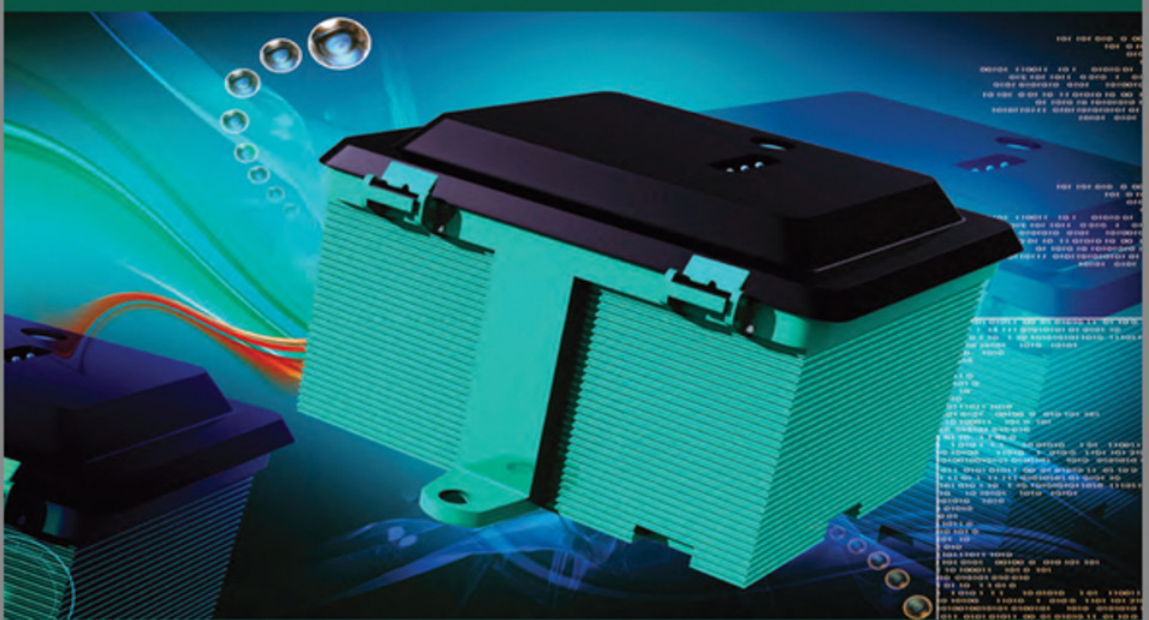
ELECTRICAL ENGINEERING SERIES

Electrochemical Components

Marie-Cécile Péra, Daniel Hissel
Hamid Gualous and Christophe Turpin



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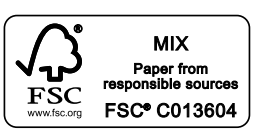

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Preface

"You can't store electricity! …"

Many of us have heard this phrase before, or indeed hear it regularly said still. At present, when there is a great deal of debate and reflection about the necessity of making a switch in our energy provision, this phrase is often even used as an excuse for the holders of one vision or another of that transition. Indeed, if electricity cannot be stored, we must at all times be able to balance supply and demand, and therefore we need to be able, to control either supply … or demand – or indeed both – in a highly dynamic way.

Yet this phrase is not entirely true. In fact, everyone knows this. On a daily basis, we all use objects, tools or mobile systems using an electrical supply (mobile telephones, laptop computers, portable electric tools, electrical vehicles, etc.). Thus, *de facto*, we know that electricity can be stored. Nevertheless, it is relatively difficult to store it, more difficult to store it over long periods of time, and more difficult still to store it in extreme environmental conditions.

Nevertheless, almost paradoxically, there are many technological solutions that can be envisaged in terms of electricity storage. In particular, we can cite electrochemical or electrostatic storage means (electrochemical accumulators, supercapacitors, etc.), but also magnetic means of energy storage (such as superconductors) or mechanical ones (such as flywheels). We can even envisage storing electricity by means of another energy vector, such as hydrogen. The purpose of this book is not to give an overview of all these means for the storage of electricity; rather, our aim here is to devote our attention to those methods of storage which are commonly used in hybrid systems, whether intended for stationary applications or use in transport.

