2 - SIMPLIFIED DESCRIPTION OF ELECTROCHEMICAL SYSTEMS

When studying an electrochemical system, the first vital step is to understand the rules that define its current/voltage working point at each instant. This chapter focuses on simple systems to illustrate the thermodynamic and kinetic aspects of the phenomena occurring in those heterogeneous systems. For these purposes, an explanation, though without demonstration, will be given of the two main quantitative laws of basic electrochemistry: NERNST and FARADAY's laws. Then, on a qualitative level, we will explain how to understand the working points of an electrochemical system thanks to the current-potential curves[1].

2.1 - CHARACTERISTICS OF SYSTEMS IN THERMODYNAMIC EQUILIBRIUM

In thermodynamics it is important to establish the precise definition of a system, i.e., its boundaries and exchanges with its surroundings. In the description adopted here, the electrochemical system is confined to the metallic materials that make up the two electrodes. If heat exchanges are not taken into account, then this open-circuit system is isolated, with neither energy nor mass exchanged with the surroundings. The aim of this section is to define the thermodynamic equilibrium state of this isolated system. However, excluded from the current issue will be the description of a system that supplies energy to a device, as with a discharging battery. In the latter case, given that electrons and electric energy exchanges occur with the surroundings, then these exchanges trigger a transformation, that is to say a progression towards a new equilibrium state. Here an analogy can be drawn with a gas system: the isolated system in equilibrium is equivalent to the gas when contained in a cylinder under pressure, with fixed temperature and pressure. If a hole is drilled allowing the gas to expand in an initially empty volume, then the transformation towards a new equilibrium state can be seen.

The thermodynamic equilibrium of an electrochemical chain, which itself is rigorously defined by the equilibria within all the phases and at all the interfaces, cannot necessarily be observed on a usual time scale.

2.1.1 - DISTRIBUTION OF THE ELECTRIC POTENTIALS AT EQUILIBRIUM

In equilibrium, no current flows through the electrochemical chain and each conducting volume is equipotential. The voltage between the terminals is the algebraic sum of the

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[1] *Other authors also use the term polarisation curve, as will be seen in section 2.3.*

C. Lefrou et al., *Electrochemistry: The Basics, With Examples*, DOI 10.1007/978-3-642-30250-3_2,

junction voltages and/or of the voltages of the electrochemical interfaces. This is illustrated in figure 2.1 which presents a simplified example of a plausible potential profile inside a Daniell cell in open-circuit conditions[2].

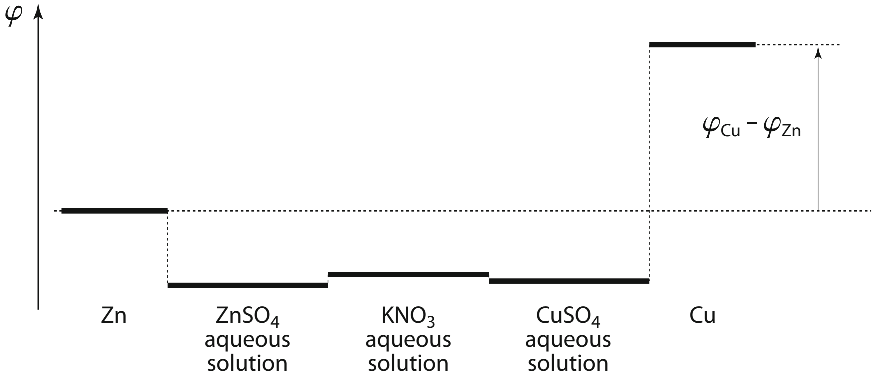

Figure 2.1 - Potential profile inside an open-circuit Daniell cell

Each of the five conducting volumes inside the electrochemical chain is equipotential. However, there is a potential difference at each interface (in this simplified representation the thickness is assumed to be insignificant), including for ionic junctions.

In numerous electrochemical systems, especially where compartments need to be separated (see example above), ionic junctions appear in the electrochemical chain between solutions with different compositions. Strictly speaking, the thermodynamic equilibrium of such a system amounts to the perfect mixing of all the solutions[3]. Therefore all junction voltages are strictly equal to zero in thermodynamic equilibrium. However, the experimental setup is designed in such a way that actually establishing the equilibrium state is considerably slowed down by the fact of implementing a porous frit, a membrane or a gel[4]. Therefore from an experimental point of view, we are interested in the quasi-steady state, which can be reached rapidly by such a system and thus observed on a usual time scale. However this state differs from the equilibrium state. Moreover, we will admit that, when a salt bridge is used, as illustrated in the example above, the fact of opting for an intermediate electrolyte with a much higher concentration than that of the ion concentrations in each of the two other compartments, leads to the ionic junction voltages being minimised in the quasi-steady state.

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[2] *The actual potential profile is not measurable in an experiment. To draw this diagram, we therefore had to make arbitrary choices for the signs of the various junction or interface voltages. On the other hand, the overall voltage is easily measurable. Its sign, which is positive if copper is chosen as the working electrode, is therefore correctly indicated in figure 2.1. As for the voltages at the electrochemical interfaces, their signs can be determined only if one knows the relative positions of the open-circuit potential of the electrode and that of its zero charge potential. However this discussion stretches well beyond the scope of this document.*

[3] *Detailed study of the thermodynamic equilibrium of the interfaces is given in section 3.3. The result stated here will be demonstrated in section 3.3.5.*

[4] *Section 4.4.2 will describe some aspects of mass transport phenomena in electrochemical systems with two compartments separated by a membrane, a gel or a porous frit.*

Let us recall the convention stating that the voltage of the electrochemical chain is defined as the difference between the potentials of the working electrode and the counter-electrode:

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

When the system is in thermodynamic equilibrium, this voltage is called the emf of the electrochemical cell[5]. It is an algebraic quantity expressed in volts (V).

2.1.2 - POTENTIOMETRY AT EQUILIBRIUM

2.1.2.1 - NERNST'S LAW

If you begin by expressing the equilibrium potential difference across an interface where both elements of a redox couple are present, then you can derive the NERNST law[6] which expresses the potential of the corresponding electrode *vs* a reference electrode.

This book will use the following expression of the NERNST law:

$$E_{/\mathrm{Ref}} = E^{\circ}{}_{/\mathrm{Ref}} + \frac{\mathrm{R}T}{\nu_{\mathrm{e}}\,\mathscr{F}} \ln \prod_i a_i^{\nu_i}$$

where i represents each of the species involved in the redox half-reaction apart from the electron,

with :

$E_{/\mathrm{Ref}}$	the potential of the electrode *vs* the selected reference electrode, when the relevant redox couple is present	$[\mathrm{V}_{/\mathrm{Ref}}]$
$E^{\circ}{}_{/\mathrm{Ref}}$	the standard potential of the relevant redox couple, *vs* the selected reference,	$[\mathrm{V}_{/\mathrm{Ref}}]$
R	the ideal gas constant	$[\mathrm{J\,K^{-1}\,mol^{-1}}]$
T	the temperature	$[\mathrm{K}]$
ν_{e}	the algebraic stoichiometric number of the electron	
a_i	the activity of species i	
ν_i	the algebraic stoichiometric number of species i	
$\mathscr{F}$	FARADAY's constant[7] $1\,\mathscr{F} = 96\,485\ \mathrm{C\,mol^{-1}} \approx 96\,500\ \mathrm{C\,mol^{-1}}$	$[\mathrm{C\,mol^{-1}}]$

In most documents, the expression of the NERNST law that is commonly chosen uses the number n of electrons exchanged. This expression then implicitly corresponds to a half-reaction written in the direction of oxidation (the activity of the oxidant is in the numerator). We prefer a more general expression involving the algebraic stoichiometric

---

[5] *Section 3.4.1.1 will describe the thermodynamic equilibrium of the electrochemical systems and interfaces and explain the link to be made between the emf and the standard GIBBS energy of reaction. Strictly speaking, U is the potential difference between the metallic connections made of the same metal inside the voltmeter on the WE side and on the CE side.*

[6] *The description of the thermodynamic equilibrium of electrochemical interfaces leading to the demonstration of the NERNST law is given in sections 3.3.4.2 and 3.4.1.2.*

[7] *$\mathscr{F}$ represents the absolute value of the molar electron charge: $1\,\mathscr{F} = \mathscr{N}\,|e|$ with $\mathscr{N}$ the AVOGADRO constant, $\mathscr{N} = 6.02\times10^{23}\ \mathrm{mol^{-1}}$ and e the elementary charge of the electron, $e = -1.6\times10^{-19}$ C.*

number of the electrons in the half-reaction. In fact, with this form of expression the NERNST law can be presented without having to consider the direction in which the half-reaction is written, as illustrated in the examples commented below:

- in the direction of oxidation : $\nu_{\text{Ox}} > 0 \qquad \nu_{\text{e}} = n > 0 \qquad \nu_{\text{Red}} < 0$,
- in the direction of reduction : $\nu_{\text{Ox}} < 0 \qquad \nu_{\text{e}} = -n < 0 \qquad \nu_{\text{Red}} > 0$.

