4.2. *Enthalpy, entropy and free energy of formation*

The variation in enthalpy at standard pressure during the course of the formation of a mole of a compound is called its enthalpy of formation. Hereafter in this chapter, it is denoted as Δh_f^0: the lowercase letter indicates that we are dealing with a mole of the substance; the superscript ^{0} reminds us that we are at standard pressure. In [ATK 96], the reader can find values of Δh_f^0 tabulated according to the temperature. If the reaction temperature T is different from that which is referenced T_{ref}, we can calculate the value of Δh_f^0 on the basis of its calorific capacity C_p for an isobaric transformation (meaning with no variation in pressure, as is the case in electrochemical components) [FEI 06].

$$\Delta h_f^0(T) = \Delta h_f^0(T_{ref}) + \int_{T_{ref}}^{T} C_p d\theta \qquad [1.4]$$

Similarly, the variation in entropy at standard pressure during the formation of a mole of a compound is called its entropy of formation. Hereafter in this chapter, it is denoted as Δs_f^0. Likewise for enthalpy, there are tables which show values for Δs_f^0 on the basis of the temperature. For a different temperature, we can calculate the value of Δs_f^0 as a function of the calorific capacity for an isobaric transformation C_p.

$$\Delta s_f^0(T) = \Delta s_f^0(T_{ref}) + \int_{T_{ref}}^{T} \frac{C_p}{\theta} d\theta \qquad [1.5]$$

Thus, we can deduce the free energy of formation at temperature T, $\Delta g_f^0(T)$, i.e. the energy which is “free” to be transformed into a form of energy other than the heat given off during the reversible reaction (e.g. electrical energy during discharge).

$$\Delta g_f^0(T) = \Delta h_f^0(T) - T\Delta s_f^0(T) \qquad [1.6]$$

1.5. Potential or voltage of an electrode

Between the electrode and the electrolyte a difference in potential exists, referred to as the absolute voltage of the electrode. In practice, we do not measure the potential of the electrode but rather a difference in potential in relation to a reference electrode defined during the phase of design and characterization of the electrode. The electrode potential is thus defined in relation to a reference whose potential is zero.[2]

If the system is at electrochemical equilibrium at standard pressure P_0= 1 bar, the potential of the electrode with zero current is the reversible redox potential E^0.

Consider a redox reaction during which n electrons are exchanged to form one mole of product [LAR 00]. Hence, the electrical charge exchanged is:

$$q = -nF \tag{1.7}$$

where F is the charge of a mole of electrons.[3]

At standard pressure, the voltage at the limits of the system being the standard potential E^0, the electrical energy produced (during discharge of an accumulator, for example) or consumed (during charging of an accumulator, for instance) during the course of the formation of one mole of product is therefore:

$$W_{elec} = -E^0 \times nF \tag{1.8}$$

If we consider that all of the Gibbs free energy is converted into electricity (when charging), or that all the electricity is converted into Gibbs free energy (when discharging), this means that the reaction is without loss, so:

$$W_{elec} = \Delta g_f^0 \tag{1.9}$$

Thus, we get an expression of the standard potential:

$$E^0 = -\frac{\Delta g_f^0}{nF} \tag{1.10}$$

1.6. Reversible potential of a cell

When we consider a whole cell inserted into an electrical circuit, the half redox reactions are no longer balanced, because the electrons and ionic species are exchanged between one electrode and the other. The electrodes are no longer at

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[2] The electrode with zero potential is the Normal Hydrogen Electrode (NHE). Experimentally, we choose an electrode for which we know the relative voltage in comparison to the NHE, tabulated for all temperatures.

[3] F is known as the Faraday constant, expressed in Coulombs (C): $F = 96485$ C

thermochemical equilibrium and their potential is altered. At one electrode – the anode – electrons are produced by the oxidation reaction; at the other – the cathode – the electrons are captured by the reduction reaction. If the cell is functioning as a generator, it produces current in a load, and cedes electrical power to that load; this is what happens in a fuel cell battery or in an accumulator during discharge. The potential of the anode is then lesser than the potential of the cathode. If the cell is functioning as a receiver, it receives power from an electrical source, as happens in the case of an electrolyzer cell or an accumulator on charge. The potential of the anode is then greater than the potential of the cathode (Figure 1.3) [DIA 96].

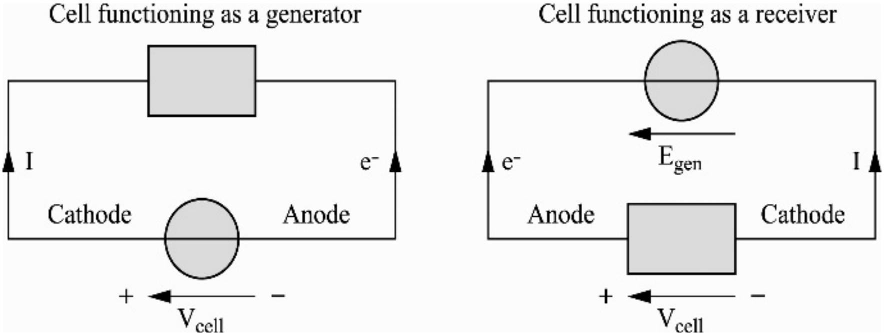

Figure 1.3. *Operation of a cell functioning as a generator (discharge of an accumulator) and as a receiver (charge of an accumulator)*

Thus:

– during charge, the potential of the anode is greater than that of the cathode; the positive electrode is the anode and the negative electrode the cathode;

– during discharge, the potential of the cathode is greater than that of the anode; the positive electrode is the cathode and the negative electrode the anode.

Hereinafter, so as to use identical equations to describe accumulators in charge or discharge mode, fuel cells or electrolyzers, we define the reversible potential, in standard conditions, of a cell, if it were at equilibrium and lossless, as being the difference between the highest electrode potential E^+ (positive electrode) and the lowest electrode potential E^- (negative electrode) [1.11] [TUR 08].

$$E^0_{rev} = E^+ - E^- \qquad [1.11]$$

The conditions of operation may well be different from standard conditions. The potential of the cell thus obeys the Nernst equation. The reversible potential of the cell is therefore calculated as follows:

$$E_{rev} = E^0 + \frac{RT}{nF} \ln \frac{\underset{j}{\Pi}\, a_{j\text{reactants}}^{vj}}{\underset{i}{\Pi}\, a_{i\text{products}}^{vi}} \qquad [1.12]$$

R is the ideal gas constant[4], T the temperature expressed in K, a_i the activity of species i and v_i its stoichiometric coefficient. There are various values which can be used to express activity. For a species in its gaseous phase, the activity can be expressed as the partial pressure of the gas P_i (section 1.16) referenced in relation to standard pressure P_0 (or indeed the partial pressure expressed in bars). For a standard substance in the liquid phase, the activity can be taken as equal to 1. For species in an ideal solution, the activity is equal to the ratio of concentration of the species to the reference concentration of 1 mole/l^{-1} [ATK 96].

$$\begin{aligned} & a_i = \frac{P_i}{P_0} \text{ for a species in the gaseous phase} \\ & a_i = 1 \text{ for a pure substance or a solvent} \qquad [1.13] \\ & a_i = \frac{[i]}{c_0} \quad \text{where } c_0 = 1 \text{ mole/l} \end{aligned}$$

1.7. Faradaic current density and the Butler–Volmer equation

The electrochemical reactions at the electrodes give rise to charged species which move under the influence of the electrical field created by the difference in potential between the positive electrode and the negative electrode when a circuit connects the two electrodes. The electronic charges move into the electrodes and the ionic charges move into the electrolyte, with the electrode/electrolyte interface ensuring continuity between the two modes of conduction. Hence, the electrodes are no longer at electrochemical equilibrium.

