# 1 - BASIC NOTIONS

## 1.1 - INTRODUCTION

### 1.1.1 - ETYMOLOGY

The word electrochemistry derives from the terms electricity and chemistry. It applies to a scientific discipline as well as to a sector of industry. Ordinary dictionaries define it as the science which describes the interactions between chemistry and electricity, or the chemical phenomena that are coupled with reciprocal exchanges of electric energy.

More precisely, it is a science that analyses and describes the transformations of matter on the atomic scale by shifts of electronic charge which can be controlled by means of electric devices. Such transformations are called oxidation-reduction reactions[1]. It is therefore a matter of controlling oxidation-reduction reactions with an electric current[2] or with a voltage[3]. Therefore electroforming, which consists of forming an object by making a deposit with an oxidation-reduction reaction, belongs to the field of electrochemistry. On the other hand, electro-erosion or EDM (electrictrical discharge machining), in which matter is removed by electric discharges, is not considered to be a part of electrochemistry.

One of the advantages of electrochemistry over chemistry when taken in its broadest sense lies in the additional, adjustable degree of freedom offered by the voltage or current. Indeed, it is possible to vary the energy of the active species in a continuous and controlled manner, and also therefore, at room temperature for example, to attain a highly selective reactivity with acute control of the reaction and of its extent.

By extension, the term electrochemistry stretches to include systems which have no controlled exchange of electrical energy with the exterior. The overall electric current is zero: the electrochemical system is at open circuit. The term combines two very different situations. The first applies to any system in thermodynamic equilibrium, that is in which no transformation of matter occurs. This is the case with many potentiometric sensors. The second situation covers systems that are likely to react spontaneously, namely with a transformation of matter and the internal exchange of electric energy, such as in corrosion. The concepts of electrochemistry are the suitable tools to describe such systems.

The scope of the scientific field of electrochemistry, and consequently of this document, can be summarized as the search for links between current and voltage at any given

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*[1] These notions are defined in section 1.2.*

*[2] These notions are defined in section 1.3.*

*[3] These notions are defined in section 1.5.*

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time, for a given electrochemical system. Understanding these links allows one to anticipate the behaviour of electrochemical devices and improve their performance.

## 1.1.2 - THE HISTORICAL DEVELOPMENT OF IDEAS

The origins of electrochemistry in the history of science are rather difficult to determine. They are often attributed to the end of the 18th century with GALVANI's work on animal electricity. In actual fact, even before electrostatic machines were developed, similar observations on the excitation of muscles in contact with metals of a different nature had already been made by SWAMMERDAN in the middle of the 17th century. However, the link with electricity had not been clearly shown at the time. GALVANI published his results in 1791, laying out how he considered living muscles to be sorts of LEYDEN jars storing electricity which would be discharged if metals were set between two points. At that time, the link between electricity and life raised a number of questions and many scientists took an active interest in fish capable of striking down their victims by electric discharges. History records several experiments made by GALVANI which led him to observe the influential impact of the presence of two different metals. The anecdote of the frog legs hanging from the iron railing of a balcony by a copper wire is often cited: the frog legs contracted convulsively when they came into contact with the iron railing, as if exposed to an electric shock.

GALVANI's works attracted the attention of several other scientists, among whom SULTZER, who discovered the acidic taste on his tongue when put in contact with two different short-circuited metals, Pb and Ag. VOLTA also made numerous tests of the same kind, on his tongue, his ears, his eyes, his nose and his skin, either smooth or scratched. He gave a lot of himself to help science progress. Most of all he was the first to pile up two different metals in stacks, each layer separated by a wet sheet (tissue, paper, etc.) impregnated with substances such as salts or acids. From his experiments, VOLTA was able to grade the various metals according to the intensity of the electric pulses that he felt. He also connected elemental cells in series and/or in opposition and realised that the voltages were additive. He unveiled his classification of metals in 1794. We must nevertheless note that if he was indeed right to refute GALVANI's theory of animal electricity, he was himself mistaken in his interpretation. Until the end of his life, he clung to the idea that this phenomenon was only due to the difference in the nature of the metals at the metallic junction. In his view the only role of the electrolyte was to equalize the potentials. It was thanks to these discoveries, empirical as they were, that the true foundation of electrochemistry could be laid. During a conference given by VOLTA in 1801 at the *Institut de France*, he was awarded a gold medal by Napoléon BONAPARTE, thanks to his demonstration of a working battery. This was an important political event, knowing that Italy was waging war against France.

Among the major events and discoveries which followed in the field of electrochemistry, one can cite the following:

1800 NICHOLSON and CARLISLE achieved the first electrolysis of water by means of a battery and observed gas evolution, revealing the production of dihydrogen. It can be noted that VOLTA had also achieved similar findings but he did not come to any conclusion.

1807 GROTTHUS put forward a theory on the electrolytes and the movement of charges (separation of the charges on H and O in water molecule).

1807 DAVY discovered potassium using a battery (with 2 000 elements!) by electrolysing molten potash. He then discovered sodium and calcium. Moreover, he was the first to identify the role played by the reactions at the electrodes and the decomposition of the electrolyte.

1824 DAVY made use of zinc to protect against the corrosion of copper or iron parts in ships.

1826 BECQUEREL observed the polarisation effects of electrodes caused by hydrogen evolution. He then proposed the use of depolarizers in two-compartment batteries.

1833 FARADAY, a student of DAVY, introduced the vocabulary of electrochemistry[4] (electrode, anion-anode and cation-cathode) and observed the link between the mass of compound produced or consumed and the amount of charge passed (laws of electrolysis).

1836 DANIELL made up the two-compartment battery called the DANIELL cell, which is still the main reference example given of an electrochemical battery in a number of educational books. Anyway this is its only use since the electric power that this battery can provide is quite negligible.

1837 JACOBI invented galvanoplasty, which has numerous applications today.

1839 GROVE discovered the reversibility of water electrolysis reactions, and laid the basis of the first fuel cell, which was not to undergo any significant development until the NASA program in the 1960's.

1859 PLANTÉ invented the lead-acid battery, which is still widely used because it can deliver high levels of electric power at a low cost. Of course, its manufacturing process underwent many improvements, but its main principle remained unchanged.

1868 LECLANCHÉ discovered the saline battery based on zinc and manganese dioxide which is also still very successful today. Incidentally, it is interesting to note that LECLANCHÉ, having failed to secure funding in France to develop his project, expatriated himself to Belgium, where he then made his fortune.

1874 KOHLRAUSCH wrote his theory on the conductivity of electrolytes.

1886 HALL in the United States, and HÉROULT in France both developed the aluminium electrolysis process. The simultaneous nature of these discoveries did entail a certain degree of polemics, but what is even more unsettling is the fact that both men were born the same year and also died the same year. Would they now be together in Heaven with beautiful, gleaming aluminium wings?

1887 ARRHENIUS developed his theory on acido-basic reactions and on ionic dissociation.

1889 NERNST worked out the thermodynamics of electrochemistry.

1897 BOTTGER developed the hydrogen electrode (first measurements of $pH$).

1899 The first electric car (*JAMAIS CONTENTE*) was developed[5]. It reached a record speed of 100 km $h^{-1}$ (over the stretch of only a few kilometres).

1902 COTTRELL wrote the equations which rule the electrode kinetics with mass transport by diffusion.

1905 TAFEL found an empirical law of electrode overpotential as being a function of the current on various metals.

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*[4] It may be worth knowing the etymology of these terms, which are so familiar in electrochemistry. The term electrolysis means splitting a compound, namely the electrolyte, which can be unbound, and decomposed. The suffix -ode means the path: the anode is thus literally the 'path towards a hill'. It is with this electrode that the current enters the system. Before deciding on anode, FARADAY could have also used, for example, the term 'eisode' (entrance for the current), in which case the cathode should have been called 'exode'... To finish, the word ion comes from the verb 'to go' in Greek: the cations are species which move towards the cathode while the anions move towards the anode.*

*[5] See the illustrated board entitled 'The first electric vehicles'.*

1906 CREMER invented the glass bulb $pH$ electrode, which is still widely used.

1914 EDISON developed the Ni/Fe alkaline secondary battery.

1922 HEYROVSKY worked out the theory for the mercury electrode in polarography, an electrochemical analysis method which, after a few improvements, meant that ultra-traces could be analysed in heavy metals for instance. He was awarded the NOBEL prize for his work in 1959.

1924-1930 BUTLER and VOLMER laid the foundations of the charge transfer theory at an electrode.

Other more recent, important events could also be mentioned here, although it is really during these two centuries that the fundamental basis of electrochemistry was shaped. It is interesting to note that most concepts relating to the existence of ions and the reactions involving the exchange of charge were put forward before the atomic theory of matter was fully accepted. It was in 1803 that DALTON reintroduced the concept of the atom, which had been previously buried for centuries. THOMSON's work on the electron was carried out in1887, and the introduction of the BOHR model dates back to 1913.

Without the VOLTA battery, which delivered a direct current, could it ever have been possible to spot the magnetic effects of an electric current? Would FARADAY have discovered the dynamo all the same? Had GALVANI's works not existed, would VOLTA have shown any interest in these issues? What were those frog legs doing on GALVANI's balcony? It is obvious that all these discoveries are interdependent and chance plays a great part in the history of science.

## 1.1.3 - SOCIOECONOMIC IMPORTANCE

The industrial applications of electrochemistry can be classified under seven large categories: electrosynthesis, surface treatments, energy storage and conversion, analysis and measurements, the environment, corrosion and bio-electrochemistry.

### ▸▸ *Electrosynthesis*

Electrosynthesis is a process used in heavy industry because, depending on the material being produced, its energetic yield is higher than that found in thermal synthesis processes. Moreover, the processes used are selective and easy to control by means of the voltage, the current and the amount of charge, which is a very accurate indicator of the advancement rate in production. The raw materials produced in the greatest quantities by electrosynthesis are aluminium, dichlorine and sodium hydroxide.

Today, the annual world production of aluminium by means of electrosynthesis has been seen to reach up to about 38 Mt (data given for 2007) [6].

Dichlorine is a raw material used for many manufactured products such as plastics and detergents, etc. The total industrial production quantity of dichlorine through the electrosynthesis process is nowadays about 50 Mt (data given for 2007). About 56 Mt of sodium hydroxide are produced simultaneously. There exists three main dichlorine and sodium hydroxide electrosynthesis processes from aqueous solutions containing

*[6] See the illustrated board entitled ' Industrial production of aluminium in France '.*

sodium chloride: the diaphragm process, the membrane[7] process and the mercury cathode process. Figure 1.1 shows the distribution of world production for the different processes.

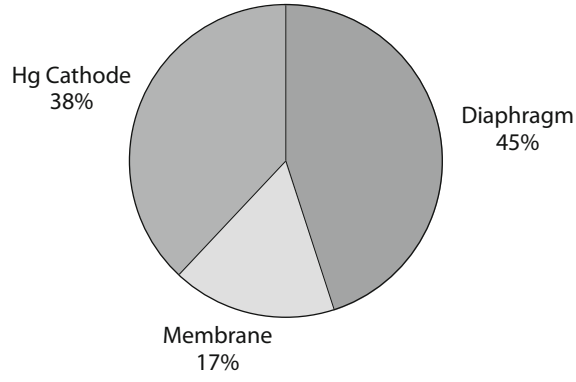


***Figure 1.1 - Distribution of the world production of dichlorine using the different electrolysis processes (data given for 2007)***

Difluorine, sodium, lithium and magnesium are also mainly produced through electrosynthesis using molten salts (figure 1.2).

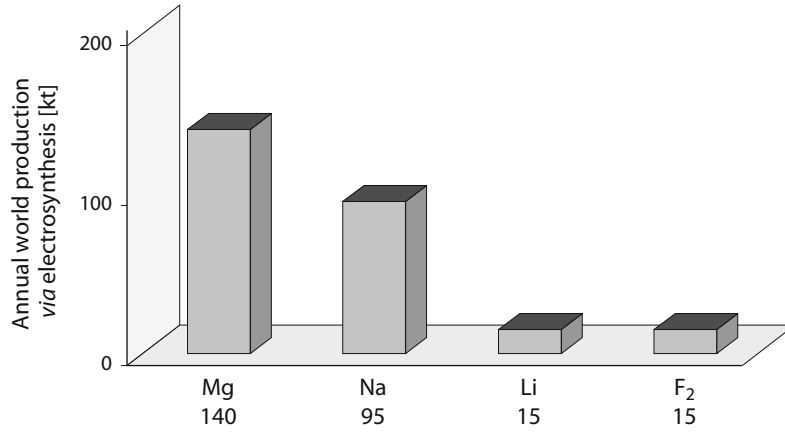


***Figure 1.2 - Annual world production via electrosynthesis of a selection of metals and halogens in 2007***

High purity dihydrogen is likewise produced by electrolysing water. It is also worth mentioning here the purification of certain metals, such as copper, zinc and aluminium, by an electrorefining process involving anodic dissolution and cathodic deposition by a selective electrolysis.

Thanks to their high selectivity, electrochemical processes also enable complex molecules to be synthesized (as used in the pharmaceutical industry, biotechnology,

*[7] More precisely an ionic conducting membrane, see section 1.3.2.2.*

perfumery, and in artificial flavouring in the food industry, etc.). Also worthy of mention is the selective synthesis of adiponitrile which is a precursor molecule in the synthesis of nylon.

### ⏩ *Surface treatments*

In electrochemical surface treatments, if the experimental conditions are suitably managed (namely current, voltage and the introduction of surfactants), then it is possible to govern the nature of the deposit formed, as well as its quality (porosity, sheen, etc.). This kind of process can be found in various applications such as polishing and electroforming objects, galvanoplasty (e.g., zinc depositing to protect against the corrosion of metal parts in the car industry) and the decorative metal coating of objects (silver, gold and chromium). Today, these techniques can also be found in the micro-electronic industry. Another original application is that of restoring ancient artefacts and managing their subsequent storage [8].

### ⏩ *Energy storage and conversion*

Batteries play an essential role in modern society. These days the use of low-power applications is increasingly on the up in portable electronic apparatus (telephones, computers, MP3 players, etc.) or in the medical sector (hearing aids, pacemakers, micro-injectors, etc.). On a domestic scale there is a growing demand for more powerful energy supplies, notably in the transport sector, for starting combustion engines, and developing electric vehicles, etc. Equally on a larger scale, very high-power supplies are also used, e.g. for modulating the electric energy consumption of a village through a coupling with photoelectric cells and for supplying energy to remote areas, etc. Particularly in the latter domain, developing fuel cells [9] represents a significant stepping stone towards progress. Operational installations with power ranging from 1 to 10 MW are already in use.

### ⏩ *Analysis and measurement*

Electrochemical sensors, the most ancient of which is the $pH$ electrode, are currently undergoing development in that their prices are often low, they are easy to use and, most of all, they are easy to insert into a regulation system. In this respect, the most widely used today is the dioxygen sensor, which allows for combustion to be optimised thanks to the process of analysing the exhaust gases [10]. Several million parts per year are produced, notably for the car industry. In the biomedical field, electrochemical sensors are also used to monitor glucose and $pH$, and to measure out certain cations. New developments are also being made in the field of pollutant analysis.

Polarography is an electrochemical method using a mercury drop electrode which permits analysis of a very high number of chemical species. It is mainly used for analysing metal cations in aqueous solutions. The usual detection limits are about $10^{-6}$ mol $L^{-1}$ but they can be lowered to $10^{-12}$ mol $L^{-1}$, with inexpensive equipment.

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*[8] See the illustrated board entitled ' Conservation of archaeological artefacts '.*

*[9] See the illustrated board entitled ' Fuel cells '.*

*[10] See the illustrated board entitled ' Regulating of fuel engines '.*

### *The environment sector*

In the environment sector, electrochemistry is still of little use on a large scale, however predictions point towards significant growth in this field in the future. Electrochemical techniques can be used for:

- separation, e.g., brackish water desalination through electrodialysis (the membrane processes is capable of producing up to 2 000 $m^3$ per day), for supplying fresh water to remote areas [11],
- recovery, e.g., electrodepositing metallic elements such as copper, nickel, zinc, cobalt, silver and gold, etc.,
- concentrating or purifying effluents through electrodialysis, or cathodic deposition processes, etc.,
- destroying pollutants, e.g., the oxidation of cyanide ions into carbon dioxide and dinitrogen, disinfection by means of producing oxidizing species in situ, e.g., dichlorine or sodium hypochloride, for example for disinfecting air, or swimming pool water.