At 25 °C, using decimal logarithms in place of natural logarithms, one can also write the following with $(\mathrm{R}T/\mathcal{F})\ln 10 \approx 0.06$ V:

$$E_{/\text{Ref}} = E^{\circ}{}_{/\text{Ref}} + \frac{0.06}{\nu_{\text{e}}} \log \prod_i a_i^{\nu_i}$$

Here it is worth noting a few elementary notions of thermochemistry. The thermodynamic quantities depend on the specific state of the system. The thermodynamic state of a given system, i.e., usually a mixture of several components, is defined by the activity of each component. Let us recall the definition of the activity, which is a dimensionless number, in the case of ideal systems[8]:

- for an ideal mixture of ideal gases $a_i = P_i / P^{\circ}$
  (ratio of the partial pressure to the standard pressure P° equal to 1 bar)
- for a pure liquid $a = 1$
- for the solvent of a solution (major component of the medium) $a = 1$
- for a solute (whether ionic or not) of an ideal solution $a_i = C_i / C^{\circ}$
  (ratio of the concentration to the standard concentration C° equal to 1 mol L^{-1})
- for an element or a compound alone in its solid phase $a = 1$
- for ideal solutions or ideal solid mixtures $a_i = x_i$
  (molar fraction x_i of the constituent under study). In electrochemistry the most frequently found examples of this type are metallic alloys or solid insertion materials. In fact they are rarely ideal systems, however their thermodynamic description always uses parameters that are close to the molar fractions, such as the insertion rate in an insertion material (see example below).

◤ The use of NERNST's law is illustrated below in some examples of ideal systems:

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

  The stoichiometric numbers are: $\nu_{\text{e}} = 1 \quad \nu_{\text{Fe}^{2+}} = -1 \quad \nu_{\text{Fe}^{3+}} = +1$

  The Fe^{3+} and Fe^{2+} ions are solutes in an aqueous solution, hence:

$$E = E^{\circ}{}_{\text{Fe}^{3+}/\text{Fe}^{2+}} + 0.06 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

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

  The stoichiometric numbers are: $\nu_{\text{e}} = -2 \quad \nu_{\text{Cu}^{2+}} = -1 \quad \nu_{\text{Cu}} = +1$

  The Cu^{2+} ions are solutes in an aqueous solution, while Cu is alone in its own phase, hence:

$$E = E^{\circ}{}_{\text{Cu}^{2+}/\text{Cu}} - 0.03 \log \frac{1}{[\text{Cu}^{2+}]} = E^{\circ}{}_{\text{Cu}^{2+}/\text{Cu}} + 0.03 \log [\text{Cu}^{2+}]$$

---

[8] *These basic notions of thermochemistry are presented in more detail in section 3.1.2.1.*

- $Zn(OH)_2/Zn$: $Zn(OH)_2 + 2\,e^- \rightleftharpoons Zn + 2\,OH^-$

  The stoichiometric numbers are: $\nu_e = -2 \quad \nu_{Zn(OH)_2} = -1 \quad \nu_{Zn} = +1 \quad \nu_{OH^-} = +2$

  The OH^- ions are solutes in an aqueous solution, Zn and $Zn(OH)_2$ are solid single components belonging to two distinct phases[9]:

$$E = E^\circ_{Zn(OH)_2/\,Zn} - 0.03\,\log[OH^-]^2 = E^\circ_{Zn(OH)_2/\,Zn} - 0.06\,\log[OH^-]$$

- Let us consider the interface between an organic electrolyte containing Li^+ ions and the cobalt oxide Li_xCoO_2, which is a solid insertion material of lithium. The redox half-reaction can be written in various different forms, such as:

$$Li_xCoO_2 \rightleftharpoons CoO_2 + x\,e^- + x\,Li^+,$$
$$LiCoO_2 \rightleftharpoons Li_{1-x'}CoO_2 + x'\,e^- + x'\,Li^+$$

  Ideally, the two extreme states of this material should correspond to the $CoO_2/LiCoO_2$ couple. To express the NERNST law in this material in a simplified manner, one can consider only the equilibrium of lithium ions which keep their oxidation number +I. This implies that the insertion material is a sufficiently good electronic conductor for the insertion limit to be ruled by the ionic insertion sites. The redox half-reaction can then be written:

$$\langle Li \rangle \rightleftharpoons \langle\ \rangle + e^- + Li^+_{electrolyte}$$

  where the symbol $\langle\ \rangle$ represents an insertion site of the host material: $\langle\ \rangle$ for a free site and $\langle Li \rangle$ for an occupied site. The NERNST law can then be written as:

$$E = E^\circ_{CoO_2/\,LiCoO_2} + 0.06\,\log\frac{a_{Li^+}\,a_{\langle\ \rangle}}{a_{\langle Li \rangle}} = E^\circ_{CoO_2/\,LiCoO_2} + 0.06\,\log a_{Li^+} + 0.06\,\log\frac{1-y}{y}$$

  where y is the ratio between the insertion rate of the material and its maximal value, in this simplified expression.

- For the electrochemical chain corresponding to the DANIELL cell (see figure 2.1 in section 2.1.1):

  Zn | aqueous solution of $ZnSO_4$ | | aqueous solution of $CuSO_4$ | Cu

  neglecting junction voltages and assuming that both interfaces are at thermodynamic equilibrium lead to the following equation[10]:

$$U = E^\circ_{Cu^{2+}/\,Cu} + 0.03\,\log[Cu^{2+}] - (E^\circ_{Zn^{2+}/\,Zn} + 0.03\,\log[Zn^{2+}])$$

---

[9] *Given the half-reaction written in this example, the standard state that is of particular relevance is that of a solution with an activity for OH^- equal to 1: in other words with $pH = 14$. The standard potential for the half-reaction written with H^+ ions would be different, in that, although it corresponds to the same couple, the standard sate corresponds to a solution with a unit activity for H^+ ($pH = 0$). Therefore, the values of E° in both equations written with OH^- or with H^+ must not be mixed up. Section 3.4.1.1 gives the same recommendation in the case of the standard GIBBS energy data. It also applies to the particular case of the apparent standard potential, which is developed in the next section.*

[10] *When a voltmeter is used for measuring a voltage, the measured quantity is always that of the potential difference between two metals of the same nature (following the measuring principle of a voltmeter). The electrochemical chain corresponding to the measure of the voltage of the DANIELL cell is:*

Cu′ | Zn | $ZnSO_4$ aqueous solution | | $CuSO_4$ aqueous solution | Cu

This point will be taken up again in the introduction of section 3.4 and set out with an example in section 3.4.1.1.

INDUSTRIAL PRODUCTION OF ALUMINIUM IN FRANCE

Document prepared with the kind collaboration of Y. BERTAUD and P. PALAU, engineers at the Rio Tinto Alcan Company, based in Voreppe, France

Aluminium was first produced between 1859 and 1887 in Salindres in the Gard region of France using the SAINTE-CLAIRE DEVILLE process. This process involved the chemical reduction of a molten mixture of chloroaluminate $NaAlCl_4$ and cryolite Na_3AlF_6 by metallic sodium Na. In 1886, P. HÉROULT filed a patent for an electrolysing process for Al_2O_3. His patent was bought in 1888 by the French *Société Electrométallurgique Française*: the first plant was built in Froges (Isère). The first cells were made up of a rotating crucible to limit interfacial depletion in alumina and to encourage liquid aluminium to gather at the bottom of the crucible. With an imposed voltage of $U = 10$ V (for $U_{eq} = 1.18$ V), the current intensity was 4000 A. Later on, with immobile crucibles and an increased anode area, the voltage could be lowered to 8 V for the same current value.