As the reactions take place at the interface, a value that is frequently used for electrochemical components is the current density j, with I being the current of the cell and S the geometric surface area of the electrode. In view of the usual

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[4] $R = 8.314\,472$ J.mol^{-1}.K^{-1}.

dimensions of cells, the current density is often expressed in [A.cm^{-2}], but in the expressions given below, the unit used is that of the SI system [A.m^{-2}].

$$j = \frac{I}{S} \qquad [1.14]$$

Consider the notations of the redox reaction [1.1], with K_{ox} and K_{red} being the reaction constants respectively in the directions of oxidation and reduction [DIA 96].

The Faradaic current density of the electrode, i.e. the flow of electrons toward the electrode, is connected to the rate of appearance of the electrons v_o (in the direction of oxidation) and the rate of their disappearance v_r (in the direction of reduction):

$$j_f = nFv = nF\left(v_o - v_r\right) \qquad [1.15]$$

The reaction rates depend on the activities of the oxidizing and reducing species a_{Ox} and $a_{\mathrm{Re}d}$ at the electrode/electrolyte interface, and on the reaction constants K_{ox} and K_{red}, where:

$$v_o = K_o a_{\mathrm{Re}d}^{a} \text{ and } v_r = K_r a_{Ox}^{b} \qquad [1.16]$$

$$K_o = k_o e^{\frac{\alpha_o nF}{RT}E} \text{ and } K_r = k_r e^{\frac{-\alpha_r nF}{RT}E} \qquad [1.17]$$

Thus, we can express the Faradaic current density j_f as a function of the electrode potential *E*, so that:

$$j_f = nF\left(k_o a_{\mathrm{Re}d}^{a} e^{\frac{\alpha_o nF}{RT}E} - k_r a_{Ox}^{b} e^{\frac{-\alpha_r nF}{RT}E}\right) \qquad [1.18]$$

α_o and α_r are the factors of symmetry of the electron transfer reaction or the transfer coefficient respectively in the oxidation and reduction directions. A coefficient equal to 0 means that we do not need to supply energy to the reagents in order for the reaction to take place. The coefficients vary in the interval [0,1]. With a first-order reaction, they are linked by the equation:

$$\alpha_o + \alpha_r = 1 \qquad [1.19]$$

Usually, we express equation [1.18] as a function of the overvoltage η, defined as the difference between the potential of the electrode and the thermodynamic potential:

$$\eta = E - E_{rev} \tag{1.20}$$

This expression is known as the Butler–Volmer equation:

$$j_f = j_0 \left(\left(\frac{a_{red}}{a_{red,eq}} \right) e^{\frac{\alpha_o nF}{RT}\eta} - \left(\frac{a_{ox}}{a_{ox,eq}} \right) e^{\frac{-\alpha_r nF}{RT}\eta} \right) \tag{1.21}$$

j_0 is called the exchange current density. At equilibrium, the Faradaic current is null because the rate of appearance of electrons is equal to the rate of disappearance of electrons. Each of these reaction rates can be interpreted as a current density $j_0 = \frac{v_{o,eq}}{nF} = \frac{v_{r,eq}}{nF}$. The activities $a_{i,eq}$ are the activities of the products at equilibrium or a long way from the reactional interface. We can show that the exchange current density is written:

$$j_0 = nFk_0^{\alpha_r} k_r^{\alpha_o} a_{red,eq}^{\alpha_r} a_{ox,eq}^{\alpha_o} = nFk^0 a_{red,eq}^{\alpha_r} a_{ox,eq}^{\alpha_o} \tag{1.22}$$

where k^0 is the standard constant of rate of electron transfer for the redox reaction:

$$k^0 = k_0^{\alpha_r} k_r^{\alpha_o} \tag{1.23}$$

The Butler–Volmer equation expresses the fact that two phenomena are involved. The first is the transfer of electronic charge. The second phenomenon is the transport of species, which manifests itself in the terms of activity of the species at the reactional interface, which may be different from those at equilibrium or far from the reaction site (see section 1.11).

1.8. Butler–Volmer equation for a whole cell

When the system is no longer at equilibrium, the reaction is favored in the direction of oxidation at the anode (production of electrons) and in the direction of reduction at the cathode (consumption of electrons). We can write a Butler–Volmer equation at each electrode:

At the anode:

$$j_{fa} = j_{0a} \left(\left(\frac{a_{a,red}}{a_{a,red,eq}} \right) e^{\frac{\alpha_{oa} nF}{RT} \eta_a} - \left(\frac{a_{a,ox}}{a_{a,ox,eq}} \right) e^{\frac{-\alpha_{ra} nF}{RT} \eta_a} \right) \qquad [1.24]$$

At the cathode:

$$j_{fc} = j_{0c} \left(\left(\frac{a_{c,red}}{a_{c,red,eq}} \right) e^{\frac{\alpha_{oc} nF}{RT} \eta_c} - \left(\frac{a_{c,ox}}{a_{c,ox,eq}} \right) e^{\frac{-\alpha_{rc} nF}{RT} \eta_c} \right) \qquad [1.25]$$

When the cell, formed by the association of an anode with a cathode, is in operation and there is a current flowing through it, the two current densities are, of course, connected. At the anode, the current is an oxidizing current, it is inbound (see Figure 1.3) and counted positively. At the cathode, the current is a reducing current, it is outbound, and is counted negatively. Let j_f represent the Faradaic current density of the cell:

$$\begin{aligned} j_f = j_{fa} &= j_{0a} \left(\left(\frac{a_{a,red}}{a_{a,red,eq}} \right) e^{\frac{\alpha_{oa} nF}{RT} \eta_a} - \left(\frac{a_{a,ox}}{a_{a,ox,eq}} \right) e^{\frac{\alpha_{rc} nF}{RT} \eta_a} \right) \\ j_f = -j_{fc} &= j_{0c} \left(- \left(\frac{a_{c,red}}{a_{c,red,eq}} \right) e^{\frac{\alpha_{oc} nF}{RT} \eta_c} + \left(\frac{a_{c,ox}}{a_{c,ox,eq}} \right) e^{\frac{-\alpha_{rc} nF}{RT} \eta_c} \right) \end{aligned} \qquad [1.26]$$

In addition, the sign of the anodic and cathodic overvoltages is different depending on whether the cell is acting as a generator (discharge) or a receiver (charge). Also, in the interests of generality, we shall revert now to using the notation of the positive electrode and the negative electrode. The subscripts a and c are thus replaced by + and –. Hence, we have:

$$\begin{aligned} \eta_- &= E_- - E_{rev-} > 0 \\ \eta_+ &= E_+ - E_{rev+} < 0 \end{aligned} \qquad [1.27]$$

Figure 1.4 shows the plot for the Faradaic current as a function of the potential of the electrodes in the case of an accumulator on charge or an electrolyzer. The negative electrode is the cathode, for which the current is counted positively, and the positive electrode is the anode, for which the current is counted negatively. The voltage at the cell terminals is the difference between the potential of the anode and the potential of the cathode. In the above plot, we considered the activity of the reagents and the products at the electrodes to be identical to that at equilibrium or far from the electrodes; this issue will be discussed later on in section 1.11. In this case, the overvoltages are referred to as activation overvoltages (see section 1.9).

