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# Electrochemistry: Electrochemical Cell, Thermodynamic and Kinetic Aspects

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## Abstract

*The field of electrochemistry can be defined as the set of physical and chemical phenomena involved by the passage of an electric current in an ionic conductor. These phenomena involve the use of electrodes characterized by at least one interface common to two conductors of different nature. They manifest themselves in various ways in electrochemical reactors made up of two electronic conductors or electrodes separated by an ionic conductive medium. After having defined the main phenomena involved in the flow of current, the article presents the thermodynamic and kinetic aspects of electrochemistry (electrochemical cell). The main industrial applications of electrochemistry are briefly presented.*

**Key words:** Electrochemistry, Electrode, Cathode, Anode, Electrolyte, Current, Battery, Energy.

## Introduction

Electricity was known when Volta invented the electric battery [1]. Indeed, electricity was already used and studied as a laboratory curiosity: the friction of insulating materials made it possible to create some electric charges and to store them in capacitors. In 1800, when Volta stacked metallic disks separated by non-metallic materials but made conductive by impregnation with salt water, he made the first electric battery and, thanks to this first application, he also opened the door to electrochemistry.

Electrochemistry can be characterized by all the phenomena involved in the passage of an electric current in an ionic conductor, regardless of its direction. The passage of this current requires the use of an electrochemical system consisting of two electrodes in electrical contact with the ionic conductor. The material involved therefore comprises electronic conductive materials and a liquid medium made electrically conductive thanks to the presence of ions. The physical characterization of electrochemical systems mainly uses current or potential measurements.

The passage of current is generally accompanied by chemical modifications of the electrodes or of the material present on their surface. This coupling of chemical transformations with electricity occurs in two major electrochemical applications: batteries and electrolysis. The passage of current always involves a conversion of energy. Current and electrical energy are produced using a battery by consuming an oxidant and a reducing agent, respectively on a cathode and an anode. In electrolysis, it is electrical energy that is consumed and transformed into products and heat.

Since Volta, electrochemistry has developed enormously, both fundamentally and in terms of applications in various sectors: energy, synthesis and use of materials, analysis and even the living world. Depending on the nature and size of the electrodes, and depending on the intensity of the current, electrochemistry has given rise to a wide variety of industrial applications which are mentioned in this article. These applications are still the subject of active research, in particular when they are part of the objectives of sustainable development and better management of materials and energy. Indeed, the coupling of electricity with changes in matter is currently at the heart of the most credible methods of storing intermittent renewable energies.

## Definition Of Some Commonly Used Words

### Capacitive Current

Electric current associated with the charge or discharge of the electrochemical double layer. The capacitive current appears as soon as the potential of the electrode is modified. The same is true when there is a modification of the surface of an electrode maintained at constant potential. The capacitive current does not cause a change in the chemical composition, but only in the distribution of electric charges.

### Faradic Current

current associated with the transfer of charge at a metal / solution interface. This transfer accompanies the oxidation or reduction reactions which lead to a modification of the chemical composition. The latter obeys Faraday's law.

### Cathode

In an electrolysis cell, the cathode is the electrode connected to the negative terminal of the direct current generator. The reduction reaction on this electrode consumes electrons. In a battery, the electrode which is the seat of the reduction is also a cathode and constitutes the positive electrode of the generator.

### Anode

In an electrolysis cell, the anode is the electrode connected to the positive terminal of the direct current generator. The oxidation reaction on this electrode releases electrons. In a battery, the electrode which is the site of oxidation is also an anode and constitutes the negative electrode of the generator.

### Negative and Positive Poles

Negative and positive terminals of a direct current generator. These polarities are used to define the conventional direction of current flow outside this generator.

### Electrochemical Reduction

Reaction located on the cathode of an electrolysis cell or on the positive electrode of an electrochemical generator. The reduction involves the decrease in an oxidation number in the oxidant consumed.

### Electrochemical Oxidation

Reaction located on the anode of an electrolysis cell or on the negative electrode of an electrochemical generator. Oxidation involves an increase in an oxidation number in the reducing agent consumed.

### Battery Reaction

In an electrochemical generator, the battery reaction is the chemical balance of the two reactions on the electrodes. This balance corresponds to a spontaneous reaction whose chemical energy can be released in electrical form.

### Chemical Balance of an Electrolysis

In an electrolysis cell, writing the balance of the two reactions at the electrodes does not reveal electrons. Depending on the nature of the electrochemical reactions, electrolysis can be a method of energy storage. These storages are frequently used when recharging electric batteries.

### Electrochemistry Historic

The birth of electrochemistry is in 1800 when Volta invented the electric battery by stacking metal disks [2]. This battery quickly established itself as a direct current generator, essential for carrying out a multitude of experiments in the fields of electricity, magnetism and electrochemistry.

Long before Volta's experiment, Galvani had shown in 1791, with the involuntary collaboration of frogs, that muscle contractions were caused by the contact of two metals and that these contractions were of variable intensity depending on the nature of the metals used [3]. In particular, the contractions were more intense when the metals were copper and zinc. Galvani and Volta disagreed on interpretations of their experiences. Since then, we know that the two different metals constitute a galvanic battery which generates a current and that the muscle of the frog is a detector of this current. This experience is not only anecdotal because it finds medical applications in cardiac pacemakers.

Electrochemistry has developed both on fundamental and applied aspects. It is difficult to evoke all the outstanding facts of the 19th century. The main scientists who helped establish the foundations of electrochemistry are still present in theoretical presentations: Faraday, Kohlrausch, Joule, Gibbs, Helmholtz, Nernst and many others.

The first industrial applications made it possible, with batteries and accumulators, to provide direct current electrochemical generators necessary for the development of electrometallurgy. But large industrial applications were only able to develop thanks to the availability of electrical energy when the electric dynamo imposed itself in the transformation of mechanical energy into electricity.

Energy and, in particular, its transformation into electricity are a determining element for the industrial vitality of electrochemistry. Currently, in France, electricity production is largely based on the exploitation of uranium fission energy and, to a lesser extent, on the combustion of fossil fuels (petroleum, coal, natural gas) [4]. Electricity can also be produced marginally by photovoltaic and the piezoelectric effect, as well as by exploiting wind energy, tidal energy, or even geothermal energy. These energies, intermittent for the most part, are very likely to develop by benefiting from electrochemical storage processes
[5].