First electrolysis cells in Froges in 1889
(© Institut pour l'histoire de l'aluminium - all rights reserved)

Subsequently, the electrolysis processes of alumina underwent major technological changes (with the automation of machines, recycling fumes, overcoming the electrolyte and metal stirring problems due to magnetic field, which made a considerable current increase possible). However the principle of the process remained the same.

The electrolyte is a liquid phase made up of molten cryolite Na_3AlF_6 with additional AlF_3 in which alumina is dissolved at a continuous rate. This electrolyte also contains a small % of CaF_2 and possibly LiF and MgF_2. Alumina dissolves based on the following overall reaction:

$$2\ Al_2O_3 + 2\ AlF_6^{3-} \rightleftharpoons 3\ Al_2O_2F_4^{2-}$$

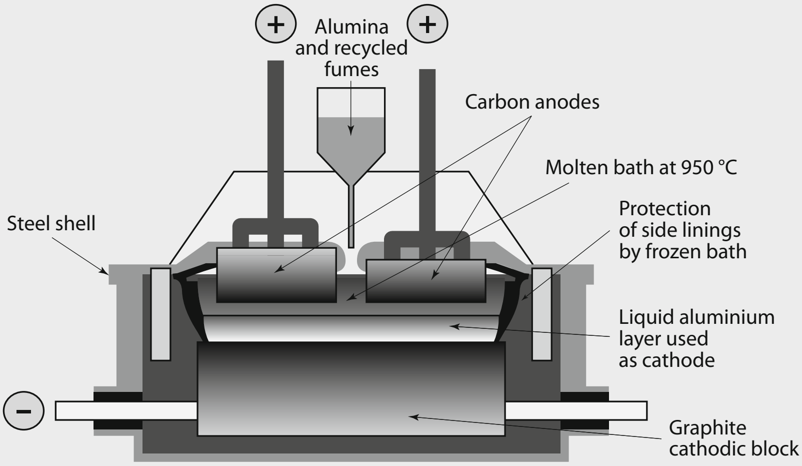
During the electrolysis process, the electrode reactions are:

at the anode $Al_2O_2F_4^{2-} + 4\ F^- + C \longrightarrow CO_2 + 2\ AlF_4^- + 4\ e^-$

at the cathode $AlF_6^{3-} + 3\ e^- \longrightarrow Al + 6\ F^-$

Therefore, when taking into account the equilibrium between AlF_6^{3-} and AlF_4^-, the following overall reaction for the main electrolysis reactions is:

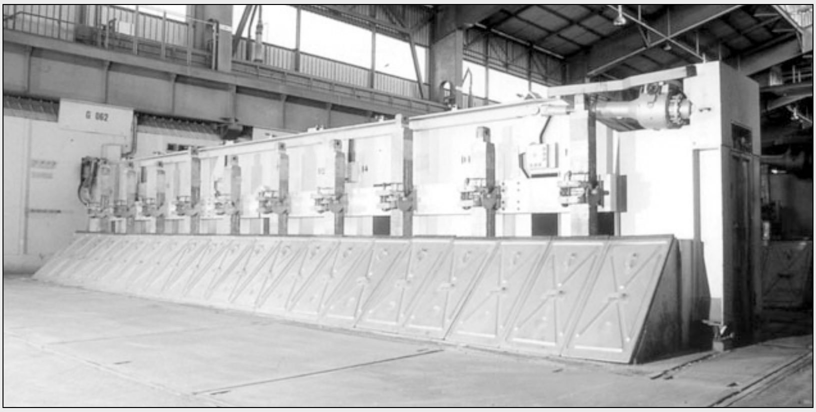
$$2\ Al_2O_3 + 3\ C \longrightarrow 4\ Al + 3\ CO_2$$



Block diagram of a modern cell for producing aluminium *(© Rio Tinto Alcan, with permission)*

The anode therefore sees a decrease in the $Al_2O_2F_4^{2-}$ ions content. If the solubility of the alumina is too low, or if its dissociation kinetics is too slow, the interfacial concentration may reach zero, depending on the anodic current density. Here, an 'anode effect' occurs and causes unwanted production of CF_4.

In modern cells, the supplied electric power between the cell terminals and the fact of regulating the inter-electrode distance both lead to a current intensity of about 300 000 A and to a voltage of about 4 V for each cell, including a 1.7 V ohmic drop within the electrolyte, with an energy yield value of about 0.5 and a faradic yield close to 0.95. The difference to 1 comes mainly from a ' chemical shuttle ', which is caused by the process of metal aluminium being dissolved in the electrolyte, and then followed by a re-oxidation process by dissolved CO_2 in the vicinity of the anode.



Series of 'AP 30' cells (300 000 A) *(© Rio Tinto Alcan, with permission)*

The key parameters that govern the technological developments are: current, faradic yield, energy consumption, the kinetics of alumina dissolution and, from more recent analysis, temperature. Moreover, in a bid to avoid CO_2 emissions, researchers are looking into replacing carbon anodes with dimensionally stable anodes which should produce dioxygen. However this would cause the energetic yield to decrease.

2.1.2.2 - APPARENT STANDARD POTENTIAL

It is important to know the thermodynamic characteristics of redox couples in order to understand and qualitatively draw the current-potential curves[11]. Mentioned here are some particular cases which are frequently seen in practice. When protons or hydroxide ions take part in the redox half-reaction and when the solution is buffered, one can assume that the proton or hydroxide ion activity remains constant whatever extent the reaction has reached. This is also the case when components present in large quantities take part in the half-reaction. In this instance therefore, the NERNST law is expressed by defining an apparent standard potential for this specific medium. These types of example are frequently found in systems involving highly acidic or highly basic solutions where the pH can be considered constant. Here apparent standard potentials are therefore defined, corresponding to aqueous solutions with fixed pH.

◤ For example, in the case of the IO_3^-/I^- couple, the redox half-reaction is:

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

We therefore have: $\nu_{I^-} = -1 \quad \nu_{H_2O} = -3 \quad \nu_{IO_3^-} = +1 \quad \nu_{H^+} = +6 \quad \nu_e = +6$

NERNST's law at 25 °C is:

$$E = E^\circ_{IO_3^-/I^-} + \frac{0.06}{6}\log\frac{(a_{H^+})^6\, a_{IO_3^-}}{a_{I^-}(a_{H_2O})^3}$$

Since H_2O is the solvent, its activity is taken to be equal to1. The end result is:

$$E = E^\circ_{IO_3^-/I^-} + 0.01\log\frac{a_{IO_3^-}}{a_{I^-}} - 0.06\ pH$$

If the solution under study is highly acidic (or highly basic) or if the solution is buffered, the NERNST law can be written as follows:

$$E = E^\circ_{app_{IO_3^-/I^-}} + 0.01\log\frac{a_{IO_3^-}}{a_{I^-}}$$

with

$$E^\circ_{app_{IO_3^-/I^-}} = E^\circ_{IO_3^-/I^-} - 0.06\ pH$$

Therefore, when numerical values are ascribed to apparent standard potentials, the relevant medium must necessarily be specified (for instance, in the preceding example, the pH value has to be given). ◢

A similar situation is also found in systems using insertion materials where there is a high concentration of the ion being exchanged. The notion of apparent standard potential is again used in writing the NERNST law, in which only the insertion rate appears. One also refers to insertion isotherm.