### *Corrosion*

Corrosion is the phenomenon whereby a metallic part is destroyed [12]. It generally occurs spontaneously, e.g., *via* a reaction with dioxygen dissolved in water in the case of wet corrosion. Attempts are generally made to fight against this phenomenon which engenders a considerable economic cost and also poses security and toxicity problems. Such is the case for the corrosion of lead tubing which can cause serious health problems. The economic cost of corrosion is estimated today as being 2% of the GNP [13] in developed countries. Sometimes however, corrosion can be beneficial. For example, in the process of dismantling of nuclear plants, corrosion can be used to reduce the quantity of contaminated matter that has to be stored.

### *Bio-electrochemistry*

Biology is an additional field in which electrochemistry plays an important role in the development processes. A significant number of phenomena in the living world involve oxidation-reduction reactions or controlled ionic movements through membranes. In addition to its list of increasing widespread uses in the field of biosensors [14], bio-electrochemistry is likely to grow in other sectors, such as in the development of new processes.

## *1.2 - OXIDATION-REDUCTION*

Oxidation-reduction is a notion that has been developed over the course of centuries, as outlined in the brief historic account given above. In the first notion introduced by

*[11] See the illustrated board entitled ' Electrodialysis '.*

*[12] See the illustrated board entitled ' Corrosion of reinforced concrete '.*

*[13] GNP: Gross National Product.*

*[14] See the illustrated board entitled ' Electrochemistry and neurobiology '.*

LAVOISIER, oxidation was considered to be the reaction between chemical species and dioxygen, e.g.:

$$2\,Hg + O_2 \longrightarrow 2\,HgO$$

The modern notion which we will define and use in the following section was rooted at the start of the 20th century, with the discovery of the electron.

## 1.2.1 - THE MODERN NOTION OF OXIDATION-REDUCTION

An oxidation-reduction reaction (redox reaction) involves transforming matter *via* electron shifts at the atomic level. When a species, or more exactly a chemical element of this species, loses one or more electrons, this species is said to undergo oxidation. When it gains electrons, it is said to undergo reduction.

Such a transformation is called an oxidation-reduction half-reaction or a redox half-reaction [15]. It concerns two species for which a given element exists under two different forms. These two species are called the oxidant (or oxidizing agent) and the reductant (or reducing agent) denoted by Ox and Red respectively. They make up a redox couple usually denoted by Ox/Red.

***The overall equation of the redox half-reaction for the Ox/Red couple is the following:***

$$Red \underset{reduction}{\overset{oxidation}{\rightleftharpoons}} Ox + n e^-$$

***where Ox is the oxidant, i.e., the form that is capable of gaining electrons,***
***Red is the reductant, i.e., the form that is capable of giving electrons.***

Although the terms oxidant and reductant (or oxidizing and reducing agents) are the most commonly used, one can also use the terms oxidized form and reduced form of the couple. It is then necessary to keep in mind the fact that Ox is both an oxidizing agent and the oxidized form of the couple Ox/Red, whereas Red is the reducing agent and the reduced form of the couple.

When the direction of the transformation actually occurring is not the main interest [16], which is the case here, then the direction in which the reaction is written should be considered immaterial. This reaction can be written by choosing the direct orientation for oxidation as well as for reduction [17].

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*[15] According to the authors, the terms half-reaction or oxidation-reduction reaction can be used for this electron exchange reaction. The term half-reaction, which is often used in this document, stresses the fact that if a redox couple reacts, e.g., in the direction of oxidation, at least one other couple must react in the direction of reduction. This term is derived from redox-chemistry in solution-based reactions, however it is still of educational interest for electrochemists given that at least two half-reactions are always occurring simultaneously, one at the anode and the other at the cathode.*

*[16] Predicting the direction of the redox half-reactions actually occurring in an electrochemical system is an important question which will be dealt with in section 2.4.*

*[17] Certain authors are in favour of the reaction being written in the direction of reduction for a redox couple, because of the highly observed convention which places Ox in first position for writing the couple Ox/Red. We will not systematically adhere to this convention here but rather we will show how an entire algebraic form of relationships stemming from thermodynamics can allow one to*

As in other areas of chemistry, key numbers appear in these balanced equations. In thermodynamics or in kinetics, stoichiometric numbers[18] are therefore defined for the reaction, which are algebraic and denoted by $\nu_i$. They are set up as being positive for the products (on the right side of the balanced reaction) and negative for the reactants (on the left side of the balanced reaction), as shown in the following generalised expressions, as well as in the ensuing examples, with $A_i$ representing the chemical constituents in the reaction:

$$0 \rightleftharpoons \sum_i \nu_i A_i$$

or most commonly:

$$\sum_{i\,=\,\text{reactants}} |\nu_i|\, A_i \rightleftharpoons \sum_{j\,=\,\text{products}} |\nu_j|\, A_j$$

The redox half-reaction of the $Cu^{2+}/Cu$ couple can be written for example in the direction of reduction:

$$Cu^{2+} + 2\,e^- \rightleftharpoons Cu$$

The stoichiometric numbers of the species are then:

$Cu$ $\quad \nu_{Cu} = +1$

$Cu^{2+}$ $\quad \nu_{Cu^{2+}} = -1$

$e^-$ $\quad \nu_e = -2$

This example shows that the usual form of writing the balanced reaction uses absolute values for the stoichiometric numbers. In some books, one finds a more mathematical form of these equations, in which algebraic stoichiometric coefficients are used directly:

$$0 \rightleftharpoons \sum_i \nu_i A_i$$

In the case of the $Cu^{2+}/Cu$ couple, this writing form therefore corresponds to:

$$0 \rightleftharpoons Cu - Cu^{2+} - 2\,e^-$$

Taking these definitions into account, when a redox half-reaction is written in the oxidation direction then the algebraic stoichiometric number of electrons corresponds to the positive number ($n > 0$) of the electrons exchanged:

- in the oxidation direction, the electrons are counted among the products of the balanced reaction:

$$\nu_{Ox} > 0 \quad \nu_e = n > 0 \quad \nu_{Red} < 0$$

- in the reduction direction, they are among the reactants:

$$\nu_{Ox} < 0 \quad \nu_e = -n < 0 \quad \nu_{Red} > 0$$

Some of the species involved are ionic, i.e., they have a charge which is a multiple of the absolute value of the charge of the electron, $|e| = 1.6\times10^{-19}$ C. The factor of proportionality, which is therefore a positive or negative integer, is called the charge number and will be denoted by $z_i$ in this book.

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*do away with the written notation of the direction of the chemical reaction chosen in this context. In fact, this direction does not correspond to any physical reality in the equilibrium state (see sections 2.1.2.1 and 3.4.1).*

*[18] Sometimes also named stoichiometric coefficients.*

# THE ORIGINS OF THE VOLTA BATTERY

*Document written with the kind collaboration of M. COMTAT,*
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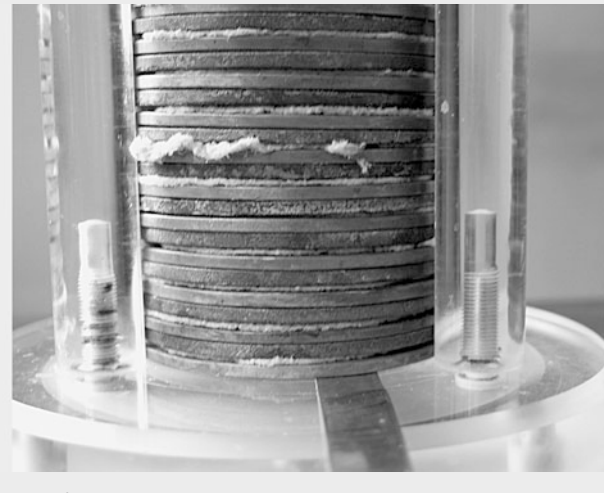
GALVANI or VOLTA, who was right, who was wrong?

Luigi GALVANI (1737-1798), an anatomy professor at the University of Bologna, showed great interest in the influence of electricity on the nerves and on muscle stimulation. Between 1780 and 1791, he focused his numerous experiments on frogs which he prepared by leaving only the lower limbs attached to the spinal cord. In his laboratory, he happened to notice that muscular contractions were caused when he touched a nerve with a metallic scalpel in his hand. However these contractions occurred only when an electric machine, switched on in the room generated a spark. GALVANI pursued the experiment on the terrace of his house, where he showed the effects of atmospheric electricity. He also noticed that when ' specially prepared frogs ', with a copper hook stuck in the spinal cord, were laid on the iron bars of the balcony, the contractions occurred when he placed the copper hook in contact with the iron bar, even when the weather was good. He reproduced this experiment in his laboratory. Thus no external electricity source was necessary for stimulating the muscles, as the contact created between nerve and muscle via two different metals was sufficient. Herein lies the origin behind the theory of animal electricity, whereby a current is discharged when the nerves and the muscles are linked by metals.

At the end of his long, meticulous study, he published a memoir in latin in 1791 (the common medical language in use at that time), entitled *De viribus electricitatis in motu musculari commentarius* (*Notes on the electric forces in muscular motion*).



***Example of a demonstration model of the VOLTA battery, built using zinc-copper pilings, used in practical experiments at Phelma (Grenoble-INP) by Professor D. DELABOUGLISE, who corrected in this demonstration battery a conception error made by VOLTA: in fact, only one metallic disc was needed at each end of the pile (copper at the bottom on the photographs). To keep true to VOLTA's historic conviction, an additional zinc disc should have been laid at the bottom of the pile below the copper disc.***

Alessandro VOLTA (1745-1827), a physics professor in Como then in Pavia, was already a renowned scientist in 1792. Discovering methane, inventing the electrophorus and then travelling and working with his foreign colleagues all contributed to making him famous. During his travels from 1780 to 1783, he visited Switzerland where he discussed ideas with VOLTAIRE, France where he worked on atmospheric electricity with LAVOISIER and LAPLACE, Germany where he discussed ideas with LICHTENBERG, the Netherlands where he worked with VAN MARUM, and England where he worked with PRIESTLEY. In 1792 when he first came upon GALVANI's dissertation, he was initially skeptical, but then became enthusiastic and decided to follow up the research on his own. He quickly grasped the idea that the muscle contraction was triggered by metallic electricity being generated when two different metals were brought into contact. He tried out the experiments on himself (on his tongue, in his nostrils, in his ears and on his eyelids). He observed effects that he decided to explain using the laws of physics. He would readily use the Ag-Zn, Cu-Zn couples but also Ag-Sn, Cu-Sn, Pb-Zn. He presented a classification of the effects of these couples. In doing so, he contested the very existence of animal electricity.

GALVANI reacted to VOLTA's experiments and a series of counter-experiments thereafter ensued, each following the other, further feeding the rivalry. The controversy stretched out across Europe as far as London where Galvanist and Voltaic Societies were created. Napoléon BONAPARTE unwittingly put an end to this controversy in 1797 when he invaded Italy and demanded a plea of allegiance from the State employees. VOLTA accepted but GALVANI refused and was excluded from the university. He died a few months later.

VOLTA was trying to find how to increase the effect of the contact between two different metals. Inspired by GALVANI's study of the electric organ of the torpedo fish, and its description as a sequence of small flat hexagons, he decided to build his own generator by piling up elements. Each element was made out of a zinc disc with a silver disc laid on top, itself covered with a cardboard disc soaked in brine. The suffused cardboard disc was meant to represent the muscle. He managed to pile up as many as 20 elements and then connected several piles in series. In 1800, he sent his results via a letter addressed to the President of the Royal Society in London. When invited by BONAPARTE in 1801 to the *Académie des Sciences* in Paris to give a presentation of his battery, VOLTA was awarded a gold medal and given a pension. Later he was made senator of the French Empire. Subsequently, BONAPARTE created an award bearing the name of the italian scientist. The award was meant to encourage others to make ' a leap forward in the field of electricity and galvanism comparable to the contribution made to these sciences by FRANKLIN and VOLTA '. BONAPARTE later convinced GAY-LUSSAC and THÉNARD to build an enlarged version of the VOLTA battery at the *Ecole Polytechnique* in Paris. This same battery was at the heart of quite a significant number of theoretical and experimental developments.

Given the success of his battery, VOLTA appeared to be the clear winner in his competition against GALVANI. However, he was incorrect in his interpretation of the working principle of the battery since he thought that it was the mere contact between two different metals that produced electricity. As for GALVANI, he had been similarly mistaken in his interpretation, but was nevertheless the precursor of electrophysiology, a science that emerged a few decades later and that was to undergo considerable development before eventually becoming a major field as we know it today.

The species is an anion when its charge has the same sign as that of the electron ($z_i < 0$); it is a cation in the opposite case ($z_i > 0$). However, there is no link between the charge of the ion and its oxidizing or reducing properties. An anion or a cation can be, depending on the case, an oxidant or a reductant.

The three examples below illustrate the fact that a reductant can be neutral, cationic as well as anionic:

$$Li \rightleftharpoons Li^+ + e^-$$

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

$$Fe(CN)_6^{4-} \rightleftharpoons Fe(CN)_6^{3-} + e^-$$

The charge numbers of these species are:

$Li$ $z_{Li} = 0$

$Li^+$ $z_{Li^+} = +1$

$Fe^{2+}$ $z_{Fe^{2+}} = +2$

$Fe^{3+}$ $z_{Fe^{3+}} = +3$

$Fe(CN)_6^{4-}$ $z_{Fe(CN)_6^{4-}} = -4$

$Fe(CN)_6^{3-}$ $z_{Fe(CN)_6^{3-}} = -3$

Similarly, an oxidant may bear any charge.

In other more complicated situations, several species are involved in the redox half-reaction [19]. By convention, only those having actually exchanged electrons are mentioned in the name of the redox couple.

For example, the redox half-reaction of the AgCl/Ag couple is:

$$AgCl + e^- \rightleftharpoons Cl^- + Ag$$

where the $Cl^-$ species is neither oxidized nor reduced but plays a role in the reaction.

It may happen that a given species is the oxidant in one couple and the reductant in another couple: this case is similar to that of amphoteric species in acido-basic equilibria.

For example, $Fe^{2+}$ an oxidant in the $Fe^{2+}/Fe$ couple and a reductant in the $Fe^{3+}/Fe^{2+}$ couple:

$$Fe^{2+} + 2\,e^- \rightleftharpoons Fe$$

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

## 1.2.2 - OXIDATION NUMBER

The definition given by the IUPAC [20] for the oxidation number or oxidation degree of an element in a compound, denoted by o.n. is "*the charge that would be left on an atom*

*[19] The method for establishing the balanced expression of a redox half-reaction is described in section 1.2.3.*

*[20] IUPAC: International Union of Pure and Applied Chemistry.*

*if all the electrons of each bond ending up at that atom were attributed to the most electronegative atom "* [21].

This is a formal definition since the bonds in polyatomic structures are generally partially covalent. The electrons are therefore only partially shifted towards the most electronegative atom. Moreover, this notion becomes more difficult to grasp in the case of bonds between atoms with similar electronegativities.

For any compound, the method for writing how the overall charge is preserved is illustrated with the following equation:

$$\sum_{\text{various elements}} (\text{number of elements in the compound}) \times \text{o.n.} = \text{charge number of the compound}$$

Taking into account the electronegativity values of the elements, we should keep in mind that:

- the oxidation number of hydrogen in most compounds is equal to +I (excluding dihydrogen where it is equal to 0 and the hydride ion where it is equal to –I);
- the oxidation number of oxygen in most compounds is equal to –II (except in the case of dioxygen where it is 0, peroxides where it is –I, and fluorinated compounds with O-F bonds where it is +I);
- the oxidation number of a halogen atom X (i.e., fluorine F, chlorine Cl, bromine Br, iodine I and astatine At) in most halogenated compounds is equal to –I (except in pure substances such as $X_2$ where it is 0, and in compounds having at least one bond between X and a more electronegative element such as O in $ClO^-$ or $ClO_4^-$ where it is positive);
- the oxidation number of an alkali atom (i.e., lithium Li, sodium Na, potassium K, rubidium Rb, caesium Cs and francium Fr) in most compounds is equal to +I, except in the corresponding metals where it is 0.

This short list of observations can be used to determine the algebraic value of the oxidation numbers of a large number of usual compounds.