### Electrochemical Cell

An electrode is a system made up of two phases in contact, a predominantly electronic conductor and a predominantly ionic conductor, whose interface is the place of charge transfer between the constituents of the two phases. The combination of at least two electrodes constitutes an electrochemical cell [6]. If, within an electrical circuit, the cell functions as a generator of energy, we are in the presence of a battery. On the contrary, if the cell acts as an energy receiver, it is an electrolyser. Reagents in a battery react during its discharge, and the chemical energy of the reaction is converted into electrical energy. Rechargeable generators are called accumulators (the name battery is inappropriate). During the charge / discharge cycles, an accumulator alternately plays the roles of receiver and generator. We will only talk about monopolar cells. This type of cell has a container in which there is an anode (or a set of anodes at the same potential) and a cathode (or a set of cathodes), each in contact with an electrolyte. The anode is the electrode at which an oxidation reaction (or possibly several) takes place. This is the (+) pole in an electrolyser and the (-) pole in a generator. The cathode is the electrode at which a reduction reaction (or possibly several) takes place. The cell contains one or more electrolyte (s), which are ionic conductors, most often liquid, although we will give examples of solid electrolytes. If the electrolyte in contact with the anode (anolyte) has a different composition than that in contact with the cathode (catholyte), a separator is needed to prevent mixing of the electrolytes, while ensuring the flow of current, primarily by ionic migration (see below).

## Electrode reactions

### Thermodynamic Aspects

Consider first an electrochemical system at equilibrium, comprising a redox couple Ox1 / Red1 intervening at electrode "1" and a couple Ox2 / Red2 intervening at electrode "2". For simplicity, these two pairs are assumed to involve the same number of "n" electrons per mole of reactant. It is assumed that the equilibrium potential of electrode "1", Eeq1, is greater than that of electrode "2", Eeq2. The reaction-balance (3) which takes place in the cell results from the combination of the two redox half-reactions (1) and (2): (3) = (1) - (2) so as to balance the electronic balance:

$$Ox1 + ne- = Red1 \quad (1)$$
$$Ox2 + ne- = Red2 \quad (2)$$
$$Ox1 + Red2 \rightarrow Red1 + Ox2 \quad (3)$$

Taking into account the hypothesis Eeq1> Eeq2, this reaction balance (3) is characterized by a change in the free enthalpy of negative reaction $\Delta rG3 < 0$.
It tends to take place spontaneously, from left to right, in a generator. On the other hand, in an electrolyser, we can theoretically carry out the reverse reaction (4), provided that the necessary electrical energy is supplied to the system using an external generator.

$$Red1 + Ox2 \rightarrow Ox1 + Red2 \quad (4)$$

This reaction (4) is associated with a change in positive free enthalpy: $\Delta rG4 = - \Delta rG3$. These variations of free enthalpy of reaction are related to the thermodynamic cell voltage at zero current, ΔEth, also called the equilibrium potential of the celland defined as the positive quantity resulting from the difference between the potentials of equilibrium (calculable by the Nernst relation) of the two electrodes of the cell [7]:

$$-n F \Delta Eth = -n F (Eeq1 - Eeq2) = \Delta rG3 = - \Delta rG4 \quad (5)$$

Recall that when an infinitesimal charge dq flows, the system exchanges an electrical work δW with the exterior, which is equal to the change in free enthalpy of the reversible reaction which takes place at constant pressure and temperature:

$$\delta W=-\Delta Eth\ dq = -n F \Delta Eth\ d\xi. \quad (6)$$

This quantity is negative for a spontaneous transformation (in a stack). The progress of the reaction, ξ, is expressed in mol. By convention, dξ is positive when the cell operates as a generator. This result is also found by writing the equilibrium condition in a form which involves the electrochemical free enthalpy:

$$\Delta r = \Sigma\ \nu i = 0. \quad (7)$$

with:

$$\mu = \mu°i + RT \ln ai + zi F\Phi. \quad (8)$$

μ is the electrochemical potential, μ ° i the standard chemical potential, νi the stoichiometric coefficient, ai the activity and zi the charge of species "i"; Φ is the potential of the phase considered. In an electrolyser, when several reactions can take place at an electrode due to the presence of several electroactive species, the question that arises is which one (or which) actually takes place. It should first be remembered that all the species present that may be oxidized can react to the anode. It could be:

anions (Cl- → Cl2 in a chlorine / soda cell),
uncharged species (H2O → O2 during the electrolysis of an aqueous solution of H2SO4),
cations (Fe2 + → Fe3 +).

In some textbooks, this last possibility is not considered, because the cations, positively charged species, are not "attracted" by the anode, the positive pole of the cell. This reasoning is of course completely false: admittedly, Fe2 + ions cannot arrive at the anode by migration, but the flow of these species towards the anode will originate from diffusion and convection (see below).

Likewise, at the cathode, can react all the species present which may be reduced. It could be:

cations (H + → H2; Zn2 + → Zn),

uncharged species (H2O → H2 during the electrolysis of water in a basic medium),
anions (Ag (CN) 2 - → Ag in the electrodeposition silver plating process).

In the latter case, we can make a remark similar to that made on the oxidation of cations at the anode. Suppose that the inventory of species likely to react indicates to us that, on the one hand, two species RedA and RedB are likely to react to the anode and that, on the other hand, two species OxC and OxD are likely to react to the cathode. Let us also suppose that the equilibrium potentials of the four redox couples involved are such that:EeqD < EeqC < EeqB < EeqA.

Thermodynamics allow us to make the following forecasts:
At the anode, if we apply an electrode potential E <EeqB, nothing can happen; if we have EeqB <E <EeqA, only RedB should be oxidized; finally, if E> EeqA, RedB and RedA should be oxidized. As a priority, the species for which the equilibrium potential is the lowest should react first.