Thus, after an introductory chapter – which cannot, however, be viewed as a complete *ab initio* introduction to the subject – reviewing the basics of

electrochemistry, Chapter 2 is given over to the storage of electricity in the form of hydrogen. While technological prototypes using this method are, as yet, limited, they should, in the future, come to play an increasingly significant role in storage for electrical grids or for supply of isolated sites. Electricity can be transformed into hydrogen by electrolysis of water. This is the technology which will be outlined and analyzed in Chapter 2.

Once hydrogen has been made by electrolysis and stored in *ad hoc* tanks, we have to be able to convert it back into electricity on demand. This can be done with another energy converter: a fuel cell. The description and usage of this technology will therefore be the subject of Chapter 3. Note that the complete combination of an electrolyzer, hydrogen storage facility and fuel cell can be viewed as what is known as a "hydrogen battery".

Such a system is unable to deliver significant dynamics in terms of storage and release of electricity. In hybrid systems, the time-delay is often prohibitive. Hence, we need to be able to supplement this solution with another, which is capable of dealing with the time requirements to meet storage/release of power needs. A supercapacitor is perfect for this role. Hence, a detailed study of supercapacitors is provided in Chapter 4.

While the storage systems touched upon in these three chapters (hydrogen batteries and supercapacitors) both exhibit potentially advantageous characteristics, which vindicate their usage in hybrid electrical systems, at present they are still relatively costly. In fact, the days of the electrochemical accumulator by no means appear to be numbered just yet. This will therefore be the topic of Chapter 5.

Finally, on the basis of the elements laid down in the previous chapters, Chapter 6 will focus on electrical hybridization of these storage systems, with a view to enhancing the performances (in terms of energy, lifetime, cost, etc.) of the new system thus formed.

Before getting to the heart of the matter, it is also useful to mention that the primary goal of this book is for use in teaching. It is intended for an audience of researchers, industrialists, academics, teachers, students, school students, etc., who are anxious to be informed, to gather information and to acquire the basic knowledge of physics and technology that will enable them to comprehend and appreciate these systems. Many exercises, along with corrected solutions, will therefore be provided to the reader throughout this manuscript. In addition, a carefully-considered list of pertinent bibliographical references is provided at the end of the book. We invite interested readers who wish to look more closely at the concepts evoked from a pedagogical angle in this book to refer to these other works.

Chapter 1

Basic Concepts of Electrochemistry used in Electrical Engineering

1.1. Introduction

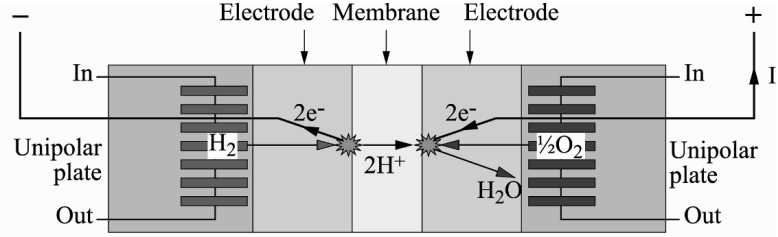
The aim of this chapter is to lay down some basic concepts of electrochemistry which are necessary in order to understand the behavior of the electrochemical components described in this book. For a detailed presentation, the reader could be helped by referring to specialized books such as [DIA 96; LEF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

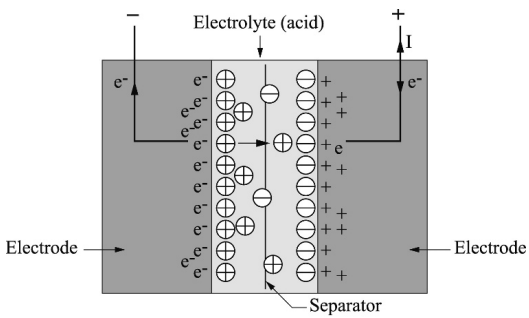
Generally speaking, an electrochemical component can operate as an electric generator or an electric load, or both if it has reversible function.