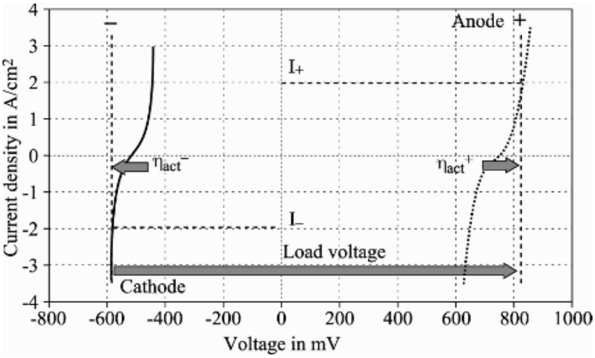

Figure 1.4. *Example of a cell of a charging accumulator or an electrolyzer for which all the symmetry coefficients are equal to 0.5, the exchange current densities 10 mA/cm* $^{-2}$ *and T = 330 K. [TUR 08]*

1.9. From the Butler–Volmer equation to the Tafel equation

The Butler–Volmer equations comprise two exponential terms. When the overvoltage η reaches a sufficiently high value, meaning that the current density is sufficiently great in comparison to j_{0-} and j_{0+}, the negative exponential term becomes negligible in comparison to the positive exponential term. Thus, the equation is simplified and becomes:

$$\begin{aligned} j_f &\approx j_{0-}\left(\left(\frac{a_{a,\text{reactant}}}{a_{a,\text{reactant,eq}}}\right)e^{\frac{\alpha_- nF}{RT}\eta_-}\right) \\ j_f &\approx j_{0+}\left(\left(\frac{a_{c,\text{reactant}}}{a_{c,\text{reactant,eq}}}\right)e^{\frac{\alpha_+ nF}{RT}\eta_+}\right) \end{aligned} \quad \text{for } j_f >> j_{0-}, j_{0+} \qquad [1.28]$$

In addition, if we discount the influence of transport of matter (see section 1.11) [SAI 04], then the ratios of the activities are equal to 1, and the equations become:

$$j_f = j_{0-}\left(e^{\frac{\alpha_- nF}{RT}\eta_{act,-}}\right) = j_{0+}\left(e^{\frac{\alpha_{r+} nF}{RT}\eta_{act,+}}\right) \qquad [1.29]$$

The corresponding overvoltages are called "activation overvoltages". This term should be viewed in the light of the "activated complex" theory [DIA 96]. In an elementary reactional stage, this theory postulates that there is an intermediary molecular state called the "transition state" or "activated complex", with a very short lifespan. In order to go from state A (e.g. oxidized state) to state B (e.g. reduced state), the reagent species thus needs to pass through an "activated complex" state AB*, whose energy is greater than A and B (Figure 1.5). Thus, in order for the state of oxidation of a species to change, the electron has to cross the "activation barrier" of the activated complex. In order for the oxidizing agent to reach its reduced form, it is necessary to supply the reduction energy ΔG^*_{red}. Similarly, in order for the reducing agent to reach its oxidized form, it is necessary to inject the oxidation energy ΔG^*_{ox}.

This enables us to offer a qualitative explanation for the inevitable loss of energy when a redox reaction occurs, i.e. when the cell emits or absorbs current.

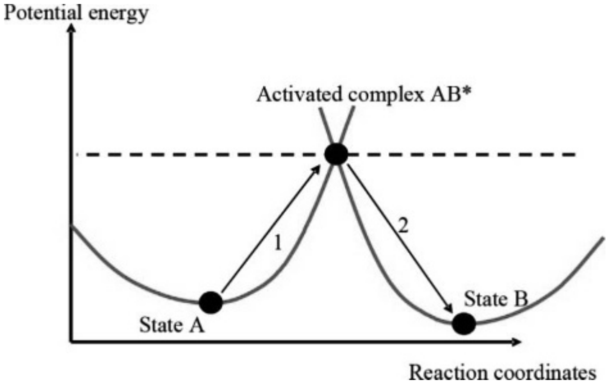

Figure 1.5. *Illustration of the activated complex theory. 1: increase of the potential energy and formation of the unstable activated complex; 2: the unstable activated complex loses some of its potential energy as kinetic energy [TUR 08]*

These equations are invertible, and we can easily express the anodic and cathodic activation overvoltages as a function of the Faradaic current density. In their inverted form, they are known as the Tafel equations:

$$\begin{aligned} \eta_{act,-} &= \frac{\alpha\_nF}{RT}\ln\left(\frac{j_f}{j_{0-}}\right) \\ \eta_{act,+} &= \frac{\alpha_+ nF}{RT}\ln\left(\frac{j_f}{j_{0+}}\right) \end{aligned} \quad \text{for } j_f >> j_{0-}, j_{0+} \qquad [1.30]$$

They can also be expressed in a semi-empirical form:

$$\left.\begin{array}{l}\eta_{act,-} = A_- \ln\left(\dfrac{j_f}{j_{0-}}\right) \\ \eta_{act,+} = A_+ \ln\left(\dfrac{j_f}{j_{0+}}\right)\end{array}\right. \text{for } j_f >> j_{0-}, j_{0+} \qquad [1.31]$$

The A_-, A_+ are called the Tafel slope respectively of the negative and positive electrodes.

1.10. Faraday's law

The exchange of electrons between two electrodes is due to redox reactions at the electrodes which consume reagents and form products. Faraday's laws can be used to calculate the flowrates of the reagents and products involved in the reactions. Let us return to the general form of the redox equation written at the negative electrode in the direction of oxidation and at the positive electrode in the direction of reduction. Balancing it so that the coefficients of stoichiometry of the reagents are equal to 1, we get:

At the anode:

$$\mathrm{Re}d_a \rightarrow b_a \; Ox_a + n_a e^- \qquad [1.32]$$

At the cathode:

$$Ox_c + n_c e^- \rightarrow a_c \; \mathrm{Re}d_c \qquad [1.33]$$

The current emitted or absorbed by the cell is the electronic charge emitted or absorbed per second; hence, it is equivalent to a molar flowrate of electrons via the Faraday constant F[5], which represents the charge of a mole of electrons in Coulombs:

$$I = q_{e-}F \qquad [1.34]$$

---

[5] The Faraday constant is denoted as *F*, expressed in Coulombs (C) and its value is F = 96485 C.