At the cathode, if we apply an electrode potential E> EeqC, nothing can happen; if we have EeqD <E <EeqC, only OxC should be reduced; finally, if E <EeqD, OxD and OxC should be reduced. As a priority, the species for which the equilibrium potential is the least weak should first react. Thus, the thermodynamic stress, ΔEth, should have the lowest possible value, i.e. (EeqB - EeqC) in our example. However, some reactions which are expected following the thermodynamic study of the system are characterized by very slow kinetics, so that they are not observed experimentally. For the reactions which actually take place, the value of ΔEth then takes a higher value. We will see such examples in the section “Applications to industrial electrolysers”. Thus, in water, reduction of cations such as Zn2 + should not be possible because reduction of protons or water molecules is thermodynamically expected. However, it is possible to electrodeposit zinc from a solution of zinc sulfate (see below) because the kinetics of this reaction are very fast, compared to that of the evolution of hydrogen. Likewise, the reduction of alkaline cations in water is characterized by a very negative equilibrium potential. However, this reaction takes place on a mercury cathode; in fact, an amalgam of the alkali metal is formed because the thermodynamically predictable hydrogen evolution reaction is blocked because of its very slow kinetics on mercury. This property is used in the electroanalytical technique called polarography and in chlorine / soda electrolysis cells. In a generator, the reactions which take place at the electrodes depend on the active materials (anode and cathode) which have been introduced. We will show, in the paragraph "Applications to electrochemical generators", that there are generators in an aqueous medium whose cell thermodynamic voltage (also called electromotive force and noted fem. below) is abnormally high. In other words, some overly reactive compounds should not be visible in the chosen solvent. Here again, kinetic considerations are decisive.

## Kinetic Aspects

The direction of spontaneous evolution of the electrochemical system symbolized by the conventional reaction-balance (3) corresponds to the oxidation of the Red2 species at the anode and the reduction of the Ox1 species at the cathode. The speed of a reaction is written: $v = d\xi/dt$

The intensity of the electric current flowing in the cell provides direct access to the speed of the electrochemical reaction: I = n F v. By convention: I> 0 for an oxidation and I <0 for a reduction. In an electrolyser, the anode is the seat of a + I current, while the -I current flows through the cathode.

When an electrode is the site of a reaction, its potential E (I) depends on the current flowing. The overvoltage of the electrode, η, is a function of ‘I’ which is defined as the difference between the potential E (I) and the equilibrium potential given by the relation of Nernst: η (I) = E (I) - Eeq. Surges are terms related to the kinetics of reactions at the electrodes which involve charge transfer and material transport.

In some cases, the Tafel relation is verified; we then have, for example for the anode overvoltage: ηa = ba log I / Io, where ba is the anodic Tafel slope and Io the exchange current. Whatever the type of electrochemical cell (generator or electrolyser), the anode overvoltage is positive and the cathodic overvoltage is negative, as shown by the Pourbaix-De Donder inequality: η I ≥ 0 [8].

## Potential difference across a cell in operation

For an electrolyser, the potential difference "U" at the terminals, when a current "I" flows, is given by the relation (9):

$$\Delta U' = \Delta Eth + \eta a + /\eta c/ + \Sigma \, Ri \, I. \quad (9)$$

The first term is the thermodynamic potential of the cell (potential difference at zero current), which is calculated using knowledge of the equilibrium potentials of the two reactions at the electrodes. ηa and ηc are the anode and cathode surges, respectively. Finally, the term ohmic drop includes losses by the Joule effect in the electrolyte, the electrodes and the possible separator. In practice, in an electrolyser, the current is limited because of the kinetics of material transfer. An electrolyser can be characterized by two dimensionless quantities: the faradic efficiency, φ, is defined as the ratio of the theoretical charge necessary to make the desired reaction-balance and of the total charge elapsed; the voltage yield, γ, is such that: γ = φ ΔEth / ΔU’. Note that ΔEth / ΔU ’is equal to the ratio of the minimum electrical energy theoretically necessary for the reaction and the electrical energy consumed. An industrialist wants the balance reaction which interests him to have a high faradic yield, close to 1. On the other hand, if the faradic yield is much less than 1, this means that there are one or more concurrent reaction (s).

taking place at a rate comparable to that of the desired reaction. The cell can no longer be characterized by a single value of ΔEth. In summary, although ΔEth is a thermodynamic quantity, its use to describe the system requires knowing the reactions which actually take place (at a sufficient speed) and not simply those which are favored by thermodynamics. For a generator, the delivered potential difference ΔU is written:

$$\Delta U = \Delta Eth - \eta a - /\eta c/ - \Sigma \, Ri \, I. \quad (10)$$

This time, the kinetic terms and the ohmic drops are cut off from the thermodynamic cell voltage. When the intensity of the current "I" increases, the overvoltage and the ohmic drops increase, therefore ΔU decreases. The maximum value of the current is obtained when the potential of the anode is equal to the potential of the cathode. The two electrodes are then shortcircuited and the current takes the maximum value icc . In practice, it is obviously not recommended, when using a generator, to achieve this extreme case, but this short-circuited battery situation is encountered in the case of electrochemical corrosion. The anodic reaction is then the oxidation of a metal, the cathodic reaction is the reduction of dissolved oxygen or protons; the short circuit current is called the corrosion current and the mixed potential involved is the corrosion potential. In this case, a new quantity is defined: the polarization of the electrode (difference between its potential when a current "I" flows and its potential at zero current). This short-circuited battery phenomenon is also involved in the case of water reduction by sodium amalgam in an "amalgam decomposer", a device used in chlorine / soda electrolysis in connection with mercury cathode electrolysers.

## Material Transport

In an electrolyte (ionic conductor), the current is transported by ions (mainly migration phenomenon). Positive ions flow in the conventional direction of current, negative ions in the reverse direction. The fraction of the current "Ii", carried by ion "i" is called the transport number ti of this ion. It is a dimensionless quantity:

$$t_i = \frac{I_i}{I_{total}} = \frac{u_i C_i |z_i|}{\sum_k u_k C_k |z_k|} \qquad \sum_k t_k = 1. \tag{11}$$

In this formula, which involves all the “k” ions in the solution, ‘u’ represents the mobility, z the charge and C the concentration. Two particular cases will hold our attention: - in the presence of a very concentrated support electrolyte compared to the electroactive ion "i", ti tends towards 0 because the denominator is very large compared to the numerator; - in the presence of a single electrolyte, the two transport numbers for the cation and the anion are written respectively t + and t- and relations (11) are simplified:

$$t^+ = \frac{u^+}{u^+ + u^-} \qquad t^- = \frac{u^-}{u^+ + u^-} \qquad t^+ + t^- = 1. \tag{12}$$

If there is a separator in the cell, it will be crossed by ions which ensure the passage of current. There are special separators which can only be crossed by one type of ion. Thus, cation exchange membranes, such as Nafion which is used in membrane chlorine / soda cells, are permeable only to cations (t + ≈ 1 and t- ≈ 0). The anion exchange membranes can only be crossed by anions. Likewise, yttrium-doped zirconium oxide ceramics have an ionic conductivity by O2- ions which is remarkable at very high temperatures (of the order of 1000 ° C). They are used as solid electrolytes in SOFC type fuel cells. We are interested in the electroactive material which is consumed at a plane electrode and which must be constantly renewed. It is brought to the electrode by three possible modes: migration, diffusion and convection.