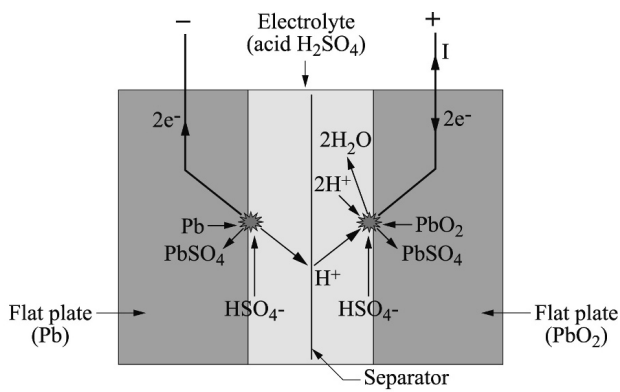
$$-\text{ electrode: } H_2 \leftrightarrow 2H^+ + 2e^- \text{ ; } + \text{ electrode: } \frac{1}{2}O_2 + 2H^+ + 2e^- \leftrightarrow H_2O$$

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

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)



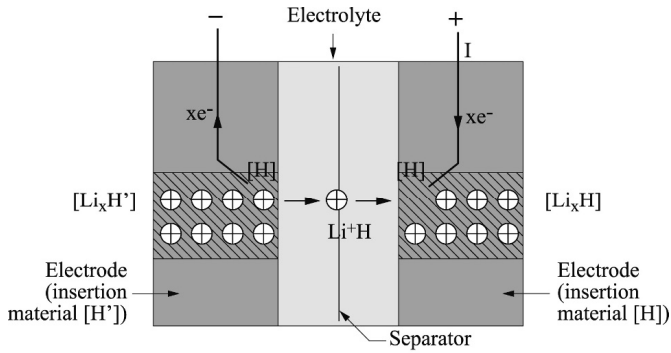
b) Diagram of the principle of a supercondenser (discharge)



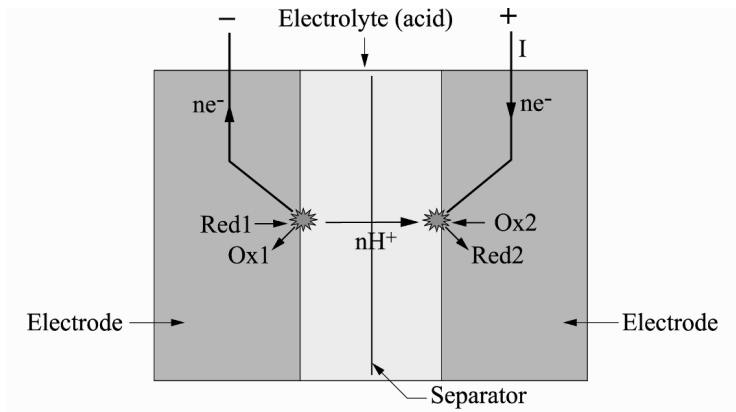
- electrode: $Pb + HSO_4^- = PbSO_4 + H^+ + 2e^-$
+electrode: $PbO_2 + HSO_4^- + 3H^+ + 2e^- = PbSO_4 + 2H_2O$
Global reaction: $Pb + PbO_2 + 2HSO_4^- + 2H^+ = 2PbSO_4 + 2H_2O$

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):

$$\text{– electrode: } a_1(\mathrm{Red}1) + nH_2O \leftrightarrow c_1(Ox1) + ne^- + nH_3O^+$$

$$\text{+ electrode: } c_2(Ox2) + ne^- + nH_3O^+ \leftrightarrow a_2(\mathrm{Red}2) + nH_2O$$

$$\text{Global reaction: } a_1(\mathrm{Red}1) + c_2(Ox2) \leftrightarrow c_1(Ox1) + a_2(\mathrm{Red}2)$$

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.