For n_a moles of electrons, one mole of reagent is consumed at the anode. Thus, to produce one mole of electrons, $\frac{1}{n_a}$ moles of reagent $\mathrm{Re}d_a$ have been consumed at the anode. Hence, in order to produce the molar flowrate of electrons q_{e-}, we consume a molar flowrate of reagent, $q_{\mathrm{Re}d_a}$:

$$q_{\mathrm{Re}d_a} = \frac{q_{e-}}{n_a} = \frac{I}{n_a F} = \frac{j_f S}{n_a F} \quad [mols^{-1}] \tag{1.35}$$

By applying the same reasoning at the cathode, we obtain Faraday's law for the anode and the cathode:

$$\begin{aligned} q_{\mathrm{Re}d_a} &= \frac{I}{n_a F} = \frac{j_f S}{n_a F} \quad [mols^{-1}] \\ q_{Oxc} &= \frac{I}{n_c F} = \frac{j_f S}{n_c F} \quad [mols^{-1}] \end{aligned} \tag{1.36}$$

These laws can also be written as the molar flowrate, by calculating the molar mass of the reagents:

$$\begin{aligned} \dot{m}_{\mathrm{Re}d_a} &= \frac{I}{n_a F} M_{\mathrm{Re}d_a} = \frac{j_f S}{n_a F} M_{\mathrm{Re}d_a} \quad [gs^{-1}] \\ \dot{m}_{Oxc} &= \frac{I}{n_c F} M_{Oxc} = \frac{j_f S}{n_c F} M_{Oxc} \quad [gs^{-1}] \end{aligned} \tag{1.37}$$

1.11. Matter transfer model: Nernst model

In order for a reaction to be able to happen continuously, the reagents need to be continuously supplied by way of matter transfer phenomena. Generally, the chemical species can move into the electrodes and the electrolyte in different ways [DIA 96]:

– by electrical migration, which consists of a movement into an electrical conductor of charged particles under the influence of an electric potential gradient;

– by diffusion, which consists of a movement of species – charged or neutral – under the influence of a concentration gradient. Thus, the species move from the most concentrated area into the least concentrated area, to tend toward equilibrium; and

– by forced or natural convection, which consists of a movement of species under the influence of the movement of the medium in which they are present. This movement may be caused by a thermal or mechanical gradient.

Thus, the modeling of matter transport is a complex subject, governed by different phenomena, different boundary conditions, different media, etc.

Here, we intend to present Nernst's model of diffusion/convection. To begin with, we consider that the reaction occurs mainly at the interface between the electrode and the electrolyte (reaction surface). Thus, the reagents need to diffuse and reach that interface in order to react (Figure 1.13). Convection can be explained by the fact that, beyond a certain distance from the reactive zone, the concentration of reagent can be deemed to be constant and independent of the distance from the reactive zone. Consider an electrode. We wish to describe the profile of concentration of an electroactive species in stationary conditions. We suppose that the transport of matter occurs only in one direction x, which is perpendicular to the plane of the electrode.

The transport of matter is governed by Fick's law:

$$D_{Xi} \frac{\partial^2 [X_i]}{\partial x^2} = \frac{\partial [X_i]}{\partial t} \qquad [1.38]$$

In a stationary regime, this law is written as:

$$D_{Xi} \frac{\partial^2 [X_i]}{\partial x^2} = 0 \qquad [1.39]$$

where D_{Xi} is the constant of diffusion of species X_i in the medium and is expressed in m^2s^{-1}. In an area sufficiently far removed from the reaction interface, $x \geq \delta_i$, where δ_i is the thickness of the diffusion zone, the concentration of species is not altered by the reaction happening at the electrode – it is a convection regime. Such is the case, for instance, in the channel in a fuel cell carrying a reagent. In this area, equation [1.39] has the following solution:

$$[X_i] = [X_i]_{eq} \text{ for } x \geq \delta_i \qquad [1.40]$$

In the stationary regime, the flow of species X_i, J_{X_i}, across the surface of the electrode *S*, is constant. The species X_i is consumed (or respectively produced) by the redox reaction, during the course of which n electrons are exchanged. The flow of the species X_i across the surface of the electrode S is thus regulated by Faraday's law.

$$J_{Xi} = \pm \frac{q_{Xi}}{S} = \pm \frac{j_f}{nF} \qquad [1.41]$$

The sign "–", or respectively "+", corresponds to a species consumed, or respectively a species produced.

In the zone of diffusion of the species X_i, of thickness δ_i, Fick's law is then written:

$$D_{Xi} \frac{d[X_i]}{dx} = -J_{Xi} \qquad [1.42]$$

At $x = \delta_i$, the boundary condition for the concentrations of reagents is:

$$[X_i](\delta_i) = [X_i]_{eq} \qquad [1.43]$$

This gives us the profile of concentration of reagents:

$$[X_i](x) = \left[X_{i,eq}\right] - \frac{J_{Xi}\delta_i}{D_{Xi}} + \frac{J_{Xi}x}{D_{Xi}} = \left[X_{i,eq}\right] - \frac{j_f(\delta_i - x)}{D_{Xi}nF} \qquad [1.44]$$

The concentration profile obtained by this model is linear in the diffusion zone, with an increasing slope for a consumed species and a decreasing one for a produced species, if the origin of the axis Ox is the reaction interface. Other types of models can be developed – particularly those of mixed diffusion, as several species can coexist in the same medium (for instance, air, a nitrogenous compound, oxygen, water vapor, in an H_2/air fuel cell).

1.12. Concept of limit current

The redox reactions at the electrodes influence the concentrations of the species. The stronger the current at an electrode, the more quickly the medium loses reagent and gains product. Indeed, the rate of disappearance of the reagents, related to the kinetics of the reaction, increases in relation to the rate of diffusion of those reagents, which bring them to the reaction site. We define the limit current as an asymptotic value of the current for which the rate of disappearance of the products is equal to the rate of their transport. It is an asymptotic value because this situation would suppose that the redox reaction occurs with a zero concentration of reagents at the interface. In reality, in this situation, other reactions occur.

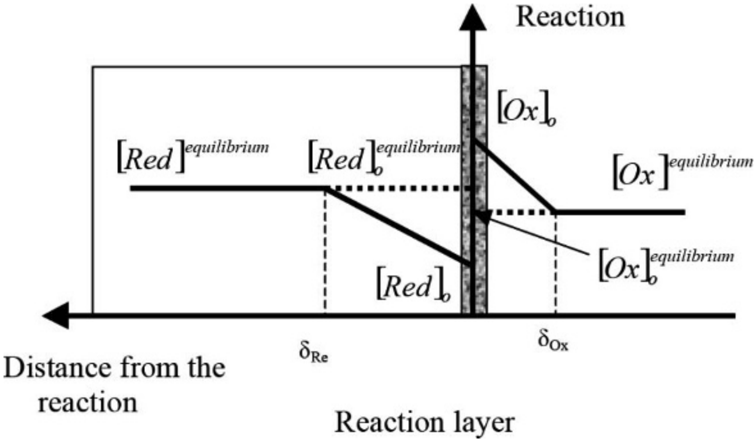

Figure 1.6. *Profile of concentration of reagent (here the reduced form) and product (here the oxidized form) from the equilibrium zone to the reactional zone [TUR 08]*

We express the limit current density by setting a zero concentration of reagent. If we use the hypothesis from Nernst's model, equation [1.44] gives us:

$$[X_i](0) = \left[X_{i,eq}\right] - \frac{j_{\lim}\delta_i}{D_{Xi}nF} = 0 \qquad [1.45]$$

$$j_{\lim} = \frac{D_{Xi}nF}{\delta_i}\left[X_{i,eq}\right] \qquad [1.46]$$

We can thus express the concentration at the reaction interface as a function of the limit current density:

$$[X_i](0) = \left[X_{i,eq}\right]\left(1 - \frac{j_f}{j_{\lim}}\right) \qquad [1.47]$$

1.13. Expression of the polarization curve

Figure 1.11 illustrates the evolution of the current density as a function of the potential of the electrodes (without taking account of diffusion) according to the Butler–Volmer equations.