The flux of a species « i », Ji, is a vector quantity which is expressed as a function of the gradient of electrochemical potential and the velocity of the liquid, v:

$$\vec{J_i} = -\frac{C_i D_i}{RT}\vec{\nabla}\bar{\mu}_i + C_i\vec{v}. \tag{13}$$

Di is the diffusion coefficient of the species, ai its activity and Ci its concentration. In Cartesian space, the operator V (vector) is:

$$\frac{\partial}{\partial x}\vec{i} + \frac{\partial}{\partial y}\vec{j} + \frac{\partial}{\partial z}\vec{k}.$$

Assume that ai = Ci (for sufficiently dilute solutions) and that the transport of matter to the plane electrode is unidirectional along the x axis. By convention, the x-axis is oriented from the surface of the electrode to the core of the solution, so any flux going to the electrode will be counted negatively. The relation (13) becomes:

$$J_i = -D_i\frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT}D_i C_i\frac{\partial \Phi(x)}{\partial x} + C_i\vec{v}(x). \tag{14}$$

In expression (14), the first term relates to diffusion, the second to migration and the third to convection. Equation (14) is difficult to solve, but can be simplified in some cases. For example, the term related to migration cancels out for uncharged electroactive species; likewise, in the presence of a "support electrolyte" which ensures the transport of the current, the migration of electroactive species is negligible and the model of the Nernst layer can be adopted. We then have a stationary convective diffusion regime with a linear gradient of concentration of the electroactive species in a zone of space, of thickness δ, close to the electrode and called the diffusion layer. This electrolyte layer adjacent to the surface of the electrode is unaffected by convection.

In the case where a Red species (such as Fe2 +) is consumed at the electrode (oxidation current), the concentration of this species at the heart of the Cred * solution is greater than that at the Cred (0) interface; the stationary flux of this species in the vicinity of the electrode see table1 (being limited to the phenomenon of diffusion) is:
Jred = -DredgradCred(15)
With

gradCred =C*red-Cred (0)(16)δred

**Table I - Partial balances (for 2 faradays passed) in the anode and cathode compartments of an electrolyser with separator comprising an anode and a copper cathode; electrolyte: CuSO4. In such a cell, the overall CuSO4 balance is zero.**

| Anode compartmentCathode compartment | |
|---|---|
| **Reaction:** Cu → Cu2+ + 2e-<br>gain of 1 mole of Cu2+<br>loss of t+ mole of Cu2+ | **Reaction:** Cu2+ + 2e- → Cu<br>loss of 1 mole of Cu2+ Migration:<br>**Migration:** gain of t+ mole of Cu2+ |
| **Partial balance:** gain of t- mole of CuSO4 | **Partial balance:** loss of t- mole of CuSO4 |

The concentration gradient is positive, so Jred is negative, which shows that the species consumed by the reaction is transported from the core of the solution to the electrode. This is the case with Fe2 + species which are involved in redox loops. The maximum value of the concentration gradient is obtained when Cred (0) = 0. The anode limit current is then reached: Ilima = nFSDred Cred * / δred.

## Material balance in an Electrolyser

When looking at the material balance in an electrolyser that does not have a separator, it suffices to take into account the reactions that take place at the electrodes. On the other hand, when a separator is present, it is necessary to carry out partial assessments in the anode compartment and the cathode compartment. Account is then taken of the ionic migration process through the separator (in general, diffusion and convection are neglected). Our words will be illustrated with three examples.

### Electro-refining of copper: soluble anode process

Or an electrolyser with a separator which contains a solution of copper sulphate of the same initial concentration in the anode and cathode compartments. Both electrodes are made of copper. The material balance for the passage of 2 faradays is given in Table I. Taking into account the counterions, it is verified that the electrical neutrality is respected in each compartment. The partial balances show a variation in the number of moles of CuSO4, and therefore in the concentration of the electrolyte, in each of the compartments. Thanks to this property, we can derive a method for determining the transport numbers: it suffices to measure by assay the variation in the concentration ΔC, which results from the passage of the current (in this example ΔC is proportional to t-). In Table I, for the sake of simplicity, the balances have been determined for an elapsed load equal to 2 faradays, i.e. almost 2 ×105 C. In practice, it will be necessary to carry out the experiments with more reasonable loads q, which will generate variations in the number of moles of copper sulphate, Δn, smaller:

Δn=qt- / 2F.

The overall balance in this electrolyser is zero because the partial balances are offset. It is a very special electrolyser in which there is no reaction-balance because the reaction which takes place at the anode is the opposite of that which takes place at the cathode. We then have ΔEth = 0 V. This type of electrolyser is used in a hydrometallurgy process: the purification of copper by the soluble anode process (see below). In practice, a separator is not used and the electrolyte consists of a mixture of sulfuric acid and copper sulphate. If we are interested in the consumption of material in the vicinity of the cathode, we see that the reaction consumes 1 mole of Cu2 + for 2 F elapsed; however, migration only brings t + mole (for CuSO4, we have: t + = 0.4 and t - = 0.6). The complement (t-mole) is supplied by diffusion.

### Electroplating of copper: insoluble anode process

In an electrolyser with a separator such as the one considered above, the same electrolyte is used, the same cathode material (copper) but the anode is unassailable (platinum, for example). The material balance in the cathode compartment for the passage of 2 F is unchanged: loss of t- mole of CuSO4 (see table II).