For instance, in the $MnO_4^-$ anion, the oxidation number of manganese is equal to +VII [because, $-1 = +VII + 4\times(-II)$].
In the $IO_3^-$ anion, the oxidation number of iodine is not equal to –I since there is a O-I bond. It is equal to +V [because $-1 = +V + 3\times(-II)$].

However, in certain cases it is also necessary to be familiar with the structure of the compound (e.g., the LEWIS structure) in order to determine the oxidation numbers.

For example, the peroxodisulfate ion $S_2O_8^{2-}$ has the following structure: $(O_3S\text{-}O\text{-}O\text{-}SO_3)^{2-}$.
It thus has an O-O peroxo bridge and each of the two sulphur atoms has an oxidation number of +VI [because, $-2 = 2\times(+VI) + 6\times(-II) + 2\times(-I)$].

*[21] The electronegativity of atoms can be defined in different manners (MULLIKEN scale, PAULING scale, etc.). But it generally refers to properties which are not outside the electrochemical sphere since it uses the energy linked to the process of extracting or adding an electron from/to an atom in the gaseous phase.*

In other cases, this method yields a virtual oxidation number which only corresponds to a mean value, though it is still useful for writing redox half-reactions. A simple example is given by the iron oxide $Fe_3O_4$, which contains $Fe^{2+}$ and $Fe^{3+}$ ions in its crystal lattice, but which can be formally considered as an iron oxide with an iron oxidation number equal to +8/3. This is also the case with numerous compounds used in batteries [22], which are called insertion materials, such as $Li_xMnO_2$, $H_xWO_3$, and $Li_xV_2O_5$, etc. Their oxidation numbers still remain a subject of discussion today.

Taking the example of $Li_xMnO_2$, we will suppose that the oxidation number of lithium is +I, that of oxygen is –II and therefore by way of deduction that of manganese is (+IV –x).

## 1.2.3 - HOW TO WRITE A REDOX HALF-REACTION

When both of the compounds in a redox couple are known, then the balanced redox half-reaction can be found in different ways. Two of these methods are briefly described below.

### First method

The first step is to write both compounds of the redox couple and when necessary to adjust the stoichiometric numbers, in order to ensure that the element with the variable oxidation number is preserved. The number of electrons exchanged is then determined from the difference between the oxidation numbers of the element in its oxidized and reduced states, taking into account the stoichiometry. Protons [23] are added if necessary to ensure that the sum of the charges on both sides of the overall equation are kept the same. Finally, water molecules $H_2O$ are added to balance the oxygen (or hydrogen) element. It is then possible to check if the hydrogen (or oxygen) element is also balanced in the overall equation.

For example, for the $Fe_2O_3$/FeO couple, preserving the iron element on both sides of the equation is written in the following way:

$$\mathbf{2}\ FeO \rightleftharpoons Fe_2O_3$$

The number of electrons exchanged can then be determined since the oxidation number of iron changes from +II in FeO to +III in $Fe_2O_3$:

$$2\ FeO \rightleftharpoons Fe_2O_3 + \mathbf{2\ e^-}$$

oxidation number: $2\times(+II) \quad 2\times(+III) + 2\times(-I)$

When the charge is preserved on both sides of the reaction by means of adding protons, then it gives the following:

$$2\ FeO \rightleftharpoons Fe_2O_3 + \mathbf{2\ H^+} + 2\ e^-$$

Preserving the oxygen element by adding water molecules finally gives:

$$2\ FeO + \mathbf{H_2O} \rightleftharpoons Fe_2O_3 + 2\ H^+ + 2\ e^-$$

The final way of writing the redox half-reaction also provides a means of checking that the hydrogen element is preserved in the equation.

---

*[22] See the illustrated board entitled ' Energy storage: the Li-Metal-Polymer (LMP) batteries '.*

*[23] Protons are usually written $H_3O^+$ or $H^+$ to simplify. The latter form will be used in this document.*

### ▸▸ *Second method*

The first step is to write the two compounds of the redox couple and to adjust their stoichiometric numbers, if necessary, in order to ensure that the element with the variable oxidation number is preserved. Water molecules, $H_2O$, and protons, $H^+$, may then be added to ensure that the O and H elements are preserved respectively. The final step consists of adding electrons in order to balance the charge on both sides of the reaction equation. This method, which is more formal than the previous one, avoids calculating oxidation numbers, but may be tricky to carry out if the redox couples are not sufficiently well-identified.

◤ Back to the $Fe_2O_3$/FeO couple, let us first express the fact of preserving the iron element as follows:

$$\mathbf{2}\ FeO \rightleftharpoons Fe_2O_3$$

Preserving the oxygen element by adding water molecules yields:

$$2\ FeO + \mathbf{H_2O} \rightleftharpoons Fe_2O_3$$

Preserving the hydrogen element by adding protons yields:

$$2\ FeO + H_2O \rightleftharpoons Fe_2O_3 + \mathbf{2\ H^+}$$

Preserving the charge by adding electrons yields:

$$2\ FeO + H_2O \rightleftharpoons Fe_2O_3 + 2\ H^+ + \mathbf{2\ e^-}$$

◢

In the preceding examples, protons were added to preserve the H element. Such a formal choice has nothing to do with the $pH$ of the medium in which the reaction occurs. One may prefer to use hydroxide ions rather than protons to ensure the hydrogen element is preserved in the reaction, e.g., in a reaction involving cyanide ions, $CN^-$, which are not stable in acidic media:

- for the first method, one can ensure the charge balance merely by adding hydroxide ions ($OH^-$) instead of protons,

◤ Let us return again to the $Fe_2O_3$/FeO couple. Once the preservation of the iron element has been taken into account, as well as the change in its oxidation number, then we have:

$$2\ FeO \rightleftharpoons Fe_2O_3 + 2\ e^-$$

The charge balance on both sides of the reaction is ensured by adding hydroxide ions instead of protons, which yields:

$$2\ FeO + \mathbf{2\ OH^-} \rightleftharpoons Fe_2O_3 + 2\ e^-$$

Preserving the oxygen element by adding water molecules yields:

$$2\ FeO + 2\ OH^- \rightleftharpoons Fe_2O_3 + \mathbf{H_2O} + 2\ e^-$$

We can check to see if the hydrogen element has also been preserved in the final redox half-reaction. ◢

- in the second method, one can add the water autoprotolysis (or autoionisation) equilibrium to the redox half-reaction simply by applying the correct multiplication coefficient, in order to eliminate the protons in the balanced reaction.

◤ In the preceding example, the water autoprotolysis equilibrium

$$H_2O \rightleftharpoons H^+ + OH^-$$

must be multiplied by –2 for the protons to be eliminated:

$$\begin{array}{rcll} (\ 2\,FeO + H_2O & \rightleftharpoons & Fe_2O_3 + \mathbf{2\,H^+} + 2\,e^-\ ) & \times \mathbf{+1} \\ (\ H_2O & \rightleftharpoons & \mathbf{H^+} + OH^-\ ) & \times \mathbf{-2} \\ \hline 2\,FeO + 2\,OH^- & \rightleftharpoons & Fe_2O_3 + H_2O + 2\,e^- & \end{array}$$

In other cases, water and/or protons are not involved when writing the equilibrium: other simple ions, such as alkali $M^+$ or halide ions $X^-$ must be involved.

This is the case for example with the redox half-reaction of the $MnO_2/Li_xMnO_2$ couple. When examining the oxidation numbers (the manganese oxidation number is what changes in this formal representation) one can see that the written form of the reaction initially gives:

$$\begin{array}{lcl} & Li_xMnO_2 \rightleftharpoons MnO_2 + \mathbf{x\,e^-} & \\ \text{oxidation number:} & (+IV\,\text{-}x) \qquad +IV\ + -x & \end{array}$$

For this half-reaction to be balanced, one needs to add a compound containing a lithium atom. Here we will choose the $Li^+$ ion so as to end up with the following balanced reaction:

$$Li_xMnO_2 \rightleftharpoons MnO_2 + x\,e^- + \mathbf{x\,Li^+}$$

In an electrochemical system, exactly as in homogeneous redox chemistry, any reduction reaction occurring is accompanied by at least one oxidation reaction with the same charge transferred. It is common in certain areas (e.g., in industrial mass balance for electrolytic processes or when describing how batteries work) to write a chemical reaction expressing the result of these two processes[24]. Writing the overall electrochemical reaction results from combining two half-reactions with the adequate multiplying coefficients so that the charges exchanged are identical. The electrons do not appear in the balanced overall redox reaction.

- For example, when writing the redox reaction between the $Ag^+/Ag$ and $Cu^{2+}/Cu$ couples, the half-reaction of the first couple must be multiplied by −2 whereas that of the second couple is multiplied by +1 in order to eliminate the electrons:

$$\begin{array}{rcll} (\ Ag & \rightleftharpoons & Ag^+ + \mathbf{e^-}\ ) & \times \mathbf{-2} \\ (\ Cu & \rightleftharpoons & Cu^{2+} + \mathbf{2\,e^-}\ ) & \times \mathbf{+1} \\ \hline Cu + 2\,Ag^+ & \rightleftharpoons & 2\,Ag + Cu^{2+} & \end{array}$$

- In certain cases, a given species acts simultaneously as both an oxidant in one of the couples and a reductant in the other couple. This reaction is called dismutation (or disproportionation). To balance such a reaction, one must first spot the fact that it is a case of dismutation, i.e., a particular chemical reaction involving two different redox couples. For example, the following equation may indeed be formally balanced, yet it does not correctly represent the chemical dismutation of diiodine because electrons appear on the right side, as in a redox half-reaction:

$$I_2 + 3\,H_2O \rightleftharpoons I^- + IO_3^- + 6\,H^+ + 4\,e^-$$

One can spot dismutation by calculating the oxidation number of the three species involved. The oxidation degree of iodine is 0 in $I_2$, −I in $I^-$ and +V in $IO_3^-$. This equilibrium is not a redox half-reaction, but an overall reaction which is the balance of the two redox half-reactions corresponding to the $IO_3^-/I_2$ and $I_2/I^-$ couples.

---

*[24] This notion of the overall reaction is of immediate use in homogeneous redox chemistry. However, in electrochemistry it must be handled with precautions as soon as several redox reactions occur simultaneously at the same interface. Those wishing to explore this question more deeply can refer to section 2.2.2.3 which deals with the faradic yield.*

These two redox couples give the following equilibria:

$$I_2 + 6\,H_2O \rightleftharpoons 2\,IO_3^- + 12\,H^+ + 10\,e^-$$
$$I_2 + 2\,e^- \rightleftharpoons 2\,I^-$$

By combining these two equilibria (with a coefficient of +5 for the second), one can finally obtain the overall dismutation reaction:

$$6\,I_2 + 6\,H_2O \rightleftharpoons 10\,I^- + 2\,IO_3^- + 12\,H^+$$

## 1.3 - THE NOTION OF CURRENT

Electric current is a macroscopic notion which was given one of its first formal definitions by AMPÈRE in 1820: *" the overall movement of charges in a conductor "*. This notion is linked to its microscopic origin: the movement of charged species, which corresponds to the charge flow rate or charge flux. Insofar as an elementary charged species has a mass, then the notion of current is consequently linked to mass transport [25].

### 1.3.1 - MACROSCOPIC QUANTITIES DEFINING THE CURRENT

#### 1.3.1.1 - CURRENT DENSITY

Most of the time, several different kinds of charged species are in movement, and the overall current is created by the movement of various charge carriers. The current density, $\mathbf{j}$, which is a vector with a modulus expressed in A m$^{-2}$, represents the overall charge flux density, i.e., the sum of the charge flux densities of each charge carrier:

$$\mathbf{j} = \sum_i \mathbf{j}_i$$

#### 1.3.1.2 - CURRENT

For any surface (S) oriented by the normal vector $\mathbf{n}$ and having an area $S$, the current intensity through that surface is equal to the quantity of charge moving across it per time unit. It is thus defined by:

$$I = \iint_{(S)} \mathbf{j} \cdot \mathbf{n}\, \mathrm{d}S = \frac{\mathrm{d}q}{\mathrm{d}t}$$

with: $I$ the current intensity through the surface (S) [ A ]
(the sign of $I$ being defined by the orientation of $\mathbf{n}$ [26])
$\mathbf{j}$ the local current density, with a modulus in [ A m$^{-2}$ ]
$\mathrm{d}q$ a small element of charge crossing (S) [ C ]
$\mathrm{d}t$ a small element of time [ s ]

---

*[25] For instance the current flowing through a metal is the result of the overall movement of the electrons. Since the electrons have a mass, then mass movement also occurs. Mass transport is mainly characterized by mass flux, and the link between mass flux and current is studied in detail in section 4.1.1.*

*[26] The link between the sign of the current and the choice of the orientation of the normal to the surface is discussed in detail in section 1.4.1.3.*

This precise definition refers to the current intensity which is a scalar corresponding to the overall charge flux or flow rate ($1\ A = 1\ C\ s^{-1}$). Naturally, it must be defined with reference to a surface. However, in certain conditions including those fulfilled in this document [27], the absolute value of the current intensity in a conductor can be defined by considering any section of the conductor. For these reasons, which is moreover usual practice in numerous documents, we will use ' current ' to stand for ' current intensity across a section of area $S$ '.

### 1.3.1.3 - ELECTRONEUTRALITY AND CONSERVATIVE CURRENT

Electroneutrality can be assumed in the bulk of all conducting media at the local level, on the macroscopic scale, only after a very short transient period, necessary in order for the charges to be rearranged (about 1 femtosecond in a metal [28]). Thanks to the property of volume electroneutrality in a conducting material, the current can be shown [29] to have the same value in any section of the conductor, whether it is normal to the current density or not. The current flowing through the conductor can then be clearly defined (except for the sign [30]), since it does not depend on the section selected, which can be any surface crossed by the overall current lines:

$$I = \iint_{(S)} \mathbf{j}\,.\,\mathbf{n}\,\mathrm{d}S = \iint_{(S')} \mathbf{j'}.\,\mathbf{n'}\,\mathrm{d}S$$

We can also say that the current is conservative.

One of the important consequences of this property is illustrated in figure 1.3 which focuses on a conductor with a variable section area.

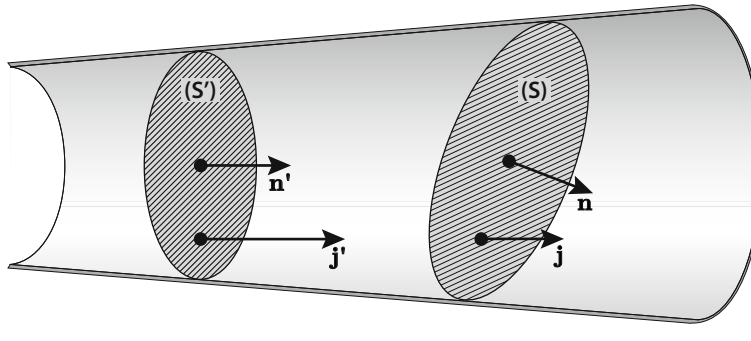



*Figure 1.3 - Diagram of a conductor volume with a variable section crossed by a current*

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*[27] These are listed in the next section (1.3.1.3); the reasoning behind this result is given in section 4.1.2.*

*[28] The order of magnitude of the transient time needed for establishing electroneutrality in a conducting medium is calculated in section 3.1.1.1.*

*[29] The reasoning behind this result is presented in section 4.1.2.*

*[30] The question of which sign to attribute to the current, an important issue in electrochemistry, is addressed in detail in section 1.4.1.3.*

The current is the same in both sections. Consequently, the current mean densities at these levels cannot be the same. The mean current density is higher for the small section than that for the larger section, resulting in the following equation:

$$I = \langle j \rangle S = \langle j' \rangle S'$$

## 1.3.2 - CONDUCTING MEDIA

Electrochemistry makes use of various electricity conducting materials. The microscopic mechanisms linked to the current flow may differ from one material to another. The various conducting materials can be classified according to the nature of the charge carriers involved.

### 1.3.2.1 - DIFFERENT CHARGE CARRIERS

A current exists as a consequence of the overall movement of charged species. It is only since the beginning of the 20th century that science has managed to gain a clear understanding of the microscopic nature of the various charge carriers.

When considering the full scope of materials in question, there are different types of charge carriers that can be distinguished:

- electrons,
- holes (fictitious particles arising from an electronic deficiency in the valence band of a solid lattice),
- ions (anions or cations, simple or complex),
- vacancies or charged defects in solid structures.