◤ Let us consider the interface between an organic electrolyte containing Li^+ ions and the Li_xMnO_2 solid oxide which is an insertion material for lithium:

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

The NERNST law can be written as a function of the insertion rate, y, of manganese oxide:

---

[11] *Section 2.3 describes the various shapes and characteristics of current-potential curves. The thermodynamic standard (possibly apparent) potential of each relevant couple is always spotted on these curves.*

$$E = E^\circ_{\mathrm{MnO_2/LiMnO_2}} + 0.06 \log a_{\mathrm{Li^+}} + 0.06 \log \frac{1-y}{y}$$

In the case of ideal materials, and if the variations of the Li^+ concentration in the solution can be disregarded, the result is the following insertion isotherm, i.e., the relationship between the insertion rate and the equilibrium potential:

$$E = E^\circ_{\mathrm{app}_{\mathrm{MnO_2/LiMnO_2}}} + 0.06 \log \frac{1-y}{y}$$

with $$E^\circ_{\mathrm{app}_{\mathrm{MnO_2/LiMnO_2}}} = E^\circ_{\mathrm{MnO_2/LiMnO_2}} + 0.06 \log a_{\mathrm{Li^+}}$$

2.1.2.3 - THE WATER REDOX COUPLES

Water, as a solvent or as a solute, can be oxidised or reduced [12]. It takes part in the two following couples:

$$O_2/H_2O \qquad \text{and} \qquad H_2O/H_2$$

One can write and balance the two corresponding redox half-reactions either with protons or with hydroxide ions:

Table 2.1 - Various ways of writing the two water redox couples

Medium	**O_2/H_2O couple**	**H_2O/H_2 couple**
Acidic	$2\,H_2O \rightleftharpoons O_2 + 4\,H^+ + 4\,e^-$	$2\,H^+ + 2\,e^- \rightleftharpoons H_2$
Basic	$4\,OH^- \rightleftharpoons O_2 + 2\,H_2O + 4\,e^-$	$2\,H_2O + 2\,e^- \rightleftharpoons 2\,OH^- + H_2$

However, whichever of the forms is selected, the elements which see their oxidation numbers change are respectively oxygen and hydrogen:

- for the O_2/H_2O couple, it is the oxidation number of oxygen that changes:
  0 in dioxygen and –II in H_2O or in OH^-;
- for the H_2O/H_2 couple, it is the oxidation number of hydrogen that changes:
  0 in dihydrogen and +I in H_2O or in H^+.

Depending on the particular case, one writing mode is preferable to the other, though the choice will not in any way change the result when applying the NERNST law. The redox couple will remain the same and equally the equilibrium potential will not be affected by the writing mode selected. Figure 2.2 represents the thermodynamic stability domain of water as a function of pH, in a diagram of the E/pH type. This diagram is calculated by applying the NERNST law, and by using the convention which states that for gases each partial pressure is equal to 1 bar [13]:

---

[12] *The same water couples often intervene in non-aqueous media (e.g., when imperfectly dehydrated organic solvents are in question). But in this case thermodynamic data adapted to these media must be used (particular attention must be paid to the reference states chosen for water).*

[13] *This type of E/pH diagram, also called POURBAIX diagram, is frequently used for redox equilibria in solutions, and also in the field of corrosion studies. It is a graphic illustration of thermodynamic data which results from applying the NERNST law. Section 3.4.1.4 focuses on the example of a particular part of the POURBAIX diagram which deals with the chlorine element in aqueous solution. Numerous other examples can easily be found in scientific literature.*

- for the couple in which water undergoes oxidation:

$$2\,H_2O \rightleftharpoons O_2 + 4\,H^+ + 4\,e^-$$

$$E = E^\circ_{O_2/H_2O} + \frac{0.06}{4}\log\left(a_{H^+}\right)^4 \times \frac{1}{1^2} = 1.23 - 0.06\ pH$$

- for the couple in which water undergoes reduction:

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

$$E = E^\circ_{H^+/H_2} - \frac{0.06}{-2}\log\left(a_{H^+}\right)^2 \times \frac{1}{1} = 0 - 0.06\ pH$$

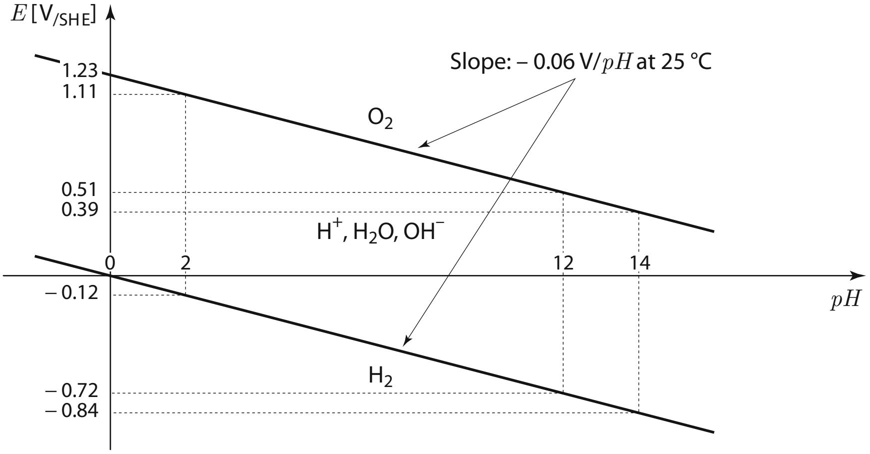


Figure 2.2 - E/pH diagram of the water couples in aqueous medium

Also noted will be the enormous impact of the pH on thermodynamic characteristics, especially in this example, since the fact of shifting from an acidic medium to a basic medium causes the potential to decrease by more than 600 mV.

When focusing on the redox reactions occurring, as opposed to when focusing on the equilibrium states, one must always take into account the two redox couples involving water[14]. This is particularly true when trying to predict and understand the reactions occurring in electrochemical systems with aqueous solutions. Here, the choice that needs to be made between the two possibilities for writing each redox couple becomes of key importance. It is an obvious choice for acidic or basic media. However it deserves particular attention when the medium is neither strongly acidic nor strongly basic. When making the choice, one needs to take into consideration the direction of the reaction in question and put the protons or hydroxide ions on the products side only and not on the reactants side. For example, keep in mind that when water is present, dihydrogen can be produced even in non-acidic media:

$$\cancel{2\,H^+ + 2\,e^- \longrightarrow H_2} \qquad\qquad 2\,H_2O + 2\,e^- \longrightarrow 2\,OH^- + H_2$$

---

[14] *In fact, as set out in sections 2.3.5 and 2.3.6, the two redox water couples play a part in the shape of the current-potential curves of the systems with aqueous electrolytes.*

or that with a neutral electrolyte, reduction of dioxygen has to be written as the following:

$$O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$$

To help remember this element, in this document we suggest the following writing mode for these two couples:

$O_2/H_2O,OH^-$ for O_2/H_2O and,or OH^-

$H^+,H_2O/H_2$ for H^+ and,or H_2O/H_2

Being able to gain a quantitative understanding of the influence of thermodynamic data of these two couples in the behaviour of systems that are not in equilibrium is a complex process[15]. This is especially true when drawing current-potential curves. We can remind ourselves that in qualitative terms, when dealing with very acidic or very basic media, it is the notion of apparent standard potential that is of key relevance. The latter is calculated by means of applying the NERNST law for a partial pressure of O_2 or H_2 equal to the standard pressure (see figure 2.2).

2.2 - CHARACTERISTICS OF SYSTEMS WITH A CURRENT FLOWING

2.2.1 - PHENOMENA OCCURRING WHEN A CURRENT IS FLOWING

In order to be able to describe the phenomena that occur when a current flows through electrochemical systems, one must first be able to describe what factor enables the current to circulate through the volumes of the various conductors and also through the various interfaces of the system. Incidentally, let us recall that current circulation, which corresponds to macroscopic charge movements, always corresponds to macroscopic mass movements.

2.2.1.1 - VOLUME CONDUCTION

The phenomena linked to the flow of current through a conducting medium can be approached at the microscopic level or from their macroscopic description. Here, we will only give a brief overview of the macroscopic description of conduction phenomena[16].

The various processes of mass transport are generally classified in three categories which are described below in a simplified manner:

- migration: the movement of charged species submitted to an electric field. Migration is generally characterised by the concentration and the molar conductivity of the charge carriers. The SI unit of molar conductivity (usually denoted by λ_i) is S m^2 mol^{-1}, but S cm^2 mol^{-1} is also used[17];

---

[15] *Appendix A.2.1 gives a detailed explanation of the shape of the current-potential curve of the $H^+,H_2O/H_2$ couple that is assumed to be fast, validating the result given here.*

[16] *A quantitative macroscopic description of volume conduction is given in section 4.2.1. Some aspects of associated microscopic phenomena are described in section 4.2.2.*

[17] *Other notations different from the Siemens, S,* can be found in other works *(Ω^{-1} or else mho) but they are not recommended.*

- diffusion: the movement of species submitted to a concentration gradient (rigorously speaking to an activity gradient). The species diffuse from the most concentrated zone towards the less concentrated zone. Diffusion is generally characterised by the diffusion coefficient (or diffusivity) of each species. The SI unit of a diffusion coefficient (usually denoted by D_i) is $m^2\ s^{-1}$, but $cm^2\ s^{-1}$ is also used;
- convection: the overall movement of the medium when it is a fluid (liquid or gaseous). This movement, characterised by a velocity in $m\ s^{-1}$, carries the species i with a concentration C_i (in $mol\ m^{-3}$). It can take the form of natural convection, caused by density gradients, or forced convection corresponding to a homogenisation process caused by mechanical agitation.