Yet what interests an electrical engineer wishing to integrate an electrochemical component into a generator is its component as a whole cell, given that an electrode does not work on its own. The quasi-static function of such a component is therefore characterized by the polarization curve, i.e. the relation linking the difference in potential V_{cell} to the boundaries of the cell, defined by $V_{cell} = E^{+} - E^{-}$, to the current or the average current density. We can obtain the polarization curve by deducing it on a pointwise basis from the curves $j_{f,i} = f\left(E_i\right),\ i = a,c,$ but from a practical point of view, it is preferable to look for an analytical or semi-analytical expression of the polarization curve by inverting the Butler–Volmer equations.

The inversion was performed in section 1.9, leading to activation overvoltages, when we can discount the influence of the variation in concentration of the species, i.e. the influence of diffusion. What about the expression which integrates this phenomenon of diffusion? Let us return to the expressions [1.28]:

$$\begin{aligned} j_f &\approx j_{0-}\left(\left(\frac{a_{-,reagent}}{a_{-,reagent,eq}}\right)e^{\frac{\alpha_{-}nF}{RT}\eta_{-}}\right) \\ j_f &\approx j_{0+}\left(\left(\frac{a_{+,reagent}}{a_{+,reagent,eq}}\right)e^{\frac{\alpha_{+}nF}{RT}\eta_{+}}\right) \end{aligned} \quad \text{for } j_f >> j_{0+}, j_{0-} \qquad [1.48]$$

We can rewrite these expressions by expressing the activity of the species as a function of the limit currents defined in section 1.12:

$$\begin{aligned} j_f &\approx j_{0-}\left(\left(1-\frac{j_f}{j_{\lim,-}}\right)e^{\frac{\alpha_{-}nF}{RT}\eta_{-}}\right) \\ j_f &\approx j_{0+}\left(\left(1-\frac{j_f}{j_{\lim,+}}\right)e^{\frac{\alpha_{+}nF}{RT}\eta_{+}}\right) \end{aligned} \qquad [1.49]$$

We invert the above expressions to express the overvoltages of the positive electrode and the negative electrode:

$$\begin{aligned}\eta_- &= \frac{RT}{\alpha_- nF}\ln\left(\frac{j_f}{j_{0,-}}\right) - \frac{RT}{\alpha_- nF}\ln\left(1-\frac{j_f}{j_{\lim,-}}\right)\\ \eta_+ &= \frac{RT}{\alpha_+ nF}\ln\left(\frac{j_f}{j_{0,+}}\right) - \frac{RT}{\alpha_+ nF}\ln\left(1-\frac{j_f}{j_{\lim,+}}\right)\end{aligned} \quad \text{for } j_f \gg j_{0-}, j_{0+} \qquad [1.50]$$

In each expression, the hypotheses made enabled us to "separate" two terms corresponding to two closely coupled phenomena, which are the charge transfer and the transport of species. Thus, we recognize the first term, identified as an activation overvoltage $\eta_{i,act}$, related to charge transfer, shown in section 1.9. The second term is related to the phenomenon of transport of matter by diffusion; it is called the "concentration overvoltage", $\eta_{i,conc}$. The overvoltage of an electrode can therefore be written as the sum of an activation term and a concentration term:

$$\eta_i = \eta_{i,act} + \eta_{i,conc} \quad \text{for} \quad i = -,+ \qquad [1.51]$$

If we wish to express the overvoltages as a function of the current rather than of the current density, we need only replace j_f with $\frac{I_f}{S}$, where S is the surface area of the electrode. Within the cell, charges move around: ions within the electrolyte and electrons into the electrodes and connections. Hence, the cell is also subject to an Ohmic drop in voltage. We can use the notation r_{cell} for the corresponding surface resistance, expressed in Ωm^2 and R_{cell} for the Ohmic resistance of a cell, expressed in Ω.

Thus, we find an expression for the voltage of the cell as a function of the current density and the current.

When operating as a generator, for $j_f \gg j_{0a}, j_{0c}$ and $I_f \gg I_{0a}, I_{0c}$:

$$\begin{aligned}V_{cell}\left(j_f\right) &= E_{rev} - \left|\eta_{a,act}\right| - \left|\eta_{a,conc}\right| - \left|\eta_{c,act}\right| - \left|\eta_{c,conc}\right| - r_{cell} j_f\\ V_{cell}\left(I_f\right) &= E_{rev} - \left|\eta_{a,act}\right| - \left|\eta_{a,conc}\right| - \left|\eta_{c,act}\right| - \left|\eta_{c,conc}\right| - R_{cell} I_f\end{aligned} \qquad [1.52]$$

When operating as a receiver, for $j_f >> j_{0a}, j_{0c}$ and $I_f >> I_{0a}, I_{0c}$:

$$\begin{aligned}
V_{cell}\left(j_f\right) &= E_{rev} + \left|\eta_{a,act}\right| + \left|\eta_{a,conc}\right| + \left|\eta_{c,act}\right| + \left|\eta_{c,conc}\right| + r_{cell} j_f \\
V_{cell}\left(j_f\right) &= E_{rev} + \sum_{i,j} \eta_{i,j} + r_{cell} j_f \\
V_{cell}\left(I_f\right) &= E_{rev} + \left|\eta_{a,act}\right| + \left|\eta_{a,conc}\right| + \left|\eta_{c,act}\right| + \left|\eta_{c,conc}\right| + R_{cell} I_f
\end{aligned} \qquad [1.53]$$

These expressions separate the overvoltages of the anode and the cathode. However, identifying these different terms and the parameters which govern them is no easy task. Even if we are able to perfectly characterize the behavior of each electrode with a half-cell experiment, we need to be certain that this behavior will not be modified when the electrode is used in a whole cell. In addition, from the point of view of an electrical engineer, who is the "user" of this component, the only possible characterization is often that for a complete cell or a collection of cells, it may prove very tricky to differentiate the contributions of each of the two electrodes. In this case, we prefer to adopt a model with non-dissociated electrodes, with ad hoc signs depending on the mode of operation:

$$V_{cell}\left(j_f\right) = E_{th} \pm \left|\eta_{act}\right| \pm \left|\eta_{conc}\right| \pm r_{cell} j_f \qquad [1.54]$$

We then define an exchange current j_0, a limit current $j_{\lim}$, and a factor of symmetry α for the whole cell. The activation- and concentration overvoltages are thus expressed in the form:

$$\begin{aligned}
\eta_{act} &= \frac{RT}{\alpha n F} \ln\left(\frac{j_f}{j_0}\right) \\
\eta_{conc} &= -\frac{RT}{\alpha n F} \ln\left(1 - \frac{j_f}{j_{\lim}}\right)
\end{aligned} \qquad [1.55]$$

In order to reach these expressions, we remove an exponential term from the Butler–Volmer equations. The approximate expression for inversion of the equations is valid only if the current density is sufficiently high. This approximation is, of course, seen again after inversion of that expression: equations [1.55] are not correct for overly low values of current density and are not defined in 0. In order to avoid numerical instability, it is usual to add a term of "internal current" j_n into the expression of the activation overvoltage:

$$\eta_{activation} = \frac{RT}{\alpha n F} \ln\left(\frac{j_f + j_n}{j_0}\right) \qquad [1.56]$$

In addition, the use of this term enables us to take account of the fact that the measured no-load voltage of an electrochemical cell is not equal to the difference in thermodynamic potentials of the electrodes. Certain authors give it a physical interpretation expressing two parasitic phenomena: a leakage of electric current into the electrolyte, and the permeation of the reagents across the electrolyte (termed "cross-over") [LAR 00].