**Table II - Partial balances (for 2 faradays passed) in the anode and cathode compartments of an electrolyser with separator comprising a platinum anode and a copper cathode; electrolyte: CuSO4.**

| Anode compartment | Cathode compartment |
|---|---|
| **Reaction:** H2O → ½O2 +2H+ + 2e-<br><br>**Migration:** loss of t+ mole of Cu2+ gain of t- mole of SO4 2- | **Reaction:** Cu2+ + 2e- → Cu loss of 1 mole of Cu2+<br><br>**Migration:** gain of t+ mole of Cu2+<br>loss of t- mole of SO4 2- |
| **Partial balance:** gain of 1 mole de H2SO4<br>and loss of t+ mole of CuSO4 | **Partial balance:** loss of t- mole of<br>CuSO4 |

On the other hand, at the anode, the reaction is different: a release of dioxygen takes place and we gain two moles of H +. The migration terms are unchanged if it is considered that the compartments are large enough that the H + ions created at the electrode, far from the separator, do not have time to reach and pass through it. The partial balance in the anode compartment is: gain of 2 moles of H +, loss of t + mole of Cu2 + and gain of t-mole of SO4 2- (i.e. 1-t + mole of SO4 2-).

We therefore have a gain of 1 mole of H2SO4 and a loss of t + mole of CuSO4. The overall balance in the cell is then a gain of 1 mole of H2SO4 and a loss of t ++ t- = 1 mole of CuSO4, which was predictable given the reaction-balance (18) which only takes into account electrode reactions:

$$H_2O + Cu^{2+} \rightarrow Cu + \tfrac{1}{2}O_2 + 2H^+ \quad (18)$$

which is also written:

$$H_2O + CuSO_4 \rightarrow Cu + \tfrac{1}{2}O_2 + H_2SO_4. \quad (19)$$

This type of cell is also used industrially (but with an anode material less expensive than platinum) to prepare copper by electrodeposition from solutions of copper sulphate. This is the insoluble anode process. The thermodynamic cell voltage is then different from 0; which egals:

$$\Delta E_{th} = E_{eq}(O_2/H_2O) - E_{eq}(Cu^{2+}/Cu).$$

This example shows us that the nature of the electrode materials has a great influence on the reactions at the electrodes (an electrode material can participate in the reaction) and therefore on the material balance that takes place in an electrolyser.

### Concept of "redox loop"

In an electrolyser, when the electrolyte contains Fe2 + impurities and when the values of the electrode potentials allow it, there can be oxidation of Fe2 + at the anode, generating Fe3 + ions which can be reduced at the cathode, to form a new Fe2 + ions, and so on. Part of the current therefore flows in pure loss because of this parasitic reaction which can take place indefinitely. It is said that the cell is the seat of a redox loop, also called an electrochemical shuttle, which contributes to the lowering of the faradic efficiency of the desired reaction-balance. The supply of electroactive substance Fe3 + to the cathode takes place by diffusion and migration, while the supply of Fe2 + to the anode takes place only by diffusion. Redox loops do not only have negative aspects: they are used in the modern technique of investigation of the local properties of electrode materials called SECM for "scanning electrochemical microscopy", which can be translated by microscopy electrochemical scanning. An ultramicroelectrode (UME) conductive probe, i.e. a disk with radius “r” of the order of a micrometer, is used to map a substrate immersed in a solution containing an Ox species. With a UME, the electroactive material is delivered to the electrode by hemispherical diffusion (and not by plane diffusion as seen previously) [9]. The UME is first placed in the electrolyte solution at a distance” d” far from the substrate. The potential which is applied to it is such that the limiting current Ilimc in reduction is reached (it is equal to -4πFDoxCox * r). We therefore have I / Ilimc = 1 for d / r > 1. When the UME is approached at a very short distance from an insulating substrate (d / r <1), the diffusion of the Ox species towards the electrode is embarrassed and the I / Ilimc ratio decreases sharply. On the contrary, if the substrate is conductive and if it is brought to an adequate potential for the oxidation reaction to take place, the detected current is amplified by the "feedback effect".We then have I / Ilimc> 1 for d / r <1. It is thus possible to detect electrochemically active zones and those which are not on the surface of a material. In conclusion of this paragraph, we will say that, in cells comprising a separator, the partial balances in the anode and cathode compartments must be taken into account; these balances strongly depend on the nature of the electrode materials. We will now give examples of applications of the concepts stated above to industrial cells (generators and electrolysers).

## Applications to Electrochemical Generators

### Generators in aqueous medium

Water participates in the redox couples (20) and (21) either as a Red species (20 couple) or as an Ox species (21 or 22 couple):

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- = H_2O \quad (20)$$

$$2H^+ + 2e^- = H_2 \quad (21)$$

the latter can be written in a basic medium:

$$H_2O + 2e^- = H_2 + 2OH^-. \quad (22)$$

The standard potentials of the pairs (20) and (21) are respectively equal to $E°_{20} = 1.23$ V and $E°_{21} = 0$ V. On all the potential-pH diagrams appear the two parallel lines of equations: $E_{20} = E°_{20} - 0.06$ pH and $E_{21} = -0.06$ pH. They define the thermodynamic stability domain of water, the width of which is 1.23 V regardless of the pH. Any redox couple characterized by the halfequation:

$$Ox + ne^- = Red \quad (23)$$

whose representative point is located, on the Pourbaix diagram(-figure1), above the stability range of water, there is an Ox species which must react with the solvent H2O according to:

$$2\,Ox + n\,H_2O \rightarrow 2\,Red + n/2\,O_2 + 2n\,H^+ \quad (24)$$

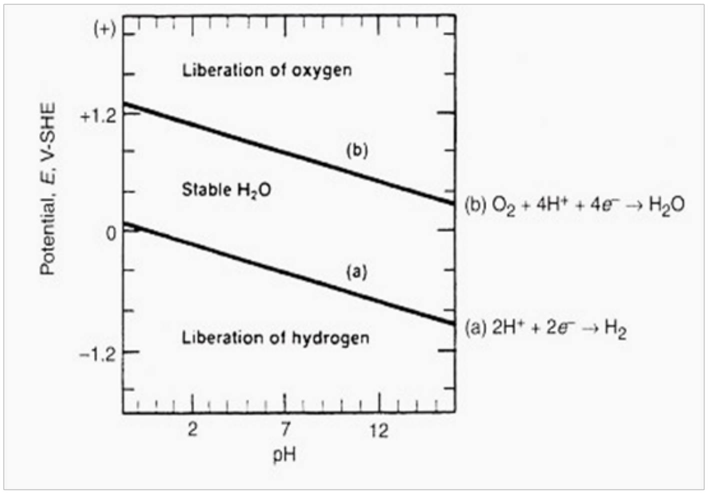

**Figure 1:**Thermodynamic stability domain of water on a potential-pH diagram at 25 ° C.

Likewise, any couple whose representative point is located, on the Pourbaix diagram, below the stability range of water has a Red species which must react with the solvent H2O according to:

$$2\ Red + n\ H2O \rightarrow 2\ Ox + n\ H2 + 2n\ OH-. \qquad (25)$$

The consequence of this is that, in water, the electromotive force of the generators should always be less than 1.23 V. If, however, there are aqueous electrolyte generators which have an e.m.f. higher than this value, it is thanks to kinetic reasons. Thus, Leclanché batteries and alkaline batteries have an e.m.f equal to 1.5 V. The negative active mass in these two batteries is zinc. This metal, characterized by a very negative value of the standard potential of the Zn2 + / Zn couple (-0.76 V) should reduce the water according to reaction (25) and generate a release of hydrogen. However, the kinetics of this reaction are slowed down with the use of an inhibitor so that corrosion of the metal is slow. However, it is inevitable; this explains the self-discharge phenomenon of this type of generator. To use the slogan of an old ad, these are actually batteries that wear out even if not in use. The situation is similar for the lead accumulator, for which the redox half-equations involve the PbIV / PbII couple at the "positive" and the PbII / Pb0 couple at the "negative":

$$PbO2 + 3H+ + 2e- + HSO4 - = 2H2O + PbSO4 \qquad (26)$$

$$PbSO4 + H+ + 2e- = Pb + HSO4 -. \qquad (27)$$

The reversible reaction-balance (28) takes place during the discharge of the accumulator. The opposite reaction takes place during its recharge.

$$PbO2 + Pb + 2\ H+ + 2\ HSO4 -\ \text{discharge}\ 2\ H2O + 2\ PbSO4 \qquad (28)$$

The thermodynamic potential of the cell is much greater than 1.23 V; it is written:

$$\Delta Eth = Eeq\ (PbIV/PbII) - Eeq\ (PbII/Pb0) \approx 2\ V.$$

This very high value suggests that at least one of the active masses is unstable in the solvent. In reality, both the negative active mass (lead) and the positive active mass (lead dioxide) are unstable in the electrolyte (aqueous solution of sulfuric acid). Reactions (29) and (30) take place "positive" and "negative" respectively, and are responsible for the self-discharge of the accumulator:

$$PbO2 + H2SO4 \rightarrow H2O + ½O2 + PbSO4 \qquad (29)$$

$$Pb + H2SO4 \rightarrow H2 + PbSO4. \qquad (30)$$

## Generators in Non-Aqueous MZedium

Lithium is a metal characterized by a very negative standard potential for the Li + / Li couple (-3 V), hence the idea of associating this redox couple with another having a high value of E ° in order to have 'a high value generator of e.m.f in addition, the low molar mass of lithium would provide a generator of high specific energy. However, in aqueous medium, lithium, like all alkali metals M, reacts strongly according to reaction (31):

$$M + H2O \rightarrow M+ + OH- + ½H2. \qquad (31)$$

We must therefore choose a non-aqueous electrolyte. This does not mean that lithium is incapable of reducing the non-aqueous solvent in question; in fact, this reaction is slow due to the formation of a passive layer on the surface of the metal which protects it from attack at depth. One of the best illustrations of this is certainly the example of the Li / SOCl2 battery. In this pile, which gave rise to significant industrial development, the e.m.f is around 3.5 V. The electrolyte is a solution of lithium tetra chloroaluminate in thionyl chloride. The following half-reactions are involved:

$$Li+ + e- = Li \qquad (32)$$

$$2\ SOCl2 + 4e- = S + SO2 + 4\ Cl- \qquad (33)$$

such that the non-reversible reaction-balance taking place during the discharge corresponds to the reduction of the solvent by lithium:

$$2SOCl2 + 4Li \rightarrow S + SO2 + 4Li+ + 4Cl-. \qquad (34)$$

Given the fact that the cathode active mass is liquid (it is the solvent itself), this cell is called a liquid cathode cell. A carbon electron collector is required for the "positive". On contact with the solvent, lithium oxidizes instantly, covering itself with a thin passivating layer of lithium chloride, compact enough to protect it from deep attack. When the battery is stressed, the layer allows Li + ions to pass through it. It behaves in a way like an ionic conductor; if necessary, it cracks if the current that is to flow is very large, and reconstitutes itself when the battery is no longer called upon. Therefore, in this example, it is thanks to the slow kinetics of reduction of the solvent by lithium that this type of efficient generator can exist. After giving an example of a non-rechargeable lithium generator (battery), let's now give an example of a rechargeable generator: the lithium-ion battery. Metallic lithium is not suitable as an anode active mass because, on recharging, dendrites form which cause short circuits. Also, lithiated carbon LixC is used as an anode material. It is an intercalator of lithium in carbon; the maximum stoichiometry is one lithium per six carbon atoms when the host material is graphite. We then have x = 1/6. Higher values can be obtained with amorpha carbon [10-11]. The cathode material is also an intercalation compound of lithium, of the metal oxide type. In lithium-ion accumulators developed by Sony in Japan, this is CoO2, but the use of Mn2O4 or even V2O5 is possible; during discharge, Li + ions penetrate the structure of the host material; they can become dis-intercalated during recharging [12]. The electrolyte is a solution of a lithium salt (LiPF6, LiClO4, LiAsF6, LiBF4 ...) in a non-aqueous solvent such as propylene carbonate or a mixture of solvents of the same type. The half-reactions are, for example in the case where the cathode material is V2O5:

$$x\,Li^+ + xe^- + C = Li_xC \tag{35}$$

$$Li^+ + V_2O_5 + e^- = LiV_2O_5 \tag{36}$$

and the reaction-balance during the discharge is:

$$Li_xC + xV_2O_5 \xrightarrow{discharge} x\,LiV_2O_5 + C \tag{37}$$

It will be noted that during reaction (37), the insertion of a lithium ion is accompanied by the variation of the oxidation number of one of the vanadium ions in the host structure (+ V → + IV) , so that the entity remains electrically neutral. In this generator, we observe that at the first charge, the quantity of electricity brought into play is greater than that observed during the following charges. This phenomenon is linked to the formation of a passivating layer at the lithiated carbon / electrolyte interface. This layer is sometimes called ISE for "interphase solid electrolyte". Its composition is often poorly known; it results from the reaction of reduction of the solvent by the anode active material.