Knowing the nature and quantities of the charge carriers in a conducting medium is an essential prerequisite for understanding conduction phenomena. However, this is not always obvious.

For example, let us consider an aqueous solution of ferrous and ferric salts. In the presence of nitrate ions, the Fe-containing charge carriers are mainly cations (aqua-complexes of $Fe^{3+}$ and $Fe^{2+}$) whereas in the presence of cyanide ions, they will mainly be anions ($Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$).

Determining the nature of charge carriers is still the goal of research in various study areas such as aqueous solutions, organic solutions (where ion pairs are frequently observed), molten salts, polymer and solid state media.

### 1.3.2.2 - DIFFERENT CLASSES OF CONDUCTORS

Starting with the main classes of charge carriers previously defined, conductors can be classified according to the nature of the major charge carriers [31]:

*[31] The macroscopic quantities characteristic of conduction and the various conduction mechanisms at microscopic level are outlined in section 4.2.*

### *Electronic conductors (ionic insulators)*

This category includes:

- metals (and superconductors)
  for example copper, with about one free electron per copper atom,
- semiconductors
  for example silicon, with a valence of IV. This is an n-type semiconductor using electrons as its main charge carriers provided it is doped with a controlled content of valence V impurities such as phosphorus atoms. It becomes a p-type semiconductor, with holes as major charge carriers, when it is doped with valence III impurities such as aluminium atoms.

### *Ionic conductors (electronic insulators) or electrolytes*

A wide variety of different examples exist:

- electrolytic solutions, such as an aqueous solution containing KCl,
- molten salts, such as NaCl at high temperature,
- solid oxides, such as $(ZrO_2)_{1-x}(Y_2O_3)_{x/2}$, used in solid oxide fuel cells SOFC [32],
- polymer electrolytes, such as $LiClO_4$ dissolved in poly(ethylene oxide) (PEO).

Today the term electrolyte refers to an ionic conducting medium, whereas in the case of solutions, it equally refers to the compound, also called the solute, which is dissolved in the solvent and which is what gives the medium its conducting properties. In this latter definition, there is a distinction to be made between strong electrolytes, whereby the quantity of charge carriers is proportional to the amount of solute introduced, and weak electrolytes, which are to be found in the other remaining cases, whereby the solute is partially dissociated.

Let us take the example of an aqueous solution containing acetic acid. The variations observed in the electric conduction properties in relation to the amount of acid introduced show that the quantity of charge carriers (acetate anion and solvated protons) is not proportional to the amount of acid introduced. This is because acetic acid is a weak acid and undergoes partial dissociation. Consequently, it is also a weak electrolyte.

Another less famous example can be found in many salts, which once dissolved in organic solvents or polymers, prove to be weak electrolytes. This can occur very frequently in such complex media, where the presence of undissociated ion pairs should generally not be ignored.

In certain applications, separating two electrolytes is a necessary precaution taken in order to avoid a rapid mixing process while ensuring the current flow by allowing the ions through [33]. To achieve this, separators must have good mechanical properties. Moreover, some of them have conduction properties that are particular to a given ion or to several types of ions, thus offering more or less selectivity.

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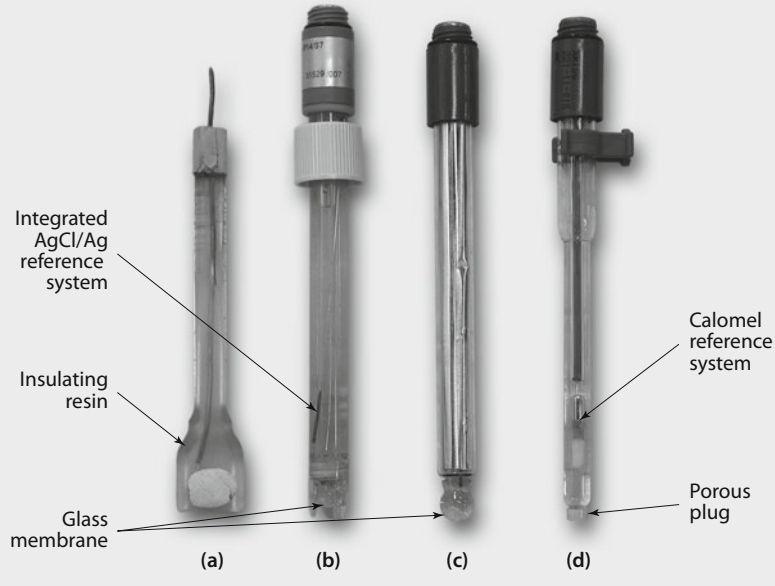
*[32] SOFC : Solid Oxide Fuel Cell, i.e., the generic term for the fuel cell devices using a solid oxide as electrolyte and working at high temperature.*

*[33] Section 4.4.2 describes certain aspects of mass transport in electrochemical systems where two compartments are separated by a membrane.*

## ON ELECTRODES




Strictly speaking, the term electrode should be restricted to defining the interface where the redox half-reaction occurs (see section 1.3.3). Generally, this term refers to the whole device: the electronic conducting material, its support and the electric connexion.

Device (**a**) pictured above is a metal electrode with its electric connexion embedded within an insulating resin, which moreover serves to delimit a well-defined surface area in contact with the electrolyte.

A reference electrode is usually a more complex device: it contains an electrochemical system which has a known and stable potential provided that the system is immersed in adequate solution. A porous material is what then ensures that contact is made with the cell's electrolyte. The calomel electrode (***d***) is an example of such a reference electrode (see section 1.5.1.2).

By extension, the term electrode usually refers to all half-cells ending in an electrical connexion, which includes specific electrodes that have an ionic membrane separating the electrochemical system from the solution. Such is the case with device (***c***) which uses a glass membrane specific to protons (membranes specific to other ions exist).

Also on the market can be found complete cells with an integrated reference electrode, generally coaxial, which is put in contact with the solution via a porous material placed on the lateral part. Such is the case with the combined pH electrode (***b***).

These include:

- porous materials (ceramics, fritted glass, felt or paper filters, etc.). Most of them are not selective: they let all the ions through but they prevent, or more precisely slow down the mixing process of the solutions. When the pore size is small enough, surface phenomena can bring about selectivity;
- permselective membranes, e.g., polymers such as Nafion®[34] or resins with ionic groups fixed on the material, often with acido-basic properties. The solutions can penetrate the structure through nanopores. The anionic (respectively cationic) groups fixed on these materials are electrically compensated by cations (respectively anions) that circulate inside the material. The selectivity of these membranes only concerns the charge of the ions able to circulate, but not the charge number or the nature of the ion. The anionic membranes let anions through and block cations at the membrane/solution interface, whereas the cationic membranes play the opposite role;
- monopolar ionic membranes, able to conduct with only one ionic species, such as Nasicon[35] or else $ZrO_2$ at high temperature. They are dense with an *a priori* zero porosity: ions move inside the material *via* conduction sites at the atomic level. In this case only one ionic species can be exchanged at the membrane/solution interface and move through the membrane. Their selectivity is therefore better than that of the materials mentioned previously. The selectivity between ionic species with the same charge is due to steric effects. These membranes are rather scarce today.

#### ⏩ *Mixed conductors (both ionic and electronic conduction)*

This category includes:

- certain oxides, such as the oxide film that builds up during the dry corrosion of metal in contact with dioxygen, or perovskites such as $LaSr_xCoO_3$ used in some fuel cells of the SOFC type,
- insertion materials such as derivatives of $K_xC$ graphite or tungsten oxide bronzes,
- plasmas (ionised gases),
- molten salts containing an alkali metal in solution,
- liquid ammonia containing dissolved sodium which reveals solvated electrons and ions resulting from the autoprotolysis of ammonia.

### 1.3.3 - ELECTRODES AND INTERFACES

Electrochemistry involves the contact between different materials which conduct electricity. The two terminals in the electrochemical system linked to the external control device must be electronic conducting materials if the electric parameter is to be controlled, for instance using a direct current (DC) power supply. This system must also include at least one ionic conducting material. To illustrate, an electronic n/p junction

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*[34] Nafion is a perfluorinated polymer with numerous $SO_3^-$ endings on the polymeric chains. It is a cationic conducting material.*

*[35] Nasicon (Natrium Super Ionic Conductor) is a ceramic material able to conduct via $Na^+$ ions at room temperature.*

cannot be classified under the field of electrochemistry. Electrochemistry always deals with heterogeneous systems with the two ends made of electronic conducting materials. Such a heterogeneous system is sometimes called an electrochemical chain [36].

The term ' electrode ' [37] is widely used in electrochemistry. However, it designates objects that can significantly vary depending on the situation. For the purposes of this document, in examples chosen to illustrate simple electrochemical systems, the term will most often refer to the metal which constitutes one of the terminals in the system in question. For instance, a platinum electrode or a copper rotating disc electrode [38]will be mentioned. When the system includes more than three materials, then the term electrode usually refers to the whole set of successive materials inserted between the metallic ending and the electrolyte material which makes up the core of the system. For instance, the term ' modified electrode ' will be used to refer to a metal whose surface has been covered with a film of conducting material or the term ' positive electrode ' in a battery will be used to refer to the composite material which is in contact with the electrolyte. In a third context, the term electrode will be used for an electrochemical half-cell [39]: this is the case with the ' $pH$ electrode ' or ' reference electrode '. In the final version of its meaning, the term electrode even stands for two half-cells combined to form the device, e.g., in the case of commercial systems for $pH$ measurements by means of a ' combined electrode '[40].

Electrochemistry often focuses on the study of the high heterogeneity zone, which is generally a very narrow area (with a typical thickness of a few nanometres) that lies between two materials with different conduction modes. This zone is called the electrochemical interface. More generally speaking, an interface is the physical separation between two phases in a heterogeneous system. Such a separation cannot be described as a simple mathematical surface of discontinuity and therefore it is more accurate to use the term interface zone or interphase. However, as is customary in most electrochemistry books, the term interface will be used in the following work. Inside this zone, parameters such as concentrations or potential undergo large spatial gradients. Therefore the profiles, i.e., the spatial variation curves, generally show a discontinuity at the interface level, on a macroscopic scale [41].

The simplest example of an electrochemical interface is the contact zone between a metal (electrode) and a solution containing species likely to react or take part in equilibrium at this interface. The latter are called electroactive species. By contrast, a non-electroactive species does not take part in the redox half-reactions, but can play a

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*[36] The term galvanic chain, linked to the early stages of electrochemistry (see section 1.1.2), is also widely used. However, considering that its precise definition depends on the authors, we prefer to avoid this term in this document. For instance some authors restrict the use of the term ' galvanic chain ' or ' galvanic cell ' to systems working as power supplies, excluding electrolysis cells.*

*[37] See the illustrated board enttitled ' On electrodes '.*

*[38] See figure 1.17 in section 1.6.4.*

*[39] A half-cell designates one part of an electrochemical system, as defined in section 1.4.1.1.*

*[40] A combined electrode for $pH$ measurement integrates the reference electrode in the body of the glass electrode (see the illustrated board entitled ' On electrodes ').*

*[41] The potential and concentration profiles at an interface in usual cases are described in section 4.3.1.*

role in carrying the current. The electrochemical interface can therefore be the highly specific zone where a redox half-reaction takes place involving electroactive species. This reaction is also called an electron transfer reaction [42], a charge transfer or indeed an electrode reaction, thus stressing the fact that it is a heterogeneous reaction localized in a very narrow zone.

***By definition, when an interface sees a single redox half-reaction occurring, the electrode where oxidation takes place is called the anode, and the electrode where reduction takes place is called the cathode*** [43]**.**

It is worth emphasizing that these terms are not defined in the case of open-circuit systems, and should not be used to designate electrodes, because the notions of anode or cathode are defined based only on the reactions occurring at the interface [44]. Interfaces in systems where the overall current value is zero behave in a heterogeneous way on a microscopic scale. This means that at any given moment certain zones behave as anodes while other zones behave as cathodes, resulting in an overall current equal to zero. This holds true for all systems in equilibrium: the notion of equilibrium is dynamic, and on a microscopic or even atomic scale it spans a range of oxidation and reduction events which cancel each other out completely. Another example of an open-circuit system, though this time not in equilibrium, is that of corrosion resulting from the galvanic coupling between two metals when put in contact with each other or resulting from the generalised or idiomorphic corrosion of a single metal. Here again, at a given instant, certain parts of the electrode behave as anodes while others behave as cathodes, the resulting overall current being equal to zero. But the overall chemical change is not zero [45].

These electrochemical interfaces still belong to an electrochemical chain comprising different conducting materials. Various types of interfaces can be seen and classified according to the nature of the conductors in contact:

- electronic junction for an interface between two electronic conductors,
- ionic junction for an interface between two ionic conductors,
- electrochemical interface for an interface between an electronic conducting medium and an ionic conducting medium,
- mixed junction in all the other cases.

Therefore, studying electrochemical systems requires one to understand the volume conduction of the conducting materials, as well as examine closely the interfaces

---

*[42] The term electron transfer may be ambiguous since it is also used for the shift of electrons from one medium to another in electrochemical systems where metals are in contact with mixed conductors. In such cases mobile electrons exist in both phases (e.g., solvated electrons in a molten salt) and the current flow corresponds partly to a simple electron transfer from one phase to the other, without any redox reaction occurring.*

*[43] As a suggestion, a mnemonic way of remembering these definitions is the following: oxidation and anode begin by a vowel whereas reduction and cathode begin by a consonant.*

*[44] Similarly, the use of the terms anode and cathode is not recommended for systems with blocking electrodes, where there is a transient current without any redox reaction occurring at the interfaces as represented qualitatively in section 2.2.1.2.*

*[45] Section 2.4.1 gives a simplified description of these phenomena using the current-potential curves.*

between two different conducting media. In the most general case which involves mixed conduction materials, the shift from an electronic conduction mode to an ionic conduction mode is not confined to a narrow zone. Such cases are frequently found in electrochemical applications, e.g., in the energy storage sector. In these instances the term ' volumic electrode ' is used, meaning that the charge transfer reaction can take place in relatively large volumes, which is quite the opposite to usual electrochemical interfaces. This document, which presents the fundamental notions of electrochemistry, will limit its scope to localised interfaces, i.e., to systems where the interfacial zone is very thin.

In certain cases direct electron transfer can occur between chemical species in a homogeneous phase, such as aqueous solution. This homogeneous redox chemistry does not, *sensu stricto*, come under the title of electrochemistry, even though correlations can be made between homogeneous and heterogeneous systems.

# 1.4 - DESCRIPTION AND OPERATION OF AN ELECTROCHEMICAL CHAIN

## 1.4.1 - GENERAL FEATURES

### 1.4.1.1 - ELECTROCHEMICAL CELL AND CHAIN

The terms electrochemical cell or electrochemical chain are used for designating an electrochemical system. The first term is generally used for a tangible, concrete object which can be handled in the lab for example. The second term underlines the heterogeneous nature of the system which is made up of different successive materials which are in contact. By convention each interface is represented by a vertical stroke.

The VOLTA battery is one of the simplest examples of an electrochemical chain, with each element made up of the following sequence of three conducting materials[46]:

Zn | NaCl aqueous solution | Cu

If the electrochemical chain includes several successive electrolyte media, then the abbreviated notation || is often used to denote the separation zone between two electrolytes. Such a notation represents either the porous material filled with a mixture of the two liquid electrolytes, or all of the various phases of a salt bridge (see example below). The nature of this intermediate zone is often such that the global zero current junction voltage can be neglected [47].

---

*[46] See the illustrated board entitled ' The origins of the VOLTA battery '.*

*[47] The junction voltage is very often mistakenly called junction potential in scientific literature. The elements needed for estimating the junction voltage between two solutions with different compositions are given in appendix A.1.1. A few numerical calculations show that the voltage is most often lower than 30 mV. When a salt bridge is implemented, the overall junction voltage can easily be made lower than 1 mV, which explains the approximation suggested here. However we must be careful and re-consider this approximation in cases where precise voltage values are required, which is notably the case in thermodynamic studies.*

To simplify matters, we will limit our scope to electrochemical cells having only two electrochemical interfaces and consequently with only two electrodes. Each system can be split into two half-cells where each of them has only one electrochemical interface.

Let us take the example of the DANIELL cell presented in figure 1.4. It includes two compartments containing respectively a $ZnSO_4$ aqueous solution in contact with zinc metal and a $CuSO_4$ aqueous solution in contact with copper metal. These two compartments are electrically connected by a third aqueous solution, e.g., a concentrated $KNO_3$ solution, which is called a salt bridge.