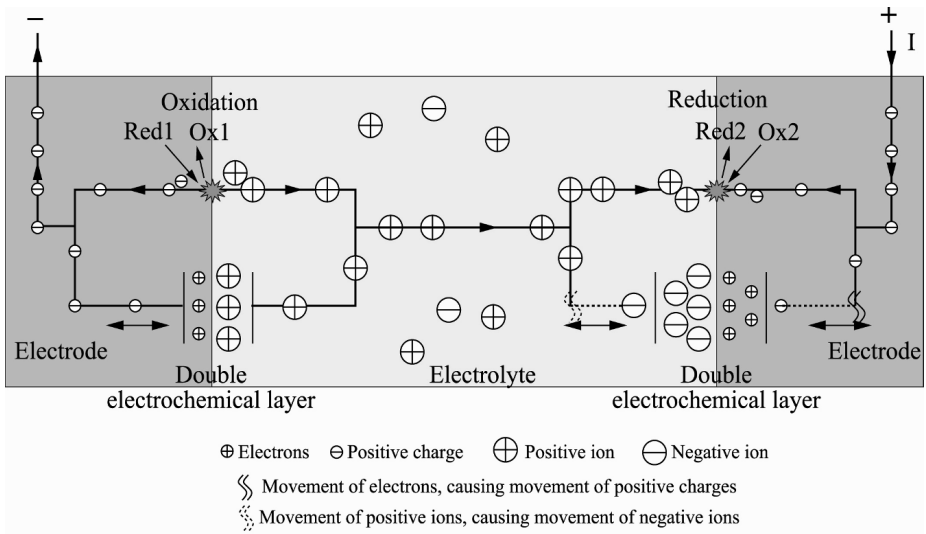
There is a wide variety of redox pairs and technologies within these broad categories, which means we have a very wide range of solutions to choose from, depending on the constraints of the technical specifications and of the system.

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.

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



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 ΔH. 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]

$$Q_{rev} = T\Delta S_{rev} \qquad [1.2]$$

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.

$$\Delta G = \Delta H - T\Delta S_{rev} \qquad [1.3]$$

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.

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:

$$q = -nF \qquad [1.7]$$

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:

$$W_{elec} = -E^0 \times nF \qquad [1.8]$$

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:

$$W_{elec} = \Delta g_f^0 \qquad [1.9]$$

Thus, we get an expression of the standard potential:

$$E^0 = -\frac{\Delta g_f^0}{nF} \qquad [1.10]$$

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

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].

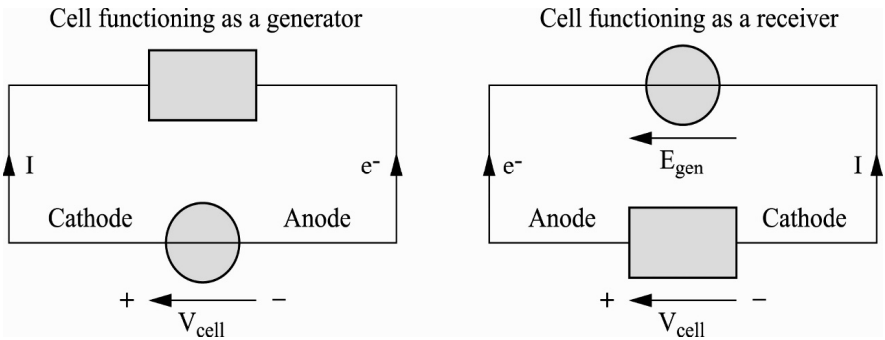


Figure 1.3. *Operation of a cell functioning as a generator (discharge of an accumulator) and as a receiver (charge of an accumulator)*

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:

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

R is the ideal gas constant[4], T the temperature expressed in K, a_i the activity of species i and ν_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].

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

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

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:

$$\eta = E - E_{rev} \qquad [1.20]$$

This expression is known as the Butler–Volmer equation:

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

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:

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

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

$$k^0 = k_0^{\alpha_r} k_r^{\alpha_o} \qquad [1.23]$$

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:

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

At the cathode:

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

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:

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

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:

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

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