The polarization curve found by the earlier study only takes account of the quasi-static behavior of an electrochemical cell. Dynamic phenomena occur, causing the passage from one point on the polarization curve to another. One such phenomenon was described in section 1.2 – the double layer capacity. The second is the electrochemical impedance, relating to the variations in current density and in the concentrations of the species.

1.14. Double-layer capacity

In the dynamic regime, the alteration of the distribution of charges, linked to the double-layer phenomenon, creates a current density which is added to the Faradaic current density:

$$j(t) = j_f(t) + j_n(t) \tag{1.57}$$

1.15. Electrochemical impedance

The double layer phenomenon means that the current of an electrode or a cell is not identical to the Faradaic current in the dynamic regime. Also, the expressions established above for the potential (or respectively the voltage) as a function of the Faradaic current are not capable of giving an account of the dynamic regime, because they express the behavior of an electrode (or respectively a cell) in steady-state conditions, with constant current or current density. By defining and calculating the electrochemical impedance, by way of certain hypotheses, we are able to give a "small-signal" description of the dynamic behavior of the cell and put forward equivalent electrical arrangements [DIA 96]. Certain elements for the calculation are outlined below.

Indeed, if we write Fick's law [1.38] in non steady-state conditions, the potential and the concentrations are time-dependent. If we consider a slight variation in Faradaic current $\Delta j_f(t)$ around a point of operation and the voltage response of the electrode $\Delta e(t)$, we can define an electrochemical impedance as:

$$Z_f = \frac{\Delta e(t)}{\Delta j_f(t)} \tag{1.58}$$

By differentiating the current density, we obtain the following expression:

$$\Delta j_f(t) = \left(\frac{\partial j_f}{\partial E}\right)_{[\mathrm{Ox}],[\mathrm{Re}d]} \Delta E(0,t)$$
$$+\left(\frac{\partial j_f}{\partial [\mathrm{Ox}]}\right)_{E,[\mathrm{red}]} \Delta[\mathrm{Ox}](0,t) + \left(\frac{\partial j_f}{\partial [\mathrm{Re}d]}\right)_{E,[\mathrm{Ox}]} \Delta[\mathrm{Re}d](0,t) \quad [1.59]$$

The Laplacian expression for this is:

$$\Delta j_f(p) = \left(\frac{\partial j_f}{\partial E}\right)_{[\mathrm{Ox}],[\mathrm{Re}d]} \Delta E(0,p)$$
$$+\left(\frac{\partial j_f}{\partial [\mathrm{Ox}]}\right)_{E,[\mathrm{red}]} \Delta[\mathrm{Ox}](0,p) + \left(\frac{\partial j_f}{\partial [\mathrm{Re}d]}\right)_{E,[\mathrm{Ox}]} \Delta[\mathrm{Re}d](0,p) \quad [1.60]$$

Hence:

$$\left(\frac{\partial j_f}{\partial E}\right)_{[Ox],[\mathrm{Re}d]} \Delta E(0,p) = \Delta j_f(p)$$
$$-\left(\frac{\partial j_f}{\partial [Ox]}\right)_{E,[red]} \Delta[Ox](0,p) - \left(\frac{\partial j_f}{\partial [\mathrm{Re}d]}\right)_{E,[Ox]} \Delta[\mathrm{Re}d](0,p) \quad [1.61]$$

By setting:

$$R_t = \frac{1}{\left(\frac{\partial j_f}{\partial E}\right)_{[Ox],[\mathrm{Re}d]}} \quad [1.62]$$

We get:

$$\begin{aligned}&\frac{\Delta E(0,p)}{\Delta j_f(p)} = R_t \\ &-R_t\left(\frac{\partial j_f}{\partial[Ox]}\right)_{E,[red]}\frac{\Delta[Ox](0,p)}{\Delta j_f} - R_t\left(\frac{\partial j_f}{\partial[\mathrm{Re}d]}\right)_{E,[Ox]}\frac{\Delta[\mathrm{Re}d](0,p)}{\Delta j_f}\end{aligned} \qquad [1.63]$$

Thus, the electrochemical impedance can be written in the form of three terms:

$$Z_f = R_t + Z_{Ox}(p) + Z_{red}(p) \qquad [1.64]$$

such that:

$$\begin{aligned}Z_{Ox}(p) &= R_t \frac{\partial j_f}{\partial[Ox]}\frac{\Delta[Ox](0,p)}{\Delta j_f(p)} \\ Z_{red}(p) &= R_t \frac{\partial j_f}{\partial[\mathrm{Re}d]}\frac{\Delta[\mathrm{Re}d](0,p)}{\Delta j_f(p)}\end{aligned} \qquad [1.65]$$

We call $\tau_X = \frac{\delta_X^2}{D_X}$ the time constant of diffusion of species X, where δ_X is the thickness of diffusion and D_X the diffusion constant from Fick's law. If we hypothesize that there is a transfer of matter in accordance with Nernst's model, we can demonstrate that Z_{ox} and Z_{red} can be put in the form [DIA 96]:

$$\begin{aligned}Z_{ox}(p) &= R_t \frac{th(\tau_{ox}p)^{1/2}}{(\tau_{ox}p)^{1/2}} \\ Z_{red}(p) &= R_t \frac{th(\tau_{red}p)^{1/2}}{(\tau_{red}p)^{1/2}}\end{aligned} \qquad [1.66]$$

R_t is called the charge transfer resistance, Z_{ox} and Z_{red} are the impedances of diffusion-convection linked to the oxidizing species and reducing species respectively. The nonlinear nature of these impedances means it is tricky to use them directly in models of complete electrical systems. Many studies have been carried out to find usable equivalent electrical arrangements [LAF 08; DEV 12].

1.16. Reagents and products in the gaseous phase: total pressure, partial pressure, molar fraction and mixture

This final section is given over to a recap of certain points concerning species in the gaseous phase, which we tend to encounter in electrolyzer cells and fuel cells. For the purposes of this book, we shall consider them to obey the ideal gas law (equation [1.67]) [ATK 96; FEI 06].

$$PV = nRT \tag{1.67}$$

P is the pressure of the gas, expressed in Pascal[6]; V is the volume occupied by the gas, expressed in m^3; n is the number of moles; R the ideal gas constant; and T the temperature expressed in K.

Consider a mixture of ideal gases. As the i^{th} gas in the mixture is ideal, we can write:

$$P_i V = n_i RT \tag{1.68}$$

V is the volume occupied by the mixture, n_i the total number of moles, and T the temperature of the mixture. P_i is the partial pressure of the i^{th} gas in the mixture. It can be interpreted as the pressure of the i^{th} gas if it were alone in the same volume V, at temperature T.

Consider n_{tot}, the total number of moles:

$$n_{tot} = \sum_i n_i \tag{1.69}$$

A mixture of ideal gases is itself an ideal gas. Thus, for a mixture, where P_{tot} is the total pressure of the mixture:

$$P_{tot} V = n_{tot} RT \tag{1.70}$$

We can therefore write, in accordance with equations [1.68]–[1.70]:

$$P_{tot} = \sum_i P_i \tag{1.71}$$

---

[6] 10^5 Pa = 1 bar.