In certain experimental conditions (see examples below), the electrolyte may have zones where diffusion plays a negligible role compared to the other mass transport modes (migration and convection). These are often called ' bulk electrolyte '. The zone(s) where diffusion cannot be disregarded is (are) then defined as the diffusion layer(s) [18]. Defining the diffusion layer volume in quantitative terms, and in particular defining its thickness, wholly depends on how precisely one chooses to observe and define the phenomena [19]. A diffusion layer, which is generally next to an interface, may see migration and convection also occur.

This can be illustrated in the example of a mechanical stirring device (forced convection) when used for homogenising the liquid electrolyte, mainly away from the zones that are next to the interfaces. The same case applies to analytical chemistry when a rotating disc electrode is involved or when a system is installed in industrial electrolysers in order to force the circulation of the electrolyte. By following a simplified model called the NERNST model [20], one can define the thickness of the diffusion layer (often denoted by δ) which is not time-dependent in this case. The order of magnitude of δ is a few µm. It increases with the viscosity of the medium and with the diffusion coefficient of the species concerned; it decreases when the stirring becomes more effective. The NERNST model is based on the simplifying hypothesis that the role played by convection in diffusion layers is insignificant, as indicated in figure 2.3, which shows the conduction modes involved in the various zones of the electrochemical system. In contrast, outside the two diffusion layers (thicknesses δ_1 and δ_2), i.e., in the bulk electrolyte, the very presence of forced convection means that the phenomenon of diffusion can be

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[18] *Care should be taken not to confuse this notion with another term also used in electrochemistry when describing the interfacial zone: the diffuse layer of the double layer (see sections 3.3.1 and 4.3.1.1).*

[19] *Section 4.3.1 focuses on the concentration profiles of several experiments that are commonly encountered in electrochemistry, serving to give a better visualization of this notion of the diffusion layer. This more detailed examination found in sections 4.3.1.3 and 4.3.1.4 helps one make a clear distinction between this general notion of a diffusion layer thickness, where diffusion represents 90, 95, 99 or 99.99%… of mass transport, and the different thickness values which result from various models (semi-infinite diffusion, NERNST's model, etc.). The latter models give precise thickness values (defined thanks to referring to the slope of the concentration profiles at the interface) which represent the right order of magnitude for the diffusion layer thickness (which itself is slightly undervalued, see for example figure 4.20 in section 4.3.1.4).*

[20] *Section 4.3.1.4 describes in more detail the results produced by the NERNST model, which uses hydrodynamic calculations as laid out by LEVICH.*

disregarded. This simplified model creates a discontinuity in the transport modes at the boundary of the diffusion layers. This discontinuity has no physical reality, but has no impact provided the aim is not to gain a precise definition of the transition zones around δ_1 and δ_2[21].

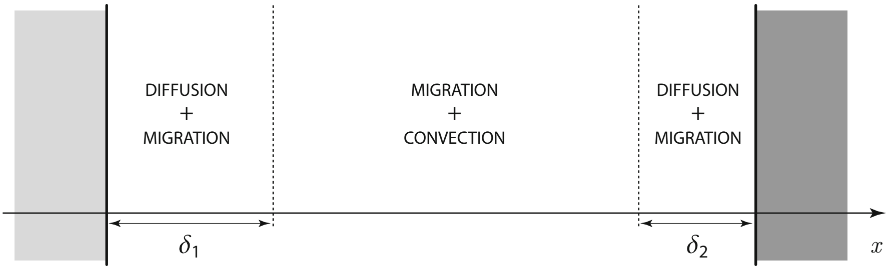

Figure 2.3 - Distribution of the conduction modes in an electrolyte when submitted to forced convection, according to the* NERNST *model

Another example is a system, initially in equilibrium, where the electrolyte is not stirred, and moreover natural convection can be disregarded. Interfacial perturbations are then imposed to this system. Figure 2.4 illustrates the conduction modes involved in these conditions. The change in concentration does not immediately reach the electrolyte zones located far from the interfaces. In between, the electrolyte has a homogeneous zone where only migration occurs. As the experiment progresses with time, the size of this non-perturbed zone decreases, while the thicknesses of the diffusion layers increase.

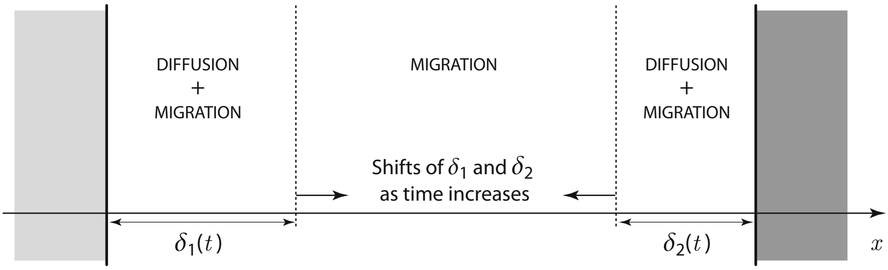

Figure 2.4 - Distribution of the conduction modes in an unstirred electrolyte
The thicknesses of diffusion layers are time-dependent.

In usual experimental conditions involving liquid electrolytes, it is impossible to prevent natural convection from occurring. In aqueous solutions at room temperature, natural convection occurs at distances of about 300 µm from the interface. Therefore the only way to keep convection negligible, is to carry out experiments for short periods, typically a few minutes[22].

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[21] *Figure 4.20 in section 4.3.1.4 illustrates the differences between the actual concentration profiles and those obtained when using the* NERNST *model.*

[22] *The order of magnitude of the diffusion layer thickness in a semi-infinite diffusion experiment is given by* $\sqrt{Dt}$ *. This is discussed in more detail in section 4.3.1.3. For a diffusion coefficient of about* 10^{-5} *cm*^{2} *s*$^{-1}$*, about 2 minutes are needed for the diffusion layer thickness to reach 300 µm, namely when natural convection phenomena begin to reach a significant scale.*

Two other particular cases are frequently found to have an effective impact on the conduction modes that occur:

- namely media which conduct using a single mobile charged species. In these media, the electroneutrality determines that there is a homogenous concentration of the unique mobile species throughout the whole volume. Therefore there is no concentration gradient, nor diffusion layer. For example, in a solid state metal, electrons only move by migration: neither convection nor diffusion occurs. In certain conditions, namely regarding temperature or partial dioxygen pressure, the same holds true in the case of numerous ionic solids which are considered to have only one charge carrier;
- solutions containing a supporting electrolyte, i.e., non-electroactive charge carriers with a concentration significantly higher than the concentration of electroactive species[23]. Here, it must be remembered that when a supporting electrolyte is present, the migration of the electroactive species can be overlooked as opposed to their convection and diffusion. For instance, in the case of forced convection with a supporting electrolyte (see figure 2.3), the conduction modes of the electroactive species are diffusion within the diffusion layers and convection outside these layers.

2.2.1.2 - PHENOMENA OCCURRING AT INTERFACES

Reactive phenomena

Let us consider the common case of the electrochemical interface between a metal and a solution. Given that a solution has no free electrons, which are what ensures the current circulation in metals, then one or several other phenomena must therefore come into play to ensure that the current is transmitted to the ionic charge carriers. The steady-state current circulation through such an interface therefore involves an electrochemical reaction.

The reactive interfaces are those where at least one chemical reaction occurs. The reactions occurring at interfaces are by nature heterogeneous reactions. The electrochemical electrode reactions always belong to this kind of reaction. Figure 2.5 illustrates the example of the reduction of Fe^{3+} ions in aqueous solution at a platinum electrode, specifying the directions in which the species move in relation to the reaction progression[24].