The cell is represented below:

$$Zn \mid ZnSO_4 \text{ aqueous solution} \mid KNO_3 \text{ aqueous solution} \mid CuSO_4 \text{ aqueous solution} \mid Cu$$

A very detailed description should also include the phases separating the various solutions. These separations are often composed of porous materials, e.g., porous plugs. It is difficult to give a precise definition of the composition of the solution inside the pores at the end of the salt bridge which is in contact with the $CuSO_4$ solution. It is a mixture of both the copper sulphate solution and the potassium nitrate solution. The same remark holds good for the solution filling the pores at the other end of the salt bridge. The brief representation is then:

$$Zn \mid ZnSO_4 \text{ aqueous solution} \mid\mid CuSO_4 \text{ aqueous solution} \mid Cu$$

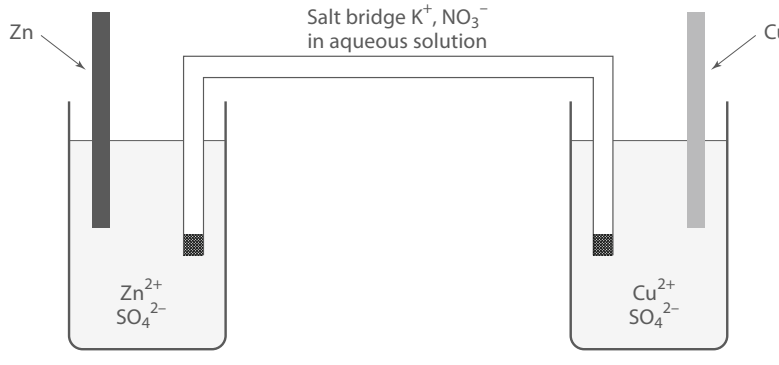



*Figure 1.4 - Diagram of a DANIELL cell*

### 1.4.1.2 - THE POLARITY OF THE ELECTRODES

The voltage of an electrochemical cell, denoted by $U$, is the potential difference between the two terminals of the cell; it is expressed in volts (V)[48]. The notation $U$ is not systematically used in scientific literature, but here it has been chosen in preference to the notation $E$ which is also frequently seen in the field of electrochemistry and also in electricity. In this document the symbol $E$ will be kept for the potentials or voltages of

---

*[48] A voltage measured by a voltmeter always represents the potential difference between two identical metals, in keeping with the measurement principle of a voltmeter. The electrochemical chain corresponding to a cell voltage should therefore be written with its electronic ending junctions included, although this thorough description of the electrochemical chain is often omitted. For instance, the voltage measurement of the DANIELL cell pictured above corresponds to the following electrochemical chain:*

*$Cu'/Zn/$ $ZnSO_4$ *aqueous solution* // $CuSO_4$ *aqueous solution* $/Cu$*

*This point will be looked at again in the introduction of section 3.4 and an example will be studied in detail in section 3.4.1.1.*

half-cells. The term emf (electromotive force) is also used in certain text-books for designating $U$. The term emf will be reserved here for the particular case of equilibrium [49], while the general term voltage will be kept for designating the parameter $U$.

When giving an algebraic value to the voltage of an electrochemical cell both of the two electrodes need to be distinguished. The privileged electrode is called the working electrode (most often noted WE or W). The other electrode is called the counter-electrode (CE) or auxiliary electrode. The algebraic voltage of the corresponding electrochemical cell is then the difference between the electric potentials of the two electrodes provided that the potential reference [50] is kept the same for both electrodes:

$$U = \varphi_{WE} - \varphi_{CE}$$

The polarity of the electrodes, which should not be confused with the polarisation [51], is defined according to the sign of the cell voltage. For example, if the voltage $U$ is positive, the polarity + is attributed to the working electrode, which is sometimes also called the positive electrode. The polarity – is attributed to the counter-electrode, which is sometimes called the negative electrode. Conversely, if $U$ is negative, then the polarity – is attributed to the working electrode.

Moreover, as soon as a current flows through the system, one of the electrodes becomes the anode and the other the cathode [52]. However there is no automatic link between the polarity of an electrode and its role as an anode or a cathode [53]. Unlike the notions of anode and cathode, the polarity of an electrode remains defined when the system is at open circuit. Finally, depending on the operating conditions of the electrochemical system in question, an electrode can be either the anode or cathode and also change its polarity [54].

#### 1.4.1.3 - SIGN CONVENTION FOR THE CURRENT THROUGH AN INTERFACE

In all operating conditions, the direction of the current flow within the whole system, i.e., the orientation of the current density vector at each point, is always unambiguously defined [53]. It is only necessary to establish a sign convention for current through the

---

*[49] The notion of thermodynamic equilibrium is addressed in chapter 3.*

*[50] The notion of reference for the potentials in electrochemistry is described in section 1.5.1. The notions of potentials are taken up again in a more detailed and rigorous way in chapter 3. In particular, the distinction between the VOLTA and GALVANI potentials is covered in section 3.1.1, and the precise description of the nature of the voltage of an electrochemical cell is given in section 3.4, in the particular case of thermodynamic equilibrium.*

*[51] The notion of polarisation, which has nothing to do with that used in physics (in electrostatics or in optics for instance), is defined in section 1.5.2.*

*[52] This sentence is not quite general but it holds for a very large majority of the systems considered in this document. It should however be handled cautiously, for example in the case of systems with so-called blocking electrodes which are crossed by a current despite the fact that no redox reaction occurs at the interfaces, as described qualitatively in section 2.2.1.2.*

*[53] The two possible cases (an electrochemical cell working as either a power source or as an electrolyser) are described in sections 1.4.2 and 1.4.3.*

*[54] The different operating conditions of an electrochemical system on the basis of current-potential curves are addressed in section 2.4.5.*

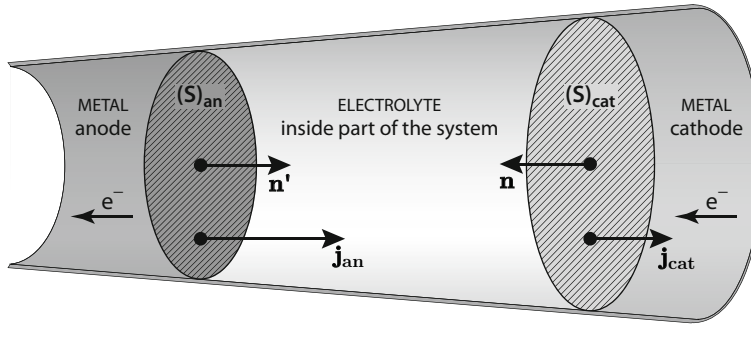
working electrode if one needs to rapidly identify if the latter is an anode or a cathode. Presenting the experimental data (the current and potential of the WE) is made easier by distinguishing between the anodic and cathodic working points. We will adopt the following convention for defining an algebraic value of the current through an interface [55]:

***The current is taken as positive if the electrode is on the overall an oxidation site***
***anode*** $I > 0$

***The current is taken as negative if the electrode is on the overall a reduction site***
***cathode*** $I < 0$

Taking into account the definition of the current through a surface, the convention adopted here comes down to orienting the normal vector to the interface from metal towards the electrolyte (see figures 1.5 and 1.7). This convention corresponds moreover to another sign convention commonly found in thermodynamics: what leaves the system (or rather what is supplied by the system) is counted negatively; what enters the system (or rather what is supplied to the system) is counted positively.

This is also consistent with the sign convention used by electricians for an electrical load [56].




$I > 0$ by convention
- surface through which current flows into the system
- normal and current density oriented in the same direction

$I < 0$ by convention
- surface through which current flows out of the system
- normal and current density oriented in opposite directions

***Figure 1.5 - Diagram of the sign convention for the current in an electrochemical system***

Due to the electroneutral nature of all conducting volumes, one can speak in terms of the current through the medium since the current is the same at whatever section [57].

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*[55] This sign convention has also been widely adopted today by European electrochemists. However, the opposite convention has been in use for a long time for historical reasons: electrochemistry underwent significant development in the 1950's with studies carried out on the mercury electrode in aqueous electrolyte where only reduction reactions could be investigated. Hence, the working electrode was frequently a cathode.*

*[56] See the illustrated board entitled ' Sign convention for current '.*

*[57] This notion, presented in section 1.3.1.3, is laid out in section 4.1.2.*

This same result can be extended throughout the electrochemical cell. It remains linked to the overall electroneutrality of the volume in question, even when it includes one or several interfaces. In particular, the current crossing the anodic interface has the same absolute value as that of the current crossing the cathodic interface. This property is of practical importance because the respective surfaces of the two electrodes are not necessarily equal. This implies that the mean current densities at each interface do not generally have the same absolute value. Throughout the rest of this document, unless otherwise specified, $j$ represents the projection of the vector $\mathbf{j}$ on the normal vector to the surface, respecting the sign convention shared by electrochemists.

***When taking into account the sign convention previously outlined, we always end up with***

$$|I| = \langle j_{an} \rangle S_{an} = -\langle j_{cat} \rangle S_{cat}$$

▸ To illustrate this property in the framework of an important case of analytical electrochemistry, let us consider the system in figure 1.6. The working electrode is a 4 mm in diameter copper disc (cross section of a metal wire embedded in an insulating material); the counter-electrode is a 1 mm in diameter platinum wire with a length $\ell$ immersed in the electrolyte.

Let us estimate the platinum wire length required for the mean current density at its surface to be 100 times smaller than the current density at the working electrode when both electrodes are connected to an external power supply.

The preserving property of the current at each electrode can be expressed with the following:

$$\left| \langle j_{\text{copper}} \rangle \right| \times \pi r^2 = \left| \langle j_{\text{platinum}} \rangle \right| \times (\pi r'^2 + 2\,\pi r'\,\ell)$$

A platinum length of about 20 cm is therefore needed.

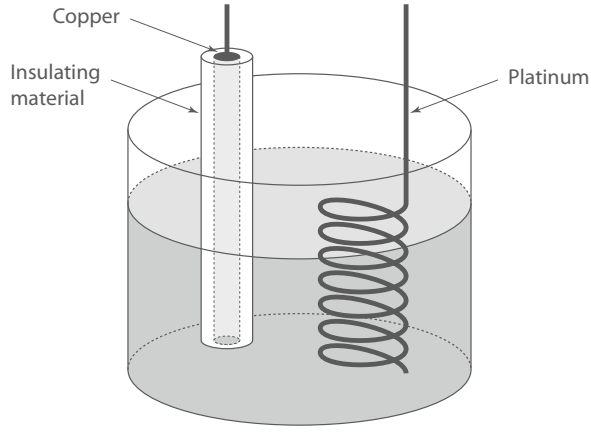


*Figure 1.6 - Diagram of an electrochemical cell with a copper disc as working electrode and a counter-electrode made of a platinum wire with an immersed length $\ell$*

▸ Let us take a second example from galvanic corrosion, an area where this property is particularly important. Imagine an ordinary steel sheet (essentially composed of iron) with an area of 6 $m^2$, fixed to a structure by means of 60 steel rivets (16 mm in diameter) with a galvanized surface, i.e., covered by a zinc layer. In moist air conditions, significant corrosion can be observed in the rivets. The reason behind this is that dioxygen reduction occurs at the surface of the iron sheet with a current density of 100 µA $cm^{-2}$ (usual value for atmospheric conditions with no forced convection).

Moreover, coupled oxidation of the zinc rivets can be seen with the equation:

$$\left| \langle j_{\text{sheet}} \rangle \right| \times 6 \times 10^4 = \left| \langle j_{\text{rivets}} \rangle \right| \times 60 \times \pi\,(0.8)^2$$

The corrosion rate of the rivets is therefore about 50 mA cm$^{-2}$ which, according to FARADAY's law (see section 2.2.2.2) corresponds to a dissolution of zinc with a rate of 85 µm h$^{-1}$ (with the molar mass of zinc equal to 65 g mol$^{-1}$ and its density equal to 7.1 g cm$^{-3}$).

When studying a single interface, one generally chooses to represent it with a vertical interface, placing the metal to the left and the electrolyte to the right (figure 1.7) [58].

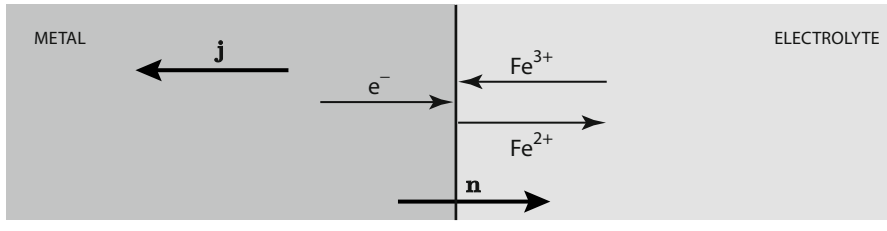


*Figure 1.7 - Diagram of an electrochemical interface with the commonly used sign convention for current: in this case the reduction of $Fe^{3+}$ ions to $Fe^{2+}$ ions, $I < 0$*

Due to the convention previously outlined, the normal vector to the surface on this diagram is always represented as a horizontal line oriented towards the right, for the anode as well as for the cathode.

## 1.4.2 - FORCED CURRENT FLOW: ELECTROLYSER MODE

In electrolysis, both terminals of the electrochemical cell are connected to an external source which supplies the energy needed to produce a non-spontaneous reaction in the electrochemical system. Therefore the latter behaves as an electric load, and the direction of the current is dictated by the external power supply. It is worth recalling that in a passive electric circuit the current flows in the direction towards the decreasing potentials: from the positive pole of the power supply towards the negative pole in the external circuit. In a simple electric representation, the circuit is as shown in figure 1.8 [59].

When dealing with batteries, the same situation corresponds to that of a recharging secondary battery [60]. The battery and the external power supply are connected in opposition, as illustrated in figure 1.9.

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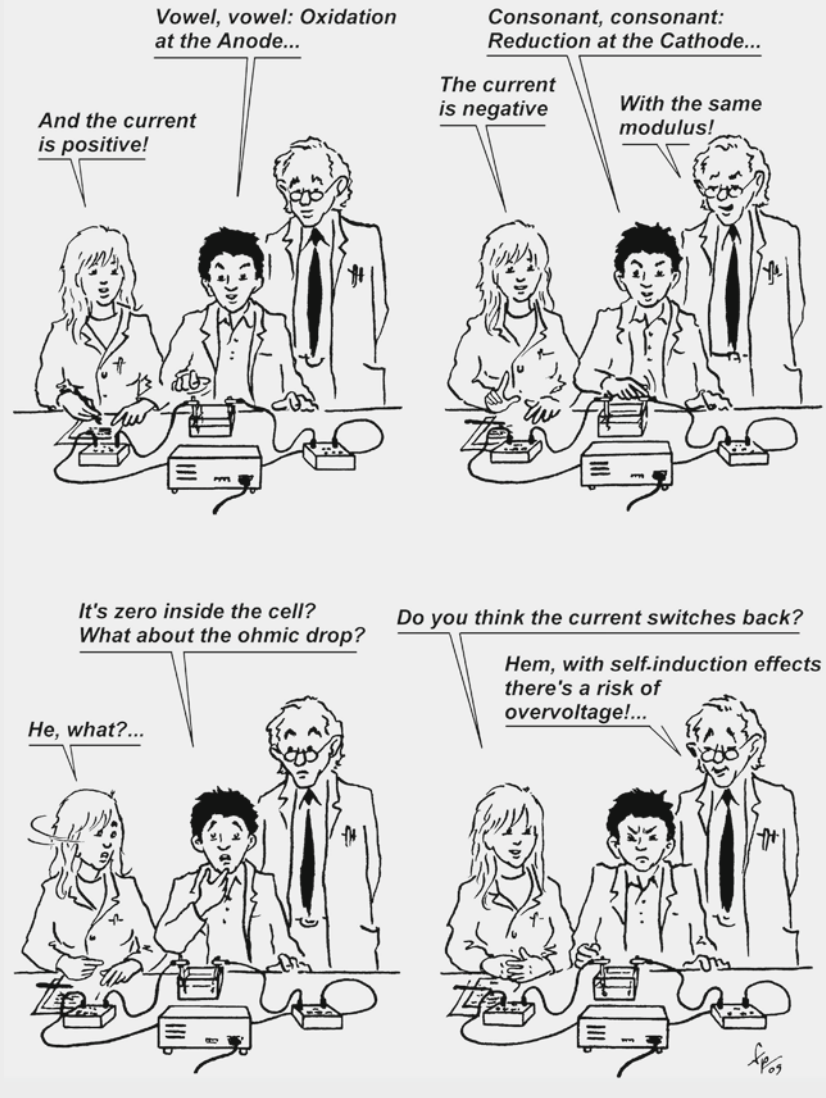
*[58] On this kind of representation which will be frequently used in describing interface phenomena, the arrows stand for the molar flux density vectors or for the velocities of the various species (here, $Fe^{2+}$, $Fe^{3+}$ ions and electrons). The length of the arrows is most often arbitrary, i.e., without any link with the actual moduli of the corresponding vectors.*

*[59] The symbol selected for the external power supply (figures 1.8, 1.9 and 1.10) is that of an ideal voltage generator, where the point of the arrow indicates the highest potential. The symbol used in figure 1.8 for the electrochemical system working as an electrolysis cell should not be mixed up with that of an electrostatic capacitor.*

*[60] One refers to a 'secondary battery', or rechargeable battery, when the system can function easily in two modes, namely that of electrolyser as well as power source (e.g., in the case of a mobile phone battery). One uses the term 'primary battery', non-rechargeable battery, or indeed disposable battery, when it is impossible or difficult to recharge, i.e., to have it working as an electrolyser.*

# SIGN CONVENTION FOR CURRENT




A magnetic needle placed either close to the anode or close to the cathode would deviate in the same manner thus indicating that the direction of the current is actually the same in both situations (as demonstrated in OERSTED experiments on magnetism). Besides, both ammeters should display identical current readings if they are connected as indicated on the drawing. To remain in keeping with the convention agreed amongst electrochemists dictating that the current entering the system is positive, and the current leaving the system is negative, the two ammeters need simply to be connected in opposition.