We define the molar fraction of the gas i by:

$$x_i = \frac{n_i}{n_{tot}} \qquad [1.72]$$

From equations [1.68], [1.70] and [1.72], we can write:

$$P_i = x_i P_{tot} \qquad [1.73]$$

1.17. Corrected exercises

1.17.1. *Calculation of the variation in enthalpy during the formation of a mole of water*

Consider a (H_2, O_2) fuel cell. During the course of the reaction, the oxygen and hydrogen are consumed and water is produced. The enthalpy of formation of the water varies in accordance with the equation where the (α_i) and (α_j) are the stoichiometric coefficients of the products and reagents respectively:

$$\Delta H = \sum_{products\ i} \alpha_i \Delta H_i - \sum_{reagents\ j} \alpha_j \Delta H_j$$

The variation in enthalpy depends on the temperature and the pressure. Let ΔH_{298}^0 be the variation in enthalpy of formation of a mole of water in standard conditions (1 bar, 25°C). Below we give the values of the variation in enthalpy for the oxygen, the hydrogen and the water.

	ΔH_{298}^0 [J.mol^{-1}]
H_2	0
O_2	0
H_2O	-285.83×10^3

Table 1.1. *Variation in enthalpy*

The variation in enthalpy at a pressure of 1 bar as a function of the temperature is written as:

$$\Delta H^0(T) = \Delta H^0_{298} + \int_{298}^{T} C_p d\theta$$

where C_p is the molar heat. The expression of C_p as a function of the temperature can be approximated by:

$$C_p(T) = \alpha + \beta T + \gamma T^2$$

	α [J.mol^{-1}.K^{-1}]	β [J.mol^{-1}.K^{-2}]	γ [J.mol^{-1}.K^{-3}]
H_2	29.038	-0.8356×10^{-3}	2.0097×10^{-6}
O_2	25.699	12.966×10^{-3}	-3.8581×10^{-6}
H_2O	30.33	9.6056×10^{-3}	1.1829×10^{-6}

Table 1.2. *Coefficient of the polynomial approximation of C_p [LAR 00]*

– write the balance equation for the reaction with the formation of one mole of water;

– write the variation in enthalpy for the formation of a mole of water;

– calculate the variation in enthalpy at 25°C;

– calculate the expression of the variation in enthalpy of a pure substance depending on the temperature as a function of the coefficients of the polynomial expression of C_p;

– calculate the expression of the variation in enthalpy for the formation of a mole of water as a function of the temperature.

<u>Solution</u>

Balance equation for the formation of one mole of water

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Expression of the enthalpy of formation of a mole of water

$$\Delta H_0 = \Delta H_{H_2O} - \Delta H_{H_2} - \frac{1}{2}\Delta H_{O_2}$$

Calculation of the enthalpy of formation of a mole of water at 298 K

$$\Delta H_0 = \Delta H_{H_2O} - \Delta H_{H_2} - \frac{1}{2}\Delta H_{O_2}$$

$$\Delta H_0 = -285.83\times 10^3 \, Jmol^{-1}$$

Calculation of the variation in enthalpy of a pure substance as a function of the temperature

$$\Delta H^0(T) = \Delta H^0_{298} + \int_{298}^{T} C_p d\theta$$

$$\Delta H^0(T) = \Delta H^0_{298} + \int_{298}^{T} \left(\alpha + \beta\theta + \gamma\theta^2\right) d\theta$$

$$\Delta H^0(T) = \Delta H^0_{298} + \alpha(T-298) + \frac{\beta}{2}\left(T^2 - 298^2\right) + \frac{\gamma}{3}\left(T^3 - 298^3\right)$$

Calculation of the enthalpy of formation of a mole of water as a function of the temperature

We use the notation
$$\alpha_{reaction} = \alpha_{H_2O} - \alpha_{H2} - \frac{1}{2}\alpha_{O2} = -11.5575$$
$$\beta_{reaction} = \beta_{H_2O} - \beta_{H2} - \frac{1}{2}\beta_{O2} = 3.9582\times 10^{-3}$$
$$\gamma_{reaction} = \gamma_{H_2O} - \gamma_{H2} - \frac{1}{2}\gamma_{O2} = 1.10225\times 10^{-6}$$

We therefore have:

$$\Delta H^0(T) = \Delta H^0_{298}$$
$$+\alpha_{reaction}(T-298) + \frac{\beta_{reaction}}{2}\left(T^2 - 298^2\right) + \frac{\gamma_{reaction}}{3}\left(T^3 - 298^3\right)$$

$$\Delta H^0(T) = -282{,}571\cdot 10^3 + \alpha_{reaction}T + \frac{\beta_{reaction}}{2}T^2 + \frac{\gamma_{reaction}}{3}T^3$$

1.17.2. *Calculation of the variation in entropy for the formation of a mole of water*

Consider an (H_2, O_2) fuel cell. During the reaction, the oxygen and hydrogen are consumed and water is produced. The entropy of formation of the water varies in accordance with the equation where the (α_i) and (α_j) are the stoichiometric coefficients of the products and reagents respectively:

$$\Delta S = \sum_{products\ i} \alpha_i \Delta S_i - \sum_{reactants\ j} \alpha_j \Delta S_j$$

The variation in entropy depends on the temperature and the pressure. Let ΔS^0_{298} be the variation in entropy of formation of a mole of water in standard conditions (1 bar, 25°C). Below we give the values of the variation in entropy of the oxygen, the hydrogen and the water.

	ΔS^0_{298} [J.mol^{-1}.K^{-1}]
H_2	130.684
O_2	205.138
H_2O	69.91

Table 1.3. *Variation in entropy*

The variation in entropy at the pressure of 1 bar as a function of the temperature is written as:

$$\Delta S^0(T) = \Delta S^0_{298} + \int_{298}^{T} \frac{C_p}{\theta} d\theta$$

where C_p is the molar heat. The expression of C_p as a function of the temperature can be approximated by:

$$C_p(T) = \alpha + \beta T + \gamma T^2$$

	α [J.mol^{-1}.K^{-1}]	β [J.mol^{-1}.K^{-2}]	γ [J.mol^{-1}.K^{-3}]
H_2	29.038	-0.8356×10^{-3}	2.0097×10^{-6}
O_2	25.699	12.966×10^{-3}	-3.8581×10^{-6}
H_2O	30.33	9.6056×10^{-3}	1.1829×10^{-6}

Table 1.4. *Coefficient of the polynomial approximation of C_p*

– write the balance equation for the reaction with the formation of one mole of water;

– write the variation in entropy for the formation of one mole of water;

– calculate the variation in entropy at 25°C;

– calculate the expression of the variation in entropy of a pure substance depending on the temperature as a function of the coefficients of the polynomial expression of C_p;

– calculate the expression of the variation in entropy for the formation of a mole of water as a function of the temperature.