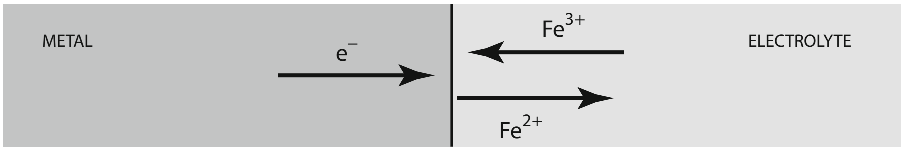

Figure 2.5 - Diagram of the reduction of Fe^{3+} at an interface with a platinum electrode

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[23] *Section 2.2.4.4 and appendix A.4.1 deal with several properties which are linked to the presence or absence of a supporting electrolyte.*

[24] *In this type of diagram, the arrows represent the molar flux density vectors, generally with arbitrary lengths.*

When a gas is produced at a metal|electrolyte interface, the phenomenon generally occurs in several steps, involving adsorbed species and the dissolution of the molecular species produced into the electrolyte (figure 2.6).

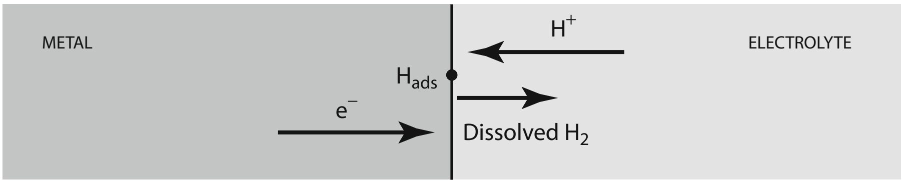

***Figure 2.6** - Diagram of the reduction of H^+ at an interface with a platinum electrode*[25]

As soon as the activity of the dissolved gas exceeds the critical solubility value, gas bubbles are formed.

This notion of a reactive electrode is used much more widely in modern science. For instance it can be found in phase transfer chemistry or in the study of liquid-liquid interfaces. Figure 2.7 represents the phase transfer reaction between a potassium chloride aqueous solution and a solution of a crown-ether (denoted by L) in an organic solvent[26].

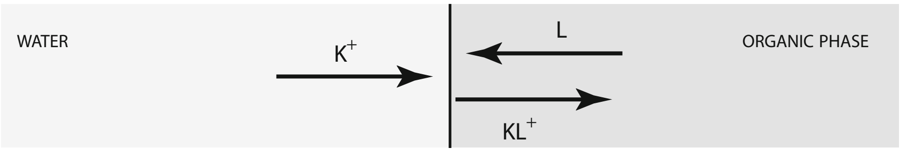

***Figure 2.7** - Diagram of the complexation reaction of K^+ by the ligand L at an interface between an aqueous solvent and an organic solvent*

Cases exist among these interfacial reactions where some of the species involved are not mobile in both phases. Figures 2.8 and 2.9 illustrate two cases in which the species produced is immobile: it gathers in the interfacial zone.

- In the case of a metal (silver) deposition reaction by reducing cations (Ag^+) in solution, the atoms formed remain on the surface (figure 2.8) and the interface continuously develops on an atomic scale as the reaction progresses.

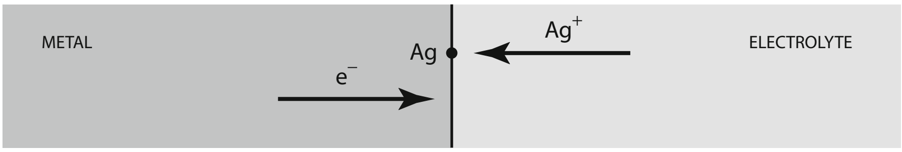

***Figure 2.8** - Diagram of the reduction of an Ag^+ ion at an interface with a silver electrode*

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[25] *Quantitatively speaking, according to FARADAY's law (see section 4.1.4), the modulus of the mass flux density of dissolved dihydrogen is equal to half that of the protons.*

[26] *Here the organic solvent is supposed to be sufficiently dissociating. If that is not the case, then this diagram should be completed by adding anions which form ion pairs (KL^+, X^-) in the organic phase.*

- In the case of an adsorption reaction of a molecule A, the adsorbed species occupies a vacant site on the electrode surface, thus partly blocking it (figure 2.9).

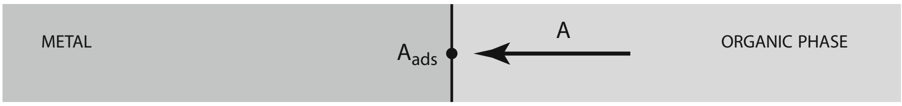

Figure 2.9 - Diagram of the adsorption reaction of a molecule A at an interface with a metal

⏩ *Exchange phenomena*

Let us consider two phases which are in contact with each other, each containing species of the same chemical nature, though with different interactions with the surroundings (figure 2.10). If these species are mobile in both phases, they can be exchanged through the interface. The interface is then said to be permeable to these species.

For instance, the ionic junction between solid silver chloride, which is an ionic solid where conduction is only due to Ag^+ ions, and an aqueous solution containing Ag^+ ions, is permeable to these ions. This is the case despite the fact that there is a difference between the interactions of these Ag^+ ions with the surrounding medium in the aqueous solutions compared to in the AgCl crystalline network.

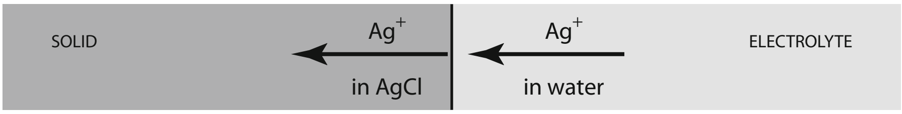

Figure 2.10 - Diagram of the exchange reaction of a silver ion at an interface between AgCl and an aqueous solution containing Ag^+ ions

These exchange phenomena constitute a particular case of reactive phenomena since the interfacial exchange can be represented here by the following overall equation:

$$Ag^+_{water} \longrightarrow Ag^+_{AgCl}$$

Depending on the number of species that can be exchanged, one can distinguish the following:

- impermeable junctions (with no mass exchange): an example of impermeable junction is the interface M metal|electrolyte containing M^+ ions. This is because M^+ ions are not mobile in the metallic lattice, at least at room temperature;
- single-exchange junctions (with a single type of species exchanged): the interface AgCl|aqueous solution containing Ag^+ ions mentioned above is an example of a single-exchange ionic junction since chloride ions are not mobile in the ionic solid. Electronic junctions are also single-exchange junctions at room temperature: electrons are the only species that are mobile in both phases;
- multiple junctions (with at least two species of different natures exchanged): junctions between two electrolyte solutions belong to this kind of junction.

Although this terminology (permeable/impermeable) is frequently used in the field of junction thermodynamics, it will not be used in the remainder of this book. In fact, it is easier to apply a common treatment for electrochemical chains where different kinds of interfaces are involved. This is notably true when treating kinetic phenomena occurring at these interfaces. If you consider all these interfaces to be impermeable interfaces, whether reactive or not, then this unification is made possible (see next example). In the case of a permeable junction, the two exchanging species (e.g., Ag^+ in solid AgCl and Ag^+ in solution) will simply be considered as two different species: the first one is transformed into the second one by a reaction at the interface.

⏩ *Accumulation phenomena*

It is important to distinguish between a ' non-reactive interface ' and an ' interface where nothing happens '. A non-reactive interface can transiently be a site of mass accumulation and consequently a site where charge accumulates if ions or electrons are concerned.

A key example of a non-reactive interface is the interface between a metal and an electrolyte which contains no electroactive species. Such a case is generally confined to a certain potential window where the electrode is said to be ideally polarisable or blocking. In such systems, applying a potential variation leads to the charge carriers moving transiently in each of the two phases. In fact, although no reaction occurs, the structure of the interfacial zone, and consequently the distribution of charge carriers, are adapted to fit the potential distribution variations. A simplified diagram of this interfacial zone would represent a capacitor where charge carriers of different signs accumulate on two planes which are placed very close to one another. This is called the electrochemical double layer[27]. It is worth mentioning that this particular feature is used in certain energy storage systems called supercapacitors[28].

From an experimental point of view it may be important to spot the particular case, notably in terms of potential, where there is no charge accumulated on both sides of the interface. This is known as the zero-charge potential.