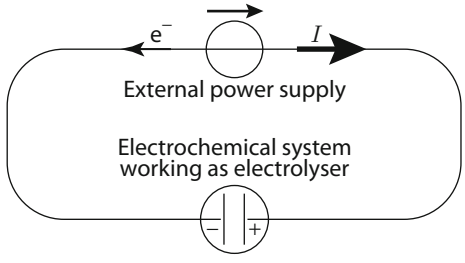



*Figure 1.8 - Circuit diagram of an electrolysis cell with its power supply*

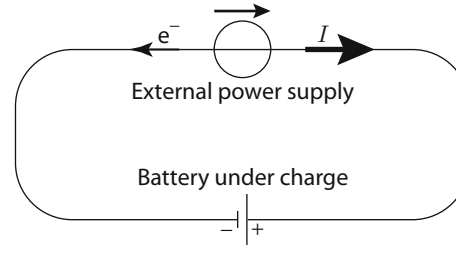



*Figure 1.9 - Circuit diagram of a battery being recharged and its external power supply*

In an electrochemical system where electrolysis is taking place (or in the case of a battery being recharged) electrons enter at the negative electrode. Because there are no free electrons in the electrolyte and because electrons cannot durably accumulate at the interface, only a reduction reaction can use the electrons arriving at the interface. The negative electrode is therefore the cathode of the electrochemical cell. This reasoning is perfectly symmetrical at the positive electrode, which is the anode. The preceding diagram can therefore be completed as illustrated in figure 1.10.

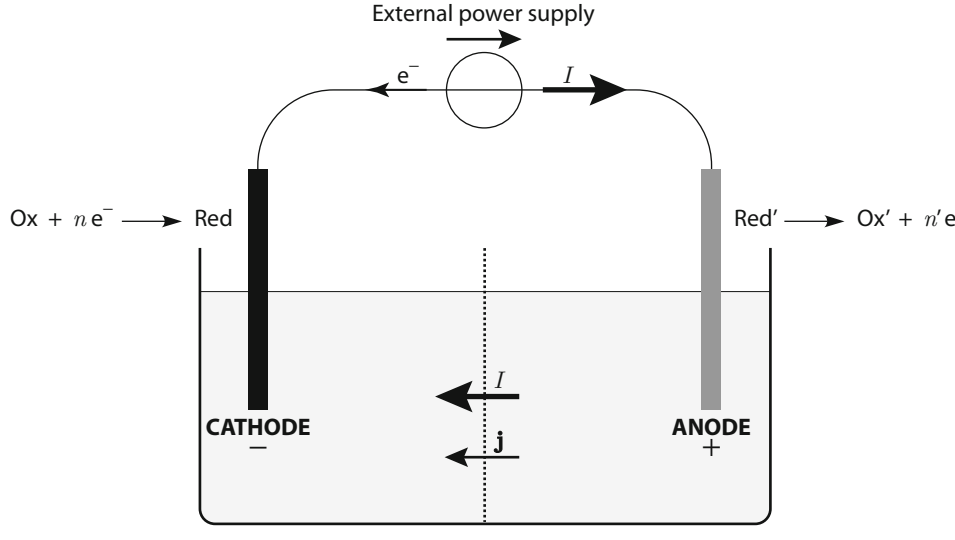



***Figure 1.10 - Diagram of an electrolyser and its external power supply***
*The dotted line represents the membrane possibly implemented to prevent the electrolytes from mixing.*

***To sum up, in the case of an electrolyser (or charging battery):***
***the positive electrode is the anode,***
***the negative electrode is the cathode***

### 1.4.3 - SPONTANEOUS CURRENT FLOW: POWER SOURCE MODE

For an electrochemical system working as a power source, (i.e., supplying energy to an external circuit) both of the two terminals of the electrochemical cell are connected, for instance by a resistance. The electrochemical system, which is where the spontaneous reaction occurs, is what imposes the direction of the current. In an external circuit, the current always flows from the positive pole of the power supply towards its negative pole. As far as batteries are concerned, it corresponds to the discharging mode. In a simple electric representation the circuit is as shown in figure 1.11.

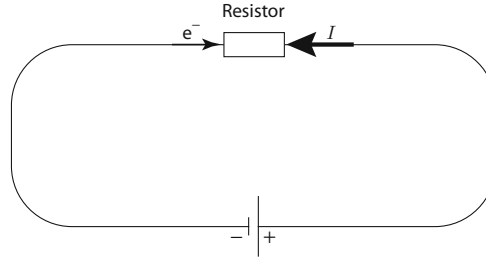



*Figure 1.11 - Circuit diagram of an electrochemical system working as a power source*

In this electrochemical system which is set in power source mode, electrons enter at the positive electrode. Because there are no free electrons in the electrolyte and because electrons cannot durably accumulate at the interface, only a reduction reaction can use the electrons arriving at the interface. The positive electrode is therefore the cathode of the electrochemical cell. The preceding diagram can be completed as illustrated in figure 1.12.

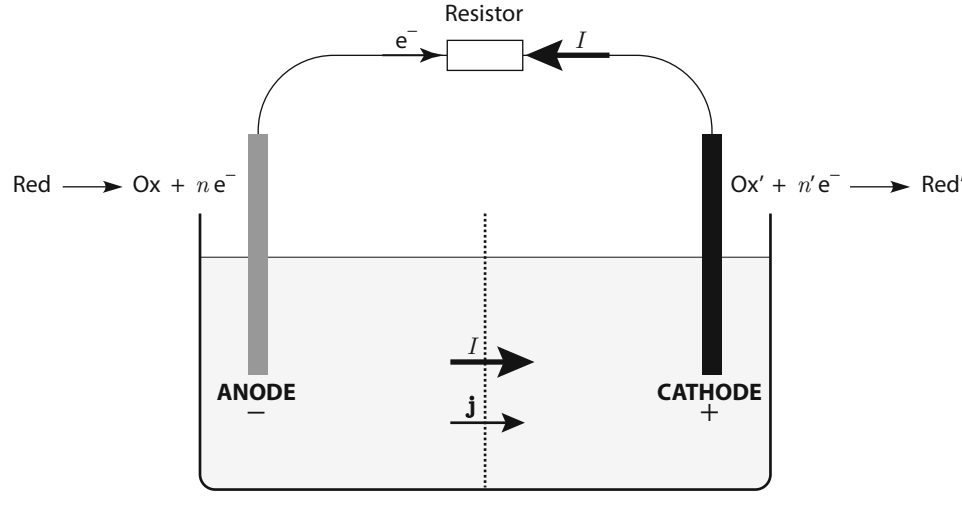



***Figure 1.12 - Diagram of an electrochemical system working as a power source***
*The dotted line represents the membrane possibly implemented to prevent the electrolytes from mixing.*

***To sum up, in the power source mode:***
***the positive electrode is the cathode,***
***the negative electrode is the anode***

### 1.4.4 - SPONTANEOUS OR FORCED CURRENT FLOW

Table 1.1 summarizes the two possible situations pertaining to an electrochemical system when crossed by a current.

***Table 1.1 – Comparing the characteristics of an electrochemical system with forced or spontaneous current flow***

| ***Operating mode*** <br> ***For a battery*** [61] | power source <br> discharge | electrolyser <br> charge |
|---|---|---|
| reactions | spontaneous | non-spontaneous |
| positive electrode | cathode (reduction) | anode (oxidation) |
| negative electrode | anode (oxidation) | cathode (reduction) |
| cathode (reduction) | positive electrode | negative electrode |
| anode (oxidation) | negative electrode | positive electrode |

## 1.5 - NOTIONS OF POTENTIAL - VOLTAGE - POLARISATION

### 1.5.1 - VOLTAGES AND POTENTIALS IN AN ELECTROCHEMICAL CELL

The word potential should be understood as an abbreviation of electric potential *vs* a reference [62]. As in physics (electrostatics or electrokinetics) the potential is always defined up to an additive constant: the absolute potential does not exist. The only quantities measurable by experiment are potential differences between two points, called voltages. The notion of potential must therefore be understood as the voltage between a given point and a reference. In physics, the most widely used references include vacuum at infinite distance (in electrostatics) and the earth (in electrokinetics). Generally, there is no ambiguity. In electrochemistry, these references are generally inappropriate and other references must be introduced. However, since several types of possible references exist, we recommend that when describing electrochemical systems, the reference that has been selected should be mentioned when indicating the unit:

a voltage, $U$, is given in V

a potential, $E$, is given in $V_{/Ref}$

*[61] It is increasingly common in current industrial and scientific literature on the subject of batteries to come across the misuse of the words anode and cathode for the negative and positive electrodes respectively. When referring to a primary battery it can be justified. However, for a secondary battery, the misuse of these words should be banned because it leads to significant confusion.*

*[62] The different notions of electric potential are laid out in section 3.1.1 (VOLTA and GALVANI potentials). Other notions making use of this term potential will also be defined in section 3.1.2 (chemical and electrochemical potentials).*

### 1.5.1.1 - STANDARD HYDROGEN ELECTRODE

In order to define a potential reference suitable for electrochemistry, a reference redox couple must firstly be chosen: the $H^+/H_2$ couple in its thermodynamic standard state. This reference system is called Standard Hydrogen Electrode (SHE). It is well-defined even though it is theoretical, and it is the reference used in all contemporary data tables in thermodynamics and electrochemistry [63].

In certain electrochemical applications (namely when semiconductors as opposed to metals are involved) it may be important to link the scale of the relative potentials *vs* SHE used in electrochemistry to the scale of the potentials commonly used in physics, where the zero reference potential is vacuum at infinite distance. Establishing that link quantitatively is no easy task because it is not simply the result of experiments: what is required is hypotheses and a model. The commonly accepted value for $H^+/H_2$ in aqueous solution is [64]:

$$\mathcal{E}_{/\text{vacuum}} = \mathcal{E}_{/\text{SHE}} - 4.5\ \text{V}$$

### 1.5.1.2 - REFERENCE ELECTRODES

Given that the SHE electrode is an ideal system, it cannot be created through any possible experiment. However, the availability of experimental reference systems are of the utmost importance when studying and characterizing electrochemical systems. Various electrochemical half-cells have therefore been developed as references for potential measurements in electrochemical systems. Some examples which are frequently used in electrochemical devices are briefly described below [65].

#### ▸▸ *Hydrogen electrode (HE)*

A hydrogen electrode, as represented in figure 1.13, is obtained by bubbling dihydrogen into a solution with a known $pH$, on a platinum (or platinised platinum [66]) electrode. The corresponding half-cell is:

Pt platinised, $H_2$ (1 bar) | $H^+$ with a concentration $C$ |

---

*[63] A few thermodynamic notions are given in section 3.1.2, including in particular the definition of the standard state for various systems.*

*[64] Comparing these quantities, here in relation to the $H^+/H_2$ couple, in different media (for example changing the solvent) involves difficult reasoning. This aspect will be briefly addressed in section 3.1.2.3.*

*[65] Section 3.4.2 goes into greater detail on certain aspects of these systems in connection with their thermodynamic characteristics. Also listed in this section are the main characteristics of redox systems that make them good candidates for being reference systems.*

*[66] Platinised platinum is obtained by forming this metal by means of electrolysis, which allows for a highly powdery deposit to be built up, and therefore creating an extremely rough surface. Photons penetrating the open porosity are trapped, resulting in a black colour. The contact area with the solution is significantly increased, which consequently decreases the current density flowing through it, as compared to a smooth platinum electrode with the same geometric area (see section 1.4.1.3). The stability of the potential of this half-cell is therefore improved because the influence of the kinetic characteristics of the redox half-reaction is decreased. The fact of obtaining a very rough metallic surface also leads to interesting properties in the context of conductivity measurements, as mentioned in section 4.2.2.2.*

It involves the $H^+/H_2$ couple:

$$H_2 \rightleftharpoons 2\,H^+ + 2\,e^-$$

If an acid is chosen with a concentration of 1 mol $L^{-1}$ then the result is a NHE (with N for ' normal ', i.e., molar for a monoacid). However, it does not quite constitute a SHE because the real compounds are not close to their standard state. For example, the proton activity of an acid with a concentration equal to 1 mol $L^{-1}$ is not equal to 1. The value of the NHE potential is about 6 $mV_{/SHE}$ at room temperature for hydrogen chloride. In practice, if one wishes to have a hydrogen electrode with a potential as close as possible to that of the SHE, then an acidic solution is implemented with a concentration slightly higher than 1 mol $L^{-1}$ [67]. Using this type of electrode is a difficult task and must be reserved to particular applications: indeed, many particular experimental precautions are necessary for ensuring an equilibrium state in such a system.