## Fuel Cells

Fuel cells are open type generators, into which a fuel and an oxidizer are introduced in order to carry out a non-reversible combustion reaction at negative ΔrG. The chemical energy of this reaction is converted into electrical energy. High hopes are currently based on the use of hydrogen as a fuel; the oxidizer is dioxygen (pure or contained in the air) and the reaction is written [13]:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \tag{38}$$

thus, generating an e.m.f of 1.23 V if working at 25 ° C. There are several types of fuel cells based on this reaction-balance; they are distinguished by the nature of the electrolyte and electrode materials and by the operating temperature. Without going into details, we will limit ourselves to illustrating the transport phenomena which take place in two types of generators.

## The Proton Exchange Membrane Fuel Cell

It is called PEMFC for “proton exchange membrane fuel cell” [14]. The electrolyte is a Nafiontype polymer, so that the current transport is mainly provided by the $H^+$ ions which migrate within it. We then have $t_+ \approx 1$. The operating temperature is less than 100 ° C.

## The Solid Oxide Fuel Cell

In this type of generator called SOFC for "solid oxide fuel cell", the solid electrolyte is a yttriated zirconia ceramicwhich is an ionic conductor at high temperature by the oxide ions $O^{2-}$ [15]. We then have $t_- \approx 1$. The operating temperature is between 750 and 1000 ° C.

## Applications To Industrial Electrolysers

Our remarks will be illustrated by two examples already briefly mentioned above: hydrometallurgy and the electrochemical preparation of chlorine and soda, because these two processes are of great economic interest [16].

### Hydrometallurgy

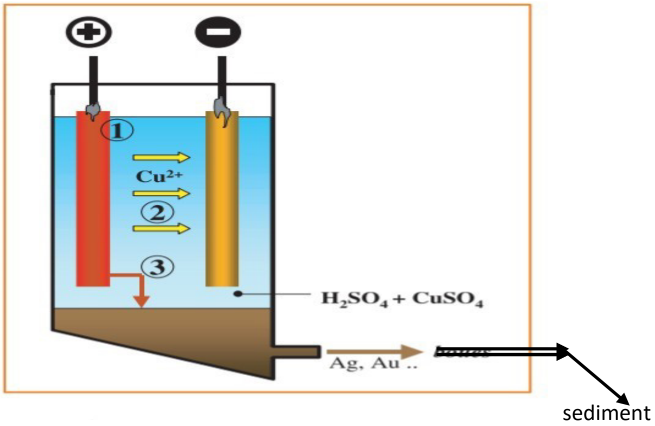

**Figure 2 :** Electro-refining of copper:1) metals less noble than copper go into solution and do not deposit at the cathode;2) copper dissolves and deposits at the cathode; 3) more noble metals than copper sediment at the bottom of the cell.

Hydrometallurgy includes all metallurgical processes involving an electrolysis step in an aqueous medium. A distinction is made, on the one hand, between the electrorefining process (which only concerns copper) and, on the other hand, the processes for preparing metals by electrolysis of aqueous solutions of metal salts. The latter are obtained, for example, by treatment with sulfuric acid of the roasting product of ores in the form of sulphides. Copper electrorefining is carried out on an industrial scale. This electrolytic process consists of bringing the anode of impure copper to a sufficient anode potential so that the copper and metals less noble than the latter are oxidized (tin, lead) and go into solution in the electrolyte (see figure 2). However, this potential is insufficient for the impurities made up of metals nobler than copper (silver and gold) to be oxidized. They then fall to the bottom of the cell and constitute the anode sludge which is recovered during a subsequent step. The potential of the cathode is such that copper is the only metal that can be deposited. The electrolyte is a solution of copper sulfate and sulfuric acid. In this type of electrolyser, the thermodynamic voltage is zero (see above). The potential difference at the "U" terminals boils down to (relatively small) overvoltage and ohmic drops. It does not exceed 0.4 V for a current density of 3 A / dm² [17]. It is also possible, from the same electrolyte, to produce copper by electrolysis with anodes insoluble in Pb / PbO2, on which the release of oxygen takes place. Copper is deposited at the cathode. The thermodynamic cell voltage is then equal to 0.9 V, and the potential difference at the terminals of the cell is greater than 2 V for a current density of the order of 1.3 A / dm². Likewise, 80% of zinc is produced today by an insoluble anode hydrometallurgical process. The electrolyte is a solution of zinc sulfate and sulfuric acid. The anode is of the Pb / PbO2 type. From a thermodynamic point of view, the deposition of zinc on a zinc cathode is not favored because the equilibrium potential Eeq (Zn2 + / Zn) is much lower than Eeq (H + / H2). On the contrary, the deposition of copper on copper from the process previously studied, for which Eeq (Cu2 + / Cu)> Eeq (H + / H2) was had, was a thermodynamically favored phenomenon. Nevertheless, zinc deposition is possible for kinetic reasons: under the above experimental conditions, the exchange current density for the Zn2 + / Zn couple is 1010 times higher than that corresponding to the H + / H2 couple. on zinc electrode .

## Chlorine / Soda Electrolysers

The production of chlorine and soda by electrolysis of concentrated aqueous solutions of sodium chloride (concentration close to 5 mol. L-1) and the production of aluminum in a molten medium are the two most important preparative electrochemistry processes. For the chlorine / soda process, three kinds of electrolytic cells are currently in use, all of which have titanium anodes coated with an electrocatalytic layer of ruthenium oxide and titanium oxide. Mercury cathode cells do not have a separator. The diaphragm cells have steel cathodes and a microporous asbestos separator; membrane cells also have steel cathodes, but the separator is a cation exchange membrane. Without going into the details of the operation of these electrolysers, described elsewhere [11], we will focus our interest on the following two points which constitute the guiding principle of this article:

Current transport in membrane cells, which is essentially provided by Na + cations. The membrane separates the anode compartment, which contains a concentrated solution of acidified sodium chloride, at pH close to 3 in order to avoid the disproportionation of the chlorine produced, and the cathode compartment, which contains a solution of concentrated sodium hydroxide (pH > 14).