Mass accumulation in the interfacial zone may or may not be a reactive phenomenon based on the chemical nature of the species in that particular zone. If chemical interactions do occur at the interface, then they are called adsorption reactions or chemisorptions. As in the case of catalysis, the notion of adsorption (or chemisorption) is only defined in relation to the order of magnitude of the interaction energy. The limit between an adsorption reaction and simple accumulation is not very clear. Electrosorption is an adsorption reaction involving an ion at the interface. In general cases, it is hard to determine the exact nature of an ion which has been specifically adsorbed, that is the effective charge of this new adsorbed species, which is generally not an integer multiple of the elementary charge.

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[27] *Section 3.3.1 describes the potential profile observed in this interfacial zone which is linked to the particular charge distribution on both sides of the interface.*

[28] *See the illustrated board entitled ' Energy storage: supercapacitors '.*

2.2.2 - The faradic phenomena

2.2.2.1 - Faradic current and capacitive current

In most cases, current flow corresponds to reactive phenomena (including possibly exchange) and/or to accumulation phenomena at the electrodes. Though it may be a complicated task, notably if adsorption[29] occurs, the current can be separated into two additive contributions:

- the faradic current (named so because this component follows the Faraday law) which is linked to the reactive phenomena with species consumed and produced at the electrodes[30];
- the capacitive current (named so because of the simplified model of a plane capacitor on the molecular scale) which is linked to the charge accumulation phenomena at the interfaces.

In numerous cases the capacitive component of the current can be disregarded, and this being so in particular in the quasi-totality of industrial applications involving current circulation in electrochemical systems.

Since this work is focused on describing simple electrochemical phenomena, we will only consider the faradic part of the current.

2.2.2.2 - Faraday's law

The faradic part of the current is a direct measure of the reaction extent rate in the case of a single reaction. Namely, this corresponds to how the system has evolved compared to the initial system, meaning that it characterises the amount of substance that has been transformed. The amount of electric charge is a measure of the reaction extent rate. This is what Faraday's law represents in quantitative terms.

The Faraday law is most often used in its integrated form which gives the following equation:

$$\Delta n_i^{\text{farad}} = \frac{\nu_i}{\nu_{\text{e}}\,\mathcal{F}}\, Q^{\text{farad}} = \frac{\nu_i}{\nu_{\text{e}}\,\mathcal{F}} \int_t^{t+\Delta t} I^{\text{farad}}(t)\,\mathrm{d}t$$

and when the current is constant, it gives:

$$\Delta n_i^{\text{farad}} = \frac{\nu_i}{\nu_{\text{e}}\,\mathcal{F}}\, I^{\text{farad}} \Delta t = \frac{\nu_i}{\nu_{\text{e}}\,\mathcal{F}}\, j^{\text{farad}} S\, \Delta t$$

with:	$\Delta n_i^{\text{farad}}$	the algebraic variation of the amount of substance of species i during the time interval Δt	[mol]
	ν_i	the algebraic stoichiometric number of species i	
	ν_{e}	the algebraic stoichiometric number of the electron	
	$\mathcal{F}$	the Faraday constant	[C mol^{-1}]

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[29] *Section 4.1.3 illustrates the consequences of adsorption phenomena at interfaces.*

[30] *The corresponding heterogeneous reaction is called a redox half-reaction or charge transfer or electronic transfer, as defined in section 1.3.3.*

Q^{farad}	the algebraic faradic charge amount exchanged during the time interval Δt	[C]
I^{farad}	the algebraic faradic current flowing through the interface	[A]
j^{farad}	the algebraic faradic current density	[A m^{-2}]
Δt	the time interval during which the current flows	[s]
S	the surface area of the electrode in question	[m^2]

FARADAY's law, as well as its expression as a local vector, will be demonstrated in greater detail later in this book[31]. This law has numerous applications, notably in industry. For instance, it forms the basis of the theoretical calculation for battery capacity, for homogeneous corrosion rates of metals, and for the amount of substance produced or consumed in electrosynthesis processes, etc.

In a fuel cell element with an area $S = 100$ cm^2 where current flows with $j = 0.20$ A cm^{-2} at room temperature, FARADAY's law enables one to determine the molar flux density of the dihydrogen consumed as well as the volume flow rate of the water produced.

The overall equation of the fuel cell is:

$$H_2 + ½\,O_2 \xrightarrow{2\mathcal{F}} H_2O$$

When using FARADAY's law, it is vital to know the respective stoichiometries in the redox half-reactions including that of the electrons in particular. This is what the number written above the reaction arrow means. It can be determined by considering the anodic half-reaction:

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

We therefore have: $\nu_e = +2 \quad \nu_{H_2} = -1$

The dihydrogen molar flow rate can be calculated from the following equation:

$$\frac{\Delta n_{H_2}}{\Delta t} = \frac{\nu_{H_2}}{\nu_e\,\mathcal{F}}\, j^{\text{farad}} S = -\frac{1}{2\mathcal{F}}\, j^{\text{farad}} S$$

$1.0{\times}10^{-4}$ mol s^{-1} or 0.37 mol h^{-1} of dihydrogen, i.e., 9.0 L h^{-1} of dihydrogen gas at room temperature and pressure ($V_{\text{molar}} = 24$ L mol^{-1}) are consumed.

The volume flow rate of water can be calculated by taking into account the stoichiometric numbers in the cathodic half-reaction:

$$2\,H^+ + 2\,e^- + ½\,O_2 \longrightarrow H_2O$$

we therefore have : $\nu_e = -2 \quad \nu_{H_2O} = +1$

$$\frac{\Delta V_{H_2O}}{\Delta t} = \frac{\nu_{H_2O}}{\nu_e\,\wedge}\, j^{\text{farad}} S\, V_{\text{molar}} = -\frac{1}{2\,\wedge}\, j^{\text{farad}} S\, V_{\text{molar}} = \frac{1}{2\,\wedge}\left| j^{\text{farad}} \right| S\, V_{\text{molar}}$$

Take the molar volume of liquid water at room temperature, that is to say 18 cm^3 mol^{-1}, then the calculated water production is 6.7 cm^3 h^{-1}.

2.2.2.3 - FARADIC YIELD

If several simultaneous, concurrent reactions occur at an electrochemical interface, the overall faradic current is the sum of the faradic currents of each redox half-reaction[32].

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[31] *Section 4.1.4 shows how the FARADAY law can be demonstrated by writing interfacial mass balances.*

[32] *Section 4.1.4 demonstrates this additive property of faradic currents in the case of an example.*

The faradic yield of a given redox half-reaction is the ratio between the variation of the amount of a given species in the medium used and the corresponding variation that should be expected from FARADAY's law if the totality of the current was used for the half-reaction to progress:

$$r_{\text{farad}} = \frac{\Delta n^{\text{effective}}}{\Delta n^{\text{farad}}}$$

This notion of faradic yield is most often used for quantifying the competition between several reactions occurring simultaneously at a given interface. It represents the fraction of the actual current used for the half-reaction in question. The faradic yield (either anodic or cathodic) of a particular half-reaction is therefore inferior to 100%.

For instance, when nickel is deposited using an acidic aqueous solution containing Ni^{2+} ions, one can observe a weak level of dihydrogen production, whilst simultaneously observing a reduction of the Ni^{2+} ions.

The thickness of the nickel layer deposited in an experiment where the current density is 50 mA cm^{-2} , and for the total duration of one hour, is equal to 60 µm.

The faraday yield of this electrochemical deposition can then be determined once the metallic deposit's molar mass, M, and the density, ρ_{vol}, are both known. A homogeneous thickness variation $\Delta\ell$ over a surface area S is linked to the variation of the amount of substance Δn by the following equation:

$$\Delta n = S\,\Delta\ell\,\frac{\rho_{\text{vol}}}{M}$$

The redox half-reaction of nickel deposition is:

$$\text{Ni}^{2+} + 2\,\text{e}^- \longrightarrow \text{Ni}$$

We therefore have: $\nu_{\text{e}} = -2 \quad \nu_{\text{Ni}} = +1$

The actual current density used for the nickel deposition reaction can be calculated using FARADAY's law:

$$j_{\text{deposition}} = \frac{\Delta\ell}{\Delta t}\,\frac{\nu_{\text{e}}\,\mathscr{F}}{\nu_{\text{Ni}}}\,\frac{\rho_{\text{vol}}}{M} = -2\,\mathscr{F}\,\frac{\Delta\ell}{\Delta t}\,\frac{\rho_{\text{vol}}}{M}$$

The current density calculated is negative, which is to be expected for a reduction reaction, following the algebraic form of FARADAY's law.