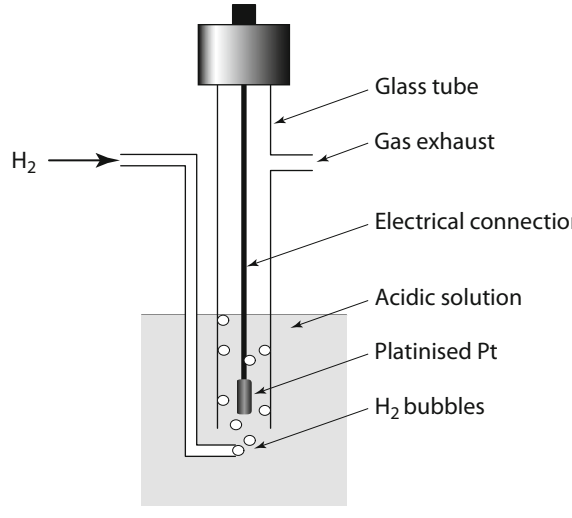



***Figure 1.13 - Diagram of a hydrogen electrode***

### ▸▸ *Silver chloride electrode*

A silver chloride electrode is made up of a silver wire coated with a solid silver chloride deposit (AgCl, scarcely soluble in water) immersed in a KCl solution. The electrochemical chain of this half-cell is therefore of the following type:

$$\text{Ag} \mid \text{AgCl} \mid \text{KCl aqueous solution with a concentration } C \mid$$

The overall equilibrium in this half-cell uses the following AgCl/Ag couple:

$$Ag + Cl^- \rightleftharpoons AgCl + e^-$$

The KCl concentration is generally set at a high value (from 1 to 3 mol $L^{-1}$), though it remains lower than the value for a KCl saturated solution [67]. This gives for example:

$$E_{AgCl/Ag}(\text{KCl, 3 mol } L^{-1}) = +0.21\ V_{/SHE}$$

*[67] The reasons behind this choice are given in section 3.4.2.2.*

### Calomel electrode ($Hg_2Cl_2$)

A calomel electrode is obtained by putting mercury with calomel (mercury(I) chloride, scarcely soluble in water) in contact with an aqueous solution containing potassium chloride. The electrochemical chain of this half-cell is therefore of the following type:

$$Hg \mid Hg_2Cl_2 \mid KCl \text{ aqueous solution with a concentration } C \mid$$

The relevant redox couple is $Hg_2Cl_2/Hg$:

$$2\,Hg + 2\,Cl^- \rightleftharpoons Hg_2Cl_2 + 2\,e^-$$

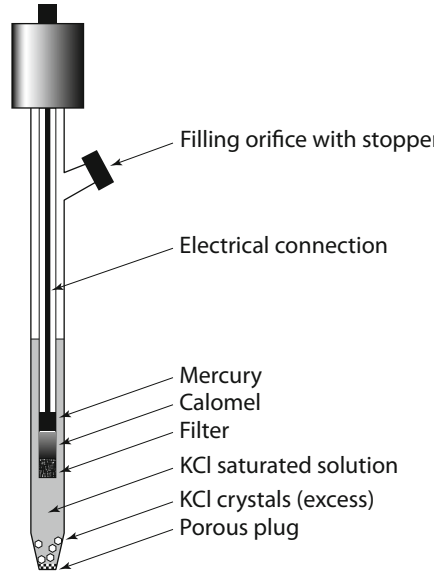



*Figure 1.14 - Drawing of a saturated calomel electrode, SCE*

A saturated KCl aqueous solution (which means about 5 mol $L^{-1}$ at room temperature) is most often used. In this instance one then refers to a saturated calomel electrode, SCE (figure 1.14). Nowadays, it is the most widespread commercial system used for potential measurements in electrochemistry. The value of its potential at 25°C is:

$$E_{SCE} = +0.24\ V_{/SHE}$$

Changing from one potential scale to another one is done *via* a translation. It is not a difficult operation. One must however be cautious about the direction of the translation. A simple procedure is to spot, on the first scale, the new reference (0 in the new scale), e.g., +0.24 V for a change from SHE to SCE, as illustrated in figure 1.15.

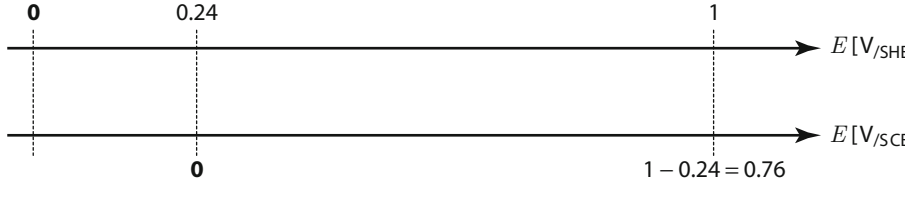



*Figure 1.15 - Illustration of the change in reference on a potential scale*

All the potentials must therefore be translated by –0.24 V to shift to the new scale: +1 V in the SHE scale corresponds to +0.76 V in the SCE scale.

This can also be expressed using the following equation to illustrate the preceding example of the shift from the SHE scale to the SCE scale:

$$\varphi - \varphi_{SCE} = \varphi - \varphi_{SHE} + \varphi_{SHE} - \varphi_{SCE} = \varphi - \varphi_{SHE} - (\varphi_{SCE} - \varphi_{SHE})$$
$$= 1 - 0.24 = 0.76 \text{ V}$$

For the experimental reference systems just described, it is important to stress the fact that the ' reference ' feature is due in particular to the presence of the inner solution which has a fixed, well-defined and well-known concentration of the relevant ion ($H^+$ for the HE, $Cl^-$ for the calomel electrode or the silver chloride electrode in the examples cited here) [68]. What is fixed and kept constant is the value of the voltage between the metallic terminal of the reference electrode and the associated internal solution, thus giving the ' reference ' quality to the system [69].

In certain experimental configurations, reference electrodes of this type, i.e., with an internal compartment, may be difficult to implement. In such cases a pseudo-reference might need to be used. For instance, it may be a metal wire (silver, platinum, etc.) or indeed the Ag,AgCl in direct contact with the electrolytic medium. In these examples the interface between the pseudo-reference and the electrolyte studied is generally not in thermodynamic equilibrium [70], in contrast to the case of the interface in usual reference systems which have a suitable internal solution. However, thanks to the use of a potentiostat [71], no current flows in the electrode, and therefore it is correct to assume that its open-circuit potential remains constant in the course of the experiment. This hypothesis has to be checked in each experimental situation. Moreover, the value of this open-circuit potential is most of the time not known in precise terms. Using a pseudo-reference therefore requires that the potential shift of this electrode be determined, e.g., by implementing a reference compound at the end of the experiment [72].

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*[68] The internal solution is in contact with the electrolyte of the system studied via a porous material. The latter is essential because it ensures contact is made with a solution having a fixed, well known concentration during the experiment. Nevertheless, it introduces an ionic junction between the internal solution and the electrolyte of the system being studied. This can be the cause of errors on the potentials measured, which are generally difficult to estimate. However, when certain experimental precautions are taken, these errors are considered insignificant most of the time (see section 3.4.2.2 and appendix A.1.1).*

*[69] As an example to shed light on this property, which may look strange at first sight, one can measure a non-zero voltage between two strictly identical reference electrodes placed in different positions in a cell. This is the case when there is a current flowing in the cell. The voltage between two points of the electrolyte, called the ohmic drop, can be measured by means of two identical reference electrodes (see figures 2.11 and 2.12, section 2.2.3). In cells with ionic and/or electronic junctions, it is possible to measure non-zero voltages between two identical reference electrodes placed at different points, even when no current is circulating.*

*[70] The potential measured at open circuit is not an equilibrium potential but a mixed potential as described in section 2.4.1.*

*[71] A potentiostat is the electric apparatus used to study electrochemical systems. Its basic principle is described in section 1.6.2 and in appendix A.1.2.*

*[72] This notion of pseudo-reference should also be used in the case of a commercial SCE immersed in an organic electrolyte, with an internal compartment filled with a saturated KCl aqueous solution. It is*

### 1.5.1.3 - THE POLARITY OF THE ELECTRODES

The polarity of the electrodes merely indicates the sign of the electrochemical cell voltage [73]. Thus, when applying a usual sign convention for voltages in electrochemical cells, which writes the voltage as the difference between the working (WE) and the counter-electrode (CE), it gives the following voltage:

$$U = \varphi_{WE} - \varphi_{CE} = E_{WE/Ref} - E_{CE/Ref}$$

The polarity of the electrodes has no relation to the sign of the voltage of the corresponding half-cells, which itself depends on the reference that has been selected. Depending on the nature of the reference electrode, the potential of the positive electrode can very well be negative. The potential of the negative electrode, in relation to the same reference electrode, will therefore also be negative, with a larger absolute value. Conversely, the potential of the negative electrode can be positive, however its value will be smaller than that of the positive electrode. Another practical consequence of these definitions is that it does not make any sense to attribute a relative precision (e.g., in percentage) to the value of an electrode potential, which depends on the selected reference.

Let us consider a copper electrode immersed in an aqueous solution containing $Cu^{2+}$ ions with a concentration of $10^{-3}$ mol $L^{-1}$. Its open-circuit potential is +0.25 $V_{/SHE}$ (close to the thermodynamic value). If this open-circuit potential is measured by means of an SCE, the value found is +0.01 $V_{/SCE}$, whereas choosing a mercurous sulphate electrode $Hg_2SO_4/Hg$ with a saturated $K_2SO_4$ solution would yield the value of −0.39 $V_{/MSE}$. A measurement error of about 1 mV on these voltages would thus yield a relative error of 10% in the first case, and of 0.3% in the second case. But this is meaningless.

## 1.5.2 - POLARISATIONS AND OVERPOTENTIALS IN AN ELECTROCHEMICAL CELL

When a current flows in an electrochemical cell, by definition the system is not in equilibrium. On the other hand, if no current flows (as in an open-circuit system), then the system could be either in thermodynamic equilibrium or not. This is because although the equilibrium state can always be defined, it is not necessarily always possible to observe. In fact the time scale of the experiment may be too short to reach the equilibrium state.

For a system which initially begins in thermodynamic equilibrium, the magnitude of the perturbation to its equilibrium state is an important parameter for describing the phenomena: it is the driving force behind the evolution. This is why the voltage between the terminals of an electrochemical cell with current flow is often compared to the open-circuit voltage [74].

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*impossible to know the precise value of the junction voltage between both electrolytes (aqueous and organic). Therefore the exact value of the potential of the reference electrode cannot be known, though it can nevertheless be used as a reference point provided it is constant.*

*[73] These notions have previously been defined in section 1.4.1.2.*

*[74] The voltage in thermodynamic equilibrium is also called emf. Its links with the thermodynamic reaction quantities are laid out in section 3.4.1.1.*

This parameter is called overpotential or overvoltage and is denoted by $\eta$:

$$\eta_{\text{overall}} = U - U(I = 0) = U - \text{emf}$$

Whatever the open-circuit state of the system, and in particular when not in equilibrium, the term polarisation [75], $\pi$, is used:

$$\pi_{\text{overall}} = U - U(I = 0)$$

This term overall overpotential or overall polarisation is often used in the industrial world because the process of cell design generally makes it impossible to differentiate the contribution of each electrode to the overpotential. This is not the case in laboratory cells where it is possible to discriminate the contribution of each electrode by implementing one or even two reference electrodes [76]:

$$\pi_{+} = E_{+/\text{Ref}} - E_{+/\text{Ref}}(I = 0) \qquad \pi_{-} = E_{-/\text{Ref}} - E_{-/\text{Ref}}(I = 0)$$

$$\pi_{\text{cat}} = E_{\text{cat/Ref}} - E_{\text{cat/Ref}}(I = 0) \qquad \pi_{\text{an}} = E_{\text{an/Ref}} - E_{\text{an/Ref}}(I = 0)$$

These values, which do not depend on the nature of the reference electrode, may depend on the spatial position of the reference electrode in the electrochemical system [77].

Such a splitting of the overall voltage in an electrochemical system leads to a better understanding of the phenomena being analysed. It is an important tool which will be developed in the following work using current-potential curves [78].

## 1.6 - EXPERIMENTATION IN ELECTROCHEMISTRY

### 1.6.1 - MEASUREMENT DEVICES

Three parameters play an important role in each electrochemical experiment: time, current and voltage. The latter parameter can be measured between different points. It is therefore necessary to have high performance voltmeters and ammeters.

Measuring a voltage can be based on various physical principles. To minimize any disturbance that may be caused to the phenomenon being studied by the measurement process itself, the current generated by that measurement must be kept extremely low. Therefore, when taking electrochemical measurements, notably at open circuit, voltmeters are used with field effect transistors with extremely high input impedance [79].

---

*[75] This term was introduced by BECQUEREL.*

*[76] It would make sense to use overvoltage for the whole cell and overpotential for a single electrode. However, the authors mostly use both terms as synonyms and not as a means of discriminating two different quantities. In the following work, we will keep the term 'overpotential'.*

*[77] Each bench scientist must keep in mind the question of the position of the reference electrode, whenever ohmic drop in the electrolyte cannot be neglected. A schematic illustration of such a situation is detailed in section 2.2.3 and figure 2.12.*

*[78] For a detailed presentation of these aspects, refer to sections 2.3 and 2.4.*

*[79] The order of magnitude of the input impedances of voltmeters used in electrochemistry is $10^{12}\Omega$.*

The characteristics of the ammeters required depend on the types of systems being studied. The current densities may vary from one system to another, however the surfaces are what constitute the parameter which varies to the largest degree. The current scale must therefore be very wide.

The following examples give various orders of magnitude.

- in an industrial cell, such as in aluminium plants, the electrolysis cells use currents about 100 000 A,
- in the starting battery of a car, the current requirements for the phase where the engine starts are about 100 A,
- in a mobile phone battery, when a call is taken the current is about 100 mA,
- in the button battery of a watch, the current is about 10 µA,
- in analytical electrochemical experiments with microelectrodes, the usual currents used are about 1 nA and can be lowered to 1 pA and even less [80].

## 1.6.2 - POWER SUPPLY AND CONTROL DEVICES

It is necessary to supply energy to the electrochemical system whenever it is working as an electric load (electrolyser mode). The most frequently used supply devices are electric current sources and voltage sources. A mere variable charge resistance can suffice to study an electrochemical system in the power supply mode.

When controlling the current in the system, we use the terms intensiostatic or galvanostatic setups. This applies even when the imposed current is time-dependent (see below), and the corresponding experiments are said to be potentiometry: in this case, the current is imposed and the voltages in the system are measured. When the voltage is imposed at the system's terminals then one refers to the term potentiostatic setup, even if the imposed voltage is time-dependent, and the corresponding experiments are called amperometry: in this case, the voltage between the system's terminals is imposed and the current passing through is measured.

Table 1.2 summarizes the terms for the main types of electrochemical experiments.

***Table 1.2 - Main categories of electrochemical experiments***

| | ***Potentiometry*** | ***Amperometry*** |
|---|---|---|
| The setup uses a source of … | controlled current (intensiostatic or galvanostatic setup) | controlled voltage (potentiostatic setup or a potentiostat) |
| The controlled parameter is… | the current $I(t)$ | the voltage $U(t)$ or the potential $E(t)$ |
| The response is in the measure of… | the voltage $U(t)$ or potential $E(t)$ | the current $I(t)$ |

*[80] See the illustrated board entitled ' Scanning electrochemical microscope '*

Opting in favour of one of these two command modes is not always straightforward.

In a number of amperometry experiments, an apparatus is used that is more sophisticated than a mere voltage generator in order to gain precise control of the voltage, $E$, between the working electrode and a reference electrode. The use of such a setup is more high-performance than the method of merely controlling the voltage $U$ between the system's two terminals: working and counter-electrodes. In fact, in the 2-electrode setup, only the overall voltage is monitored and the distribution of the voltage between the two interfaces cannot be controlled. The device essentially needed for any quantitative research study to be carried out in electrochemistry is therefore the 3-electrode setup with a potentiostat. The three electrodes used are then the working electrode (WE), the counter-electrode (CE) and a reference (Ref), through which no current flows. Figure 1.16 is a simplified diagram of an experimental electrochemical setup making use of a potentiostat[81]. The working point illustrated corresponds to a case in which the working electrode is the anode ($I > 0$ with the usual convention and the electrochemical cell works in the electrolyser mode.

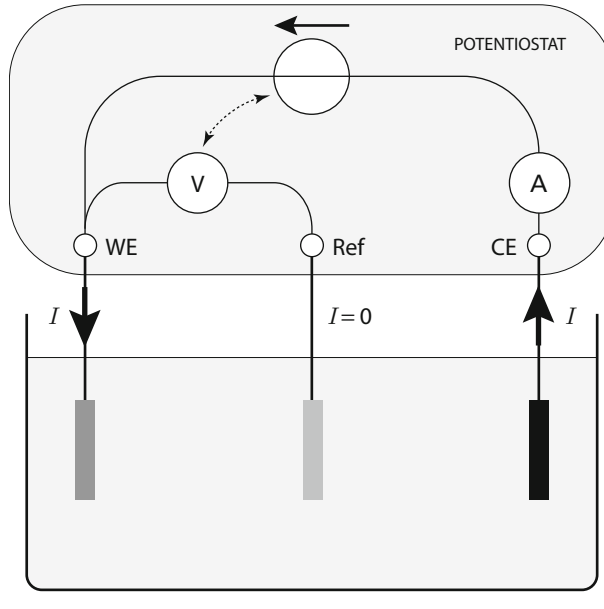



***Figure 1.16 - Simplified diagram of an electrochemical setup using a potentiostat***
*WE: working electrode; Ref: reference electrode; CE: counter-electrode*

*The dotted arrow symbolizes the existing link between the voltage indicated by the voltmeter (controlled voltage between WE and Ref) and the actual voltage delivered by the power supply between WE and CE.*

*[81] The implementation principles of these electrochemical setups are explained in appendix A.1.2. In particular, a simplified electronic circuit of a potentiostat is described (see figure A.1), underlining the use of an operational amplifier to ensure the control of $E$ and $U$ and to maintain a zero current in the portion of circuit containing the reference electrode (see also the illustrated board entitled 'Electrochemical devices').*

### 1.6.3 - DIFFERENT TYPES OF ELECTRIC CONTROL

There is a wide range of possible experiments that can be chosen for a given system depending on the type of command used and on their time dependence. The simplest example is the response given by a system where a constant voltage or current is imposed. Here one refers to the term potentiostatic or intensiostatic control. In general cases the response is time-dependent and the term transient state is then used. The response given by a system to a chronoamperomety experiment (potentiostatic control) is a curve $I(t)$; the response to a chronopotentiometry experiment (intensiostatic control) is a curve $U(t)$ or $E(t)$ [82]. It may also be of interest to note the evolution over time when the value of the command quantity applied is changed after a fixed time. In this type of experiment, depending on the kind of signal imposed, one refers to the terms single step, double step methods and other more sophisticated techniques with fixed duration pulses.