Solution

Balance equation for the formation of one mole of water

$$H_2 + \frac{1}{2} O_2 \to H_2O$$

Expression of the entropy of formation of a mole of water

$$\Delta S_0 = \Delta S_{H_2O} - \Delta S_{H2} - \frac{1}{2} \Delta S_{O2}$$

Calculation of the entropy of formation of a mole of water at 298 K

$$\Delta S_0 = \Delta S_{H_2O} - \Delta S_{H2} - \frac{1}{2} \Delta S_{O2}$$

$$\Delta S_0 = -163{,}343 \text{ JK}^{-1}\text{mol}^{-1}$$

Calculation of the variation in entropy of a pure substance as a function of the temperature

$$\Delta S^0(T) = \Delta S^0_{298} + \int_{298}^{T} \frac{C_p}{\theta} d\theta$$

$$\Delta S^0(T) = \Delta S^0_{298} + \int_{298}^{T} \left(\frac{\alpha}{\theta} + \beta + \gamma\theta \right) d\theta$$

$$\Delta S^0(T) = \Delta S^0_{298} + \alpha \ln\left(\frac{T}{298} \right) + \beta(T - 298) + \frac{\gamma}{2}\left(T^2 - 298^2\right)$$

Calculation of the enthalpy of formation of a mole of water as a function of the temperature

We use the notation

$$\alpha_{reaction} = \alpha_{H_2O} - \alpha_{H2} - \frac{1}{2}\alpha_{O2} = -11.5575$$
$$\beta_{reaction} = \beta_{H_2O} - \beta_{H2} - \frac{1}{2}\beta_{O2} = 3.9582 \times 10^{-3}$$
$$\gamma_{reaction} = \gamma_{H_2O} - \gamma_{H2} - \frac{1}{2}\gamma_{O2} = 1.10225 \times 10^{-6}$$

We therefore have

$$\Delta S^0(T) = \Delta S^0_{298}$$
$$+\alpha_{reaction} \ln\left(\frac{T}{298} \right) + \beta_{reaction}(T - 298) + \frac{\gamma_{reaction}}{2}\left(T^2 - 298^2\right)$$

$$\Delta S^0(T) = -164,5715 + \alpha_{reaction} \ln\left(\frac{T}{298} \right) + \beta_{reaction} T + \frac{\gamma_{reaction}}{2} T^2$$

1.17.3. *Calculation of the variation in free energy during the formation of a mole of water*

Using the expressions of the enthalpy and entropy of formation of a mole of water obtained in the previous two exercises:

– Give the expression of the variation in the Gibbs free energy during the formation of a mole of water as a function of the temperature.

– Calculate the variation in the Gibbs free energy at 65°C. Calculate the reversible potential of a fuel cell functioning at 65°C.

– Calculate the variation in the Gibbs free energy at 200°C. Calculate the reversible potential of a fuel cell functioning at 200°C.

– What is the influence of the temperature on the performances of a fuel cell?

– Calculate the value obtained for the reversible potential at 800°C. Draw a conclusion about the validity of the expression obtained.

<u>Solution</u>

Calculation of the Gibbs free energy of formation of a mole of water as a function of the temperature:

$$\Delta G_0(T) = \Delta H_0 - T\Delta S_0$$

$$\Delta G_0(T) = -282{,}571.10^3 + T \times 164{,}5715$$

$$+\alpha_{reaction} T\left[1-\ln\left(\frac{T}{298}\right)\right] - \frac{\beta_{reaction}}{2}T^2 - \frac{\gamma_{reaction}}{6}T^3$$

Calculation of the Gibbs free energy of formation of a mole of water at 65°C:

$$T = 65 + 273 = 338K$$

$$\Delta G_0(T) = -230{,}594 \text{ kJmol}^{-1}$$

Calculation of the potential of a fuel cell at 65°C:

$$E_{rev} = \frac{-\Delta G_0}{2F} = \frac{230.594 \times 10^3}{2 \times 96485} = 1.195\,V$$

Calculation of the variation in Gibbs free energy during the formation of a mole of water and the reversible potential at 200°C

$$\Delta G_0(T) = -208.132 \text{ kJmol}^{-1}$$

$$E_{rev} = \frac{-\Delta G_0}{2F} = 1.078\,V$$

The rise in temperature slightly decreases the reversible potential of the cell, but causes a more drastic decrease in the activation overvoltages because it improves the kinetics of the reactions. On balance, the rise in temperature is favorable for the performances of the fuel cells.

Calculation of the variation in Gibbs free energy during the formation of a mole of water and the reversible potential at 800°C

$$\Delta G_0(T) = -105.005 \text{ kJmol}^{-1}$$

$$E_{rev} = \frac{-\Delta G_0}{2F} = 0.544 \, V$$

The value obtained is much lower than the no-load voltage obtained at the limits of this type of fuel cells. This means that at 800°C, the polynomial approximation of C_p used is no longer valid.

1.17.4. *Calculation of the Nernst potential for a cell in a PEM fuel cell (PEMFC)*

Consider a cell in a hydrogen PEMFC, functioning at 65°C. Consider that water is produced in liquid form.

– write the balance reaction. Write the Nernst potential of the cell as a function of the activities of the species;

– carry out numerical application for a hydrogen pressure of 1 bar, oxygen pressure of 0.21 bar and a reversible potential equal to 1.195 V.

Solution

The balance reaction in a PEMFC is written:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

The reversible potential as a function of the activities:

$$E_{rev} = E^0 + \frac{RT}{nF} \ln \frac{\underset{j}{\Pi}\, a_{jreagents}^{vj}}{\underset{i}{\Pi}\, a_{iproducts}^{vi}}$$

The reagents are in gas form, so their activity is the partial pressure. The water is produced in liquid form, so its activity is equal to 1. Thus, we get:

$$E_{rev} = E^0 + \frac{RT}{2F}\ln\left(\frac{P_{H2}}{P_0}\right) + \frac{RT}{2F}\ln\left(\frac{P_{O2}}{P_0}\right)^{1/2}$$

$$E_{rev} = E^0 + \frac{RT}{2F}\ln\left(\frac{P_{H2}}{P_0}\right) + \frac{RT}{4F}\ln\left(\frac{P_{O2}}{P_0}\right)$$

Numerical application:

$$E_{rev} = 1.195 + \frac{8.314\times 338}{2\times 96485}\ln(1) + \frac{8.314\times 338}{4\times 96485}\ln(0,21)$$

$$E_{rev} = 1.184V$$

1.17.5. *Faraday equations for a Pb accumulator*

In the case of a discharging lead accumulator, we get the following equations:

At the anode:

$$Pb + HSO_4^- \rightarrow PbSO_4 + 2e^- + 2H^+$$

At the cathode:

$$PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$$

– write the Faraday equations linking the battery current and the molar flowrate of Pb at the anode and the molar flowrate of Pb oxide at the cathode;

– write the Faraday equation for the consumption of the electrolyte.

<u>Solution</u>

In accordance with the reaction at the anode, half a mole of Pb is consumed with the production of one mole of electrons. We can write the molar flowrate of Pb as a function of the battery current I, with F being the Faraday constant:

$$\dot{n}_{Pb} = \frac{I}{2F}$$

Similarly, we can write the molar flowrate of PbO_2:

$$\dot{n}_{PbO2} = \frac{I}{2F}$$

Half a mole of electrolyte is consumed at the anode and half a mole of electrolyte is consumed at the cathode. Thus, we have:

$$\dot{n}_{PbO2} = \frac{I}{F}$$

1.17.6. *Calculation of the mass of water consumed by an electrolysis cell*

Calculate the amount of water consumed by an electrolysis cell, when that cell consumes 10 A of power. What volume of liquid water will be consumed in 24 h by an electrolyzer comprising 100 cells? The atomic molar mass of hydrogen is 1 g, and that of oxygen is 16 g.

Solution

From the reactions taking place at the electrodes of the electrolyzer, we know that half a mole of water is consumed per mole of electrons exchanged, so:

$$\dot{n}_{H_2O} = \frac{I}{2F}$$

In 24 hours, the mass of water consumed is:

$$m_{H_2O} = N_{cell} M_{H_2O} \frac{I}{2F} \Delta t = 100 \times (2 \times 1 + 16) \times \frac{10}{2 \times 96485} \times 3600 \times 24$$
$$m_{H_2O} = 8.06\ kg$$

Thus, the electrolyzer consumes 8 liters in 24 hours.