The molar mass of nickel is equal to 59 g mol^{-1}, its density is 8.9 g cm^{-3}. The calculated value of the current density is:

$$j_{\text{deposition}} = -\,2\times 96\,500\,\frac{60\times 10^{-4}}{3600}\,\frac{8.9}{59} = -\,49\ \text{mA cm}^{-2}$$

In the end, the faradic yield obtained for nickel deposition is therefore 97%.

If the faradic yield for a given working point of the electrochemical system is close to 100% at both electrodes, then the two redox half-reactions are called main reactions. In such a case, writing the balanced results of these two half-reactions corresponds to the overall conversion of reactants to products within the system.

On the other hand, as soon as several half-reactions occur simultaneously at one of the two electrodes (or *a fortiori* at both electrodes), it is still possible to write the various overall reactions combining oxidation and reduction. However, this is of little interest since it does not represent a real overall result. A relevant example in the field of batteries is laid out below.

THE FIRST ELECTRIC VEHICLES

In the nineteenth century, there were three means of achieving propulsion competing to replace the old hackney cabs:

- steam following the invention of the steam carriage (4.8 km/h) by CUGNOT in 1769, and the construction of l'OBÉISSANTE by A. BOLLÉE in 1873, the first ever steam vehicle, designed for 12 passengers;
- electricity supplied by batteries (DAVENPORT's small-scale model in 1834, and a two-seater vehicle developed by M. FARMER in 1847);
- the internal combustion engine (the two-stroke engine developed by E. LENOIR in 1859, the four-stroke developed by E. DELAMARE-DEBOUTTEVILLE in 1883, and R. DIESEL's diesel engine in 1889).

To give a general idea, at the end of the eighteenth century, vehicles without horses were divided into three types: 40% steam vehicles, 38% electric traction vehicles and only 22% combustion engine vehicles.

La JAMAIS CONTENTE
(The electric automobile. France 1899. Manufactured by *Compagnie internationale des transports automobiles électriques* - JENATZY - 56, rue de la Victoire - Paris. Bodywork made out of partinium alloy, designed by RHEIMS and AUSCHER, with FULMEN accumulators. Photo by P. FABRY, with the kind permission of the *Musée national de la voiture et du tourisme* - Compiègne, France)

The struggle to penetrate the market manifested itself in competitions. The most legendary race against the clock was carried out in a matter of only a few months between Gaston DE CHASSELOUP and Camille JENATZY (1898-1899). JENATZY, the son of a Belgian manufacturer in the rubber industry (including tyres), won the race reaching up to a speed of 105.9 km/h over a distance of 1 km. He held this record for three years. La JAMAIS CONTENTE, which was shaped like a shell, had two rear engines and held over half a ton of lead acid batteries. Given the road conditions and the rustic state of mechanics at the time (steering, shock absorbers), this feat certainly merits applause. C. JENATZY continued to be an experienced racing driver while still managing his factory (he achieved a new speed record of 200 km/h in 1909, but with a combustion engine car).

Electric vehicles had clear benefits (silent, clean, basic maintenance, easy steering and long engine lifespan) compared to gasoline vehicles (dangerous crank start, need for a clutch, frequent maintenance, unpleasant smell, etc.). Although the first vehicles had low endurance levels in terms of autonomy, some of them could keep going for up to 300 km at a go. Large car fleets began to be developed in big cities (for taxis, the postal service, milk deliveries, garbage collection, etc.). Having eventually been taken over by gasoline or diesel (following the arrival of starters and FORD's assembly line), electric vehicles are now currently in the process of finding new life in light of prospected oil shortages.

In a nearly fully recharged lead acid battery, two half-reactions are in competition at the positive electrode (anode):

$$PbSO_4 + 2\,H_2O \longrightarrow PbO_2 + 2\,e^- + HSO_4^- + 3\,H^+$$
$$H_2O \longrightarrow ½\,O_2 + 2\,H^+ + 2\,e^-$$

At the negative electrode (cathode), in a battery which enables gases to escape (called a vented or flooded battery), competition between the following half-reactions can also occur:

$$PbSO_4 + H^+ + 2\,e^- \longrightarrow Pb + HSO_4^-$$
$$2\,H^+ + 2\,e^- \longrightarrow H_2$$

In most cases however, since there is an excess of active material at the negative electrode, the faradic yield of the positive electrode drops whereas that of the negative electrode remains very close to 100%. If we take an extreme case where the faradic yield at the cathode is 100%, then we can write the two overall reactions that are in competition at the end of the recharging operation:

$$2\,PbSO_4 + 2\,H_2O \longrightarrow PbO_2 + Pb + 2\,HSO_4^- + 2\,H^+$$
$$PbSO_4 + H_2O \longrightarrow Pb + ½\,O_2 + H^+ + HSO_4^-$$

When the recharging operation is prolonged, the second reaction gradually becomes the only one to be considered, and this corresponds to an operating mode called floating [33]. In any case it makes no sense to write the balance between the reduction and oxidation of water. However there is a lot of literature about thoses batteries where one can frequently read about how the parasitic reaction is the electrolysis of water.

2.2.3 - CELL VOLTAGE DISTRIBUTION

Generally speaking, in systems with localised interfaces, the voltage between the terminals in an electrochemical chain can be split into the sum of the interfacial voltages and the ohmic drops [34]. Let us recall that an interfacial voltage is the difference between the potentials of both sides of the interface, whose thickness is about a few nanometres most of the time. It is therefore either an ionic or electronic junction voltage or an electrochemical interface voltage. The ohmic drop is the potential difference between

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[33] *In floating mode, it is better to use VRLA (Valve Regulated Lead Acid) batteries where the reactions are water oxidation at the positive electrode and dioxygen reduction at the negative electrode. When a steady state is reached in an ideal VRLA battery, there is no mass consumption, which is not the case for a vented battery for which the floating mode leads to a continuous loss of water.*

[34] *When a voltage is measured by means of a voltmeter, the measurement represents the potential difference between two metals of the same nature (based on the measurement principle of a voltmeter). Rigorously speaking, one should add to the electrochemical chain the electronic junction(s) of the electrode connections in order to describe the distribution of the potentials which yield the voltage U that is measured between the terminals of the cell. Figure 2.11 (as well as figures 2.15 and 2.16 in section 2.2.4.2) should therefore include a first additional interface, namely an electronic junction between the copper (Cu′) and the zinc on the negative electrode side. This interface is generally omitted. But rigorously speaking, the voltage between the two extreme points that is represented in this figure is different from the voltage U measured by a voltmeter. This discrepancy corresponds to the voltage of the Cu′|Zn electronic junction. Since this value is constant whatever the cell's operating mode, this precision is not essential provided that only voltage variations are studied. In this chapter, the voltage value, shifted by the electronic junction voltage, will be simply denoted by «U»:*

$$«U» = \varphi_+ - \varphi_- = U - U_{\text{connections electronic junction}}$$

This point will be taken up again in the introduction to section 3.4 and laid out in detail in section 3.4.1.1.

the terminals of a given conductor volume that is part of a chain with a current flowing through it.

For each of the two extreme interfacial voltages, if we opt for the sign convention which writes the potential difference between the metal and the electrolyte, $\Delta\varphi = \varphi_{\text{metal}} - \varphi_{\text{electrolyte}}$, then it gives the following:

$$E_+ - E_- = \Delta\varphi_+ - \Delta\varphi_- + \sum U_{\text{ohmic drop}} + \sum U_{\text{junction}}$$

The ohmic drop terms can either be positive or negative depending on the situation[35]. In simple systems, the ohmic drop across a conducting volume is proportional to the current flowing through it[36]. It corresponds to the OHM law at the macroscopic level,

$$U = RI \qquad \text{(absolute value[35])}$$

Figure 2.11 gives a diagram representing a potential profile in a DANIELL cell:

Zn | $ZnSO_4$ aqueous sol. | KNO_3 aqueous sol. | $CuSO_4$ aqueous sol. | Cu