In another important category of electrochemical experiments, there is a command signal with a linear variation with time that is imposed. Included in this category is voltamperometry, frequently abbreviated to voltammetry, in which a linear potential sweep is imposed. The slope of the $U(t)$ or $E(t)$ curve is called the scan rate (in V $s^{-1}$). The response given by the system is usually represented by a curve $I = f(U)$ or $I = f(E)$, in which $U$ or $E$, and consequently $I$ vary with time. The direction of the potential sweep can be reversed when a given value of the potential is reached. In this case, the experiment is then called cyclic voltammetry.

Even though our main objective here is not to present all the usual techniques, it is nonetheless essential to mention the techniques where the command signal varies periodically with time. The most widely used example is electrochemical impedance spectroscopy (or abbreviated to impedance spectroscopy or impedancemetry) where the applied signal is sinusoidal with a low amplitude and a controlled frequency $f$. After a transient response, a steady-state response has to be reached whose amplitude must vary linearly with the input signal so that usual analysis can be carried out. This linearity can be obtained if the amplitude of the input signal is sufficiently low. Those performing the experiment must firstly check that the system fulfils both these criteria, regarding the steady character and the linearity before validating the data obtained, because the valid conditions can vary from one system to another. In these conditions, the response

---

*[82] Etymologically speaking, the term suggests that chronoamperometry (respectively chronopotentiometry) methods encompass all experiments in which one can expect information to emerge as an outcome of the variation with the time of the current (respectively potential) being measured. However, these terms were historically introduced for single or double-step pulses with a constant signal during each pulse. Moreover, they were restricted to experiments in which diffusion was the only transport mode for the electroactive species (such examples are presented in section 4.3.1.3). More generally speaking, the terms chronoamperometry or chronopotentiometry are used today for experiments with a constant input signal, at least for the duration of one pulse, where the mass transport modes are immaterial. For example, diffusion, migration or even forced convection, can be studied in the transient period preceding the steady state. On the other hand, experiments where the open-circuit potential is recorded, which are very useful in corrosion or titration studies, are not designated by the term chronopotentiometry, even though it would seem appropriate in etymological terms.*

is sinusoidal with the same frequency as that of the input signal. It can therefore be expressed in an impedance form which is a function of the frequency. The quantities measured can be represented on a BODE plot [83] (frequently used by electricians). However, in electrochemistry, they are more frequently presented in the form of a NYQUIST plot: the opposite of the imaginary part of the complex impedance, –Im ($Z$), is plotted as a function of the real part Re ($Z$) for various values of the frequency.

### 1.6.4 - STEADY STATE

After letting the experiment last for a reasonable duration, it is sometimes possible to reach a current/voltage point that does not change with time. In this case one refers to a steady or stationary state. The steady ($U$,$I$) or ($E$,$I$) curves that are plotted in these conditions are useful tools for analysing the behaviour of electrochemical systems [84].

This notion must not be confused with the notion of equilibrium: in other words, the terms 'steady' and 'constant' are not interchangeable. For a steady state to be established, it is merely necessary that the relevant parameters, at any point in space, do not vary with time. Strictly speaking, an electrochemical system in a steady state can therefore present spatial gradients, but the latter must not vary with time. For instance, as far as the concentrations are concerned, the steady state is expressed by the following:

$$\forall i \qquad \frac{\partial C_i}{\partial t} = 0 \qquad \text{but possibly} \qquad \frac{\partial C_i}{\partial x} \neq 0$$

Equilibrium states are particular cases of steady states in which the overall current is zero.

From an experimental point of view, what is frequently observed are ($U$,$I$) or ($E$,$I$) curves which are steady throughout the duration of the experiment. But the steady character of the various parameters, such as the concentrations in the electrolyte, is not necessarily strictly verified. Therefore one should use the more accurate term of quasi-steady state. It is very exceptional in electrochemistry to find strict steady states differing from equilibrium states. This is because no time evolution of the mean composition of each phase must then occur [85]. The systems showing steady ($U$,$I$) or ($E$,$I$) characteristics throughout the duration of the experiment are thus therefore most of the time in a quasi-steady state.

The first precondition for securing a quasi-steady state is to ensure that the system's overall chemical composition be kept practically unchanged from start to end of the experiment.

---

*[83] A BODE plot is commonly used in electronics and represents the modulus or the phase of the complex quantity as a function of the frequency on a logarithmic scale.*

*[84] Sections 2.3 and 2.4 deal with the shape of the current-potential curves and show how they can be used to understand and describe electrochemical systems.*

*[85] Examples of this type are described in appendix A.4.1 for a system where the anodic and cathodic reactions are exactly opposite. The electrolyte may then reach a steady state in the strictest sense.*

# ELECTROCHEMICAL DEVICES

*Document written with the kind collaboration of B. PETRESCU, R&D engineer for the company Bio-Logic, based in Claix in France*

All electrochemical studies require an apparatus that is capable of controlling and measuring voltages and currents between the terminals of an electrochemical cell. These instruments are often called potentiostats or galvanostats. Today manufacturers tend to provide a comprehensive response to users' needs by offering better integration and modularity on both hardware and software levels. Depending on the specific application, intelligent modules can be added to the basic potentiostat, often using the same chassis. Specific high current amplification modules (up to 100 A) meet the needs of storage or energy supply (batteries, fuel cells, photovoltaic devices), while low current devices (resolution below 1 pA) meet the needs of research on materials, biochips, sensors, etc. In addition, the number of measurement channels can be modulated and the range extends from single channel to multichannel.


***Modular multichannel potentiostat VMP3 manufactured by Bio-Logic*** *(© Biologic SAS)*

The huge technological advances that have been made in electronics and the increasingly common use of digital technology seen in recent years have collectively had a significant impact on miniaturizing and simplifying the setup around electrochemical cells. It has also opened up the door to new functions: potentiostat, galvanostat and impedance analyser configurations, intelligent recording and the possibility of having unlimited numbers of experimental recorded data, chaining techniques, analysing the peak or parametric identification in impedance, data protection, USB and Ethernet connections are just some of the possibilities that a modern potentiostat can offer. Remember that only until recently, a cyclic voltammetry experiment required the use of an analogic potentiostat coupled with a signal generator and a plotter. In order to carry out an electrochemical impedance measurement, the user often had to handle several instruments and different types of software at the same time. Today, only one instrument and only one software package are required for monitoring the experiment, recording the data and analysing the results. All this aims towards saving time for those carrying out the experiment, while improving the performance and reliability of the measurements.

This may occur in two rather different cases:

- a typical situation in analytical chemistry: the electrolyte's volume is sufficient to allow an extremely large amount of substance to be contained, compared to that produced or consumed during the experiment. Thus, the measurement causes no perturbation within the system being analysed;
- a macro-electrolysis situation in a system with a circulating electrolyte, which ensures the electrolytic cell is continuously fed with an electrolyte with a constant composition while the reaction products are being simultaneously evacuated.

This condition in terms of the system's chemical composition does not suffice to obtain quasi-steady states that are distinct from equilibrium states and that can be observed moreover under experiment for a reasonable time length. The rotating disc electrode (RDE), illustrated in figure 1.17, is an example of a device that can be used easily to obtain a quasi-steady state in the lab. The cylindrical shaft of this electrode is attached to an electric motor ensuring the rotation of the electrode around its axis. The only metallic part in contact with the electrolyte is the disc section.

In the following document, it is mostly these kinds of experimental conditions that will be selected to illustrate the various aspects of electrochemistry using the inappropriate though common expression of steady state.

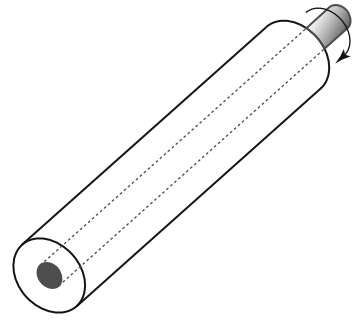
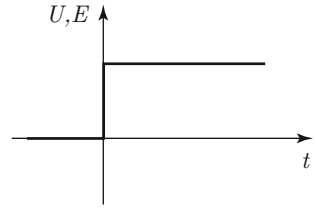
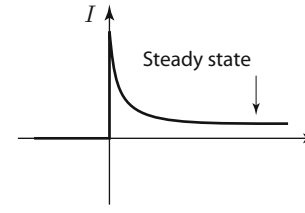
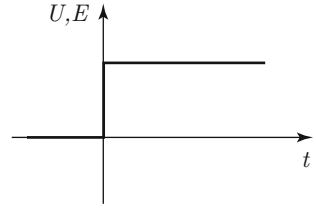
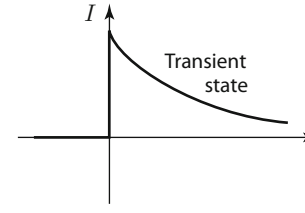
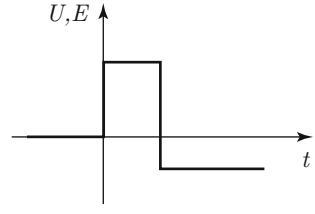
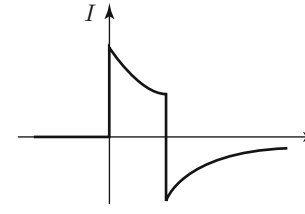
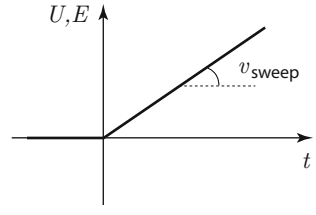
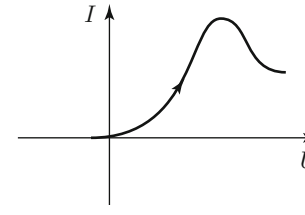
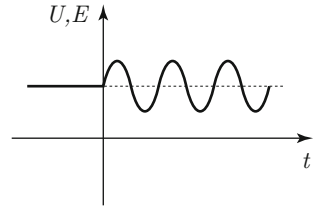
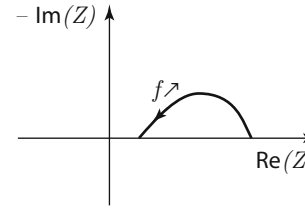


*Figure 1.17 - Schematic drawing of a rotating disc electrode, RDE*

## 1.6.5 - MAIN ELECTROCHEMICAL METHODS

Usual amperometry experiments can be briefly classified under four main categories which are shown in table 1.3. A similar table could be drawn up for usual potentiometry techniques, apart from voltammetry because its equivalent in potentiometry is not used.

*Table 1.3 - Main types of amperometry experiments found in electrochemistry*

| | Imposed voltage | Response |
|---|---|---|
| Steady state (for some experimental conditions) |  |  |
| Chronoamperometry<br>single step |  |  |
| double step |  |  |
| Voltamperometry |  |  |
| Impedancemetry |  |  |

# QUESTIONS ON CHAPTER 1

1 - An anion is always negatively charged true false

2 - An oxidant is always a cation true false

3 - In the following half-reaction:

$$Co + 4\,Cl^- \longrightarrow CoCl_4^{2-} + 2\,e^-$$

indicate:

- the redox couple involved .....
- the oxidized species of the couple .....
- the (algebraic) charge number of the oxidant .....
- the (algebraic) stoichiometric number of the reducing agent .....
- the element undergoing oxidation .....
- the oxidation number of the oxidized element .....
- the direction of the reaction oxidation reduction

4 - An anion can be reduced at the cathode true false

5 - What is the usual oxidation number of oxygen in a compound? .....

Among the following compounds, circle where oxygen features:

- at its usual oxidation number

  $H_2O$ FeO $H_2O_2$ $OH^-$ $ClO_4^-$ $F_2O$ $CO_2$ CO

- at a higher oxidation number

  $H_2O$ FeO $H_2O_2$ $OH^-$ $ClO_4^-$ $F_2O$ $CO_2$ CO

6 - What is the oxidation number of oxygen in $O_3$?

–III –I 0 +I +III

7 - Write the redox half-reaction of the $SiO_2$/Si couple in an acidic medium

.....

8 - An electrolyte is:

- an ionically conducting medium true false
- a vessel used for performing electrolysis true false
- a compound that dissolves in a solvent giving rise to ions true false
- a man performing electrolysis true false
- an electrocuted person true false

9 - Molten salts are media with mainly electronic conduction true false

10 - Semiconductors are media with an electronic conduction type true false

11 - An electrolyte can exist in a ..... state:
- solid true false
- liquid true false
- gas true false

12 - The usual order of magnitude for the width of a metal | aqueous electrolytic solution interfacial zone is a few micrometres true false

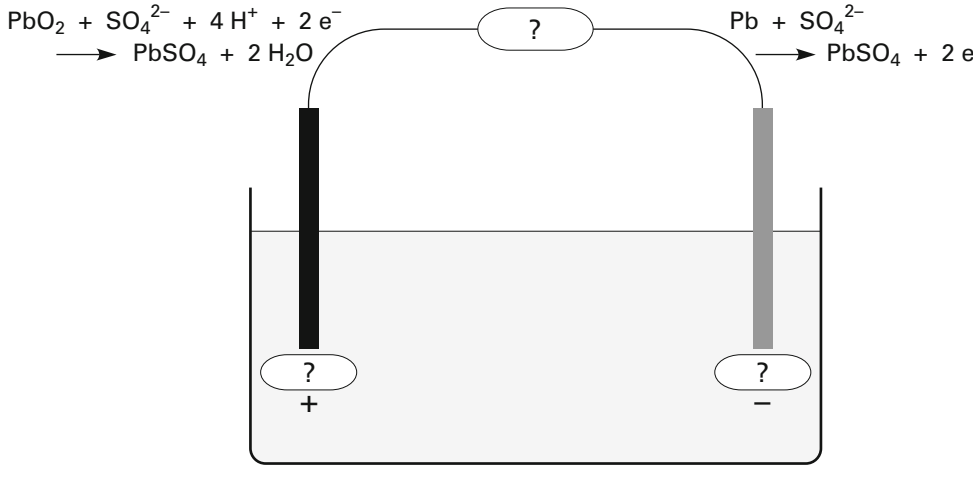
13 - In electrochemistry, the cathode:
- is always the negative electrode of the system true false
- always has a negative potential *vs* SHE true false
- is always a reduction site true false

14 - An electrolysis process is carried out between an electrode with a surface of 1 $m^2$ where the current density is equal to 1 mA $cm^{-2}$ and an electrode whose active surface is a 10 cm × 10 cm square. The absolute value of the current density at this second electrode is

$10^{-3}$ A $m^{-2}$ 1 A $m^{-2}$ $10^{3}$ A $m^{-2}$

15 - Considering the electrode reactions given below, complete the following diagram, by specifying:
- the positions of the anode and the cathode
- the direction of the current (or of the current density)
- the type of the external circuit component

(indicate your answers by replacing the question marks on the diagram)



16 - In a 3-electrode setup, these electrodes are called:

- .....
- .....
- .....

What is the name of the electronic device generally used in the lab in this case? .....

17 - In electrochemistry, an electrode playing a specific role is the SHE.

- What is this specific role? .....
- What do the initials stand for? .....
- What is the redox couple involved? .....
- A potential difference exists between SHE and NHE true false

18 - Cite two types of reference electrodes of experimental use, and specify the redox couple involved.

- .....
- .....

19 - A silver wire coated with silver chloride is dipped into an aqueous solution containing copper nitrate. This electrode can be used as reference electrode for measuring potentials that can be spotted in the potential scale true false

20 - When a system, not equilibrium at open circuit, is crossed by a current, then one must exclusively use the term polarisation overpotential

21 - Complete the diagram by showing the appropriate shape of the curves that would indicate the variations of the voltage and the current as a function of time, in a simple chronoamperometry experiment.