The thermodynamic cell voltage, which depends on the type of cell. At the anode, two reactions are in competition:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \qquad (39)$$

$$2Cl^- \rightarrow Cl_2 + 2e^-. \qquad (40)$$

Taking into account the values of the standard potentials of the two couples involved and the activities of the electroactive species, we have: Eeq ($O_2$ / $H_2O$) <Eeq ($Cl_2$ / $Cl^-$).

Thermodynamics therefore predict that the release of dioxygen is favored. However, the $O_2$ evolution kinetics are slow on many materials, in particular on Ti / $TiO_2$-$RuO_2$, an electrocatalytic material with respect to the release of chlorine. It is therefore this last reaction that takes place, and Eeq ($Cl_2$ / $Cl^-$) must be taken into account for the calculation of the thermodynamic cell voltage. The release of oxygen, although very slow, is inevitable, so that the chlorine produced always contains traces of oxygen. If the cathode is made of steel, hydrogen is formed according to the reaction (41):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (41)$$

Indeed, the reduction of sodium ions to generate a metallic sodium deposit according to (42) is not observed in an aqueous medium:

$$Na^+ + e^- \rightarrow Na \qquad (42)$$

On the other hand, if the cathode is in mercury, the sodium chloride solution in contact with the electrode is at pH = 3 and one must consider, on the one hand, the reduction of the H + ions according to (43) and, of on the other hand, the reduction of sodium ions leading to the formation of an amalgam according to equation (44):

$$2H^+ + 2e^- \rightarrow H_2 \qquad (43)$$

$$Na^+ + e^- + n\,Hg \rightarrow (Na, nHg) \qquad (44)$$

The notation (Na, nHg) in reaction (44) symbolizes a liquid sodium / mercury alloy with a low sodium content and not a compound with defined stoichiometry. The standard potentials of the two couples E ° (Na + / Na, nHg) and E ° (Na + / Na) differ slightly, but the equilibrium potentials that we calculate by knowing the activities of the electroactive species are such as Eeq (Na + / Na, nHg) << Eeq (H + / H2). Although the reaction of release of hydrogen is considerably favored by thermodynamics, this reaction is so slow on a mercury electrode that it is the formation of sodium amalgam which is observed (this property is also used in polarography to study on mercury cathode the reduction of various metal cations without being hampered by the reduction of water). Thus, the thermodynamic cell voltage is written:

$$\Delta E_{th} = E_{eq}(Cl_2/Cl^-) - E_{eq}(Na^+/Na, nHg) = 1{,}31 - (-1{,}85) = 3{,}16\ V$$

for mercury cathode cells, and:

ΔEth = Eeq (Cl2/Cl-) - Eeq (H2O/H2) = 1,31 - (-0,84) = 2,15 V

For steel cathode cells (membrane or diaphragm). This difference of the order of 1 V is also reflected by a difference of the order of 1 V on the total potential difference ΔU 'at the terminals of these two types of cells, under normal operating conditions. Finally, to illustrate the previous remarks with a final example, we will discuss the decomposition of sodium amalgams in the chlorine / soda process with a mercury cathode. In steel cathode cells, soda and hydrogen are produced directly in the cathode compartment of the electrolyser. On the contrary, in a cell with a mercury cathode, a liquid sodium amalgam is formed at the cathode. The latter is pumped continuously and treated with water in an auxiliary reactor called a decomposer.

The necessary and sufficient quantity of water is introduced into it to obtain directly salable 50% soda. The overall reaction involved (45) results from the combination of reactions (41) and (44):

2(Na, nHg) + 2H2O → 2Na+ + 2OH- + 2n Hg + H2 (45)

However, sodium amalgam does not react violently with water like metallic sodium because this reaction causes the release of hydrogen on mercury, and we know that this phenomenon has very slow kinetics. This is why the reactor is filled with graphite spheres which "catalyze" the decomposition. In practice, the kinetics of H2 evolution are considerably faster on graphite than on mercury; water is therefore easily reduced on this material while sodium otherwise oxidizes. The decomposer therefore behaves like a short-circuited battery, in which the "corrosion current" associated with the decomposition of the amalgam is very intense; this is a necessary condition for the continuous recycling of mercury in the electrolysis cell.

## Main Challenges Faced In This Area

The experimental study of systems is a difficult undertaking which requires a multidisciplinary approach. In the past, for lack of specific commercial instrumentation, the experimenter borrowed from other fields (electronics engineers, electromechanics) devices that were lacking (regulations or signal analyzers). he had to master the knowledge of its use. The average electrochemist had to know a minimum of electronic signal processing, numerical analysis of solution chemistry or hydrodynamics in order to perform and interpret their experiments. the progress made since in instrumentation, the commercialization of high-performance scientific instrumentation may lead people to believe that this investment is less necessary today. this is a decoy and many automatic electrochemical measurement benches, which remain complex measuring devices, are not always acquired or used under the best conditions. each device has its own specificity and is in principle dedicated to the implementation of a determined electrochemical method. Also it is rather difficult to have a versatile equipment allowing to implement, with equal performances, the principal methods of study of the electrochemical systems.

## Conclusion

We have illustrated, thanks to examples involving electrolysers, that the calculation of the reversible cell voltage, ΔEth, a thermodynamic quantity, requires knowledge of the kinetics of the reactions that can take place at the electrodes, because they will not be observed (and taken into account for the calculation of ΔEth) only the reactions which take place with a sufficient speed. The preparation by electrolysis of certain compounds (such as chlorine), although not favorable according to thermodynamic forecasts, is made possible by playing on the fact that the thermodynamically favorable reaction is very slow (release of dioxygen). We have also shown that the very existence of certain generators of high electromotive force was due to the fact that the active masses (anodic or cathodic) react only very slowly on the solvent. The simultaneous consideration of thermodynamics and electrochemical kinetics is therefore a necessity. Finally, we also insisted on the fact that the transport of electroactive species played a fundamental role, and that migration was not the only mode of supply of matter to the electrode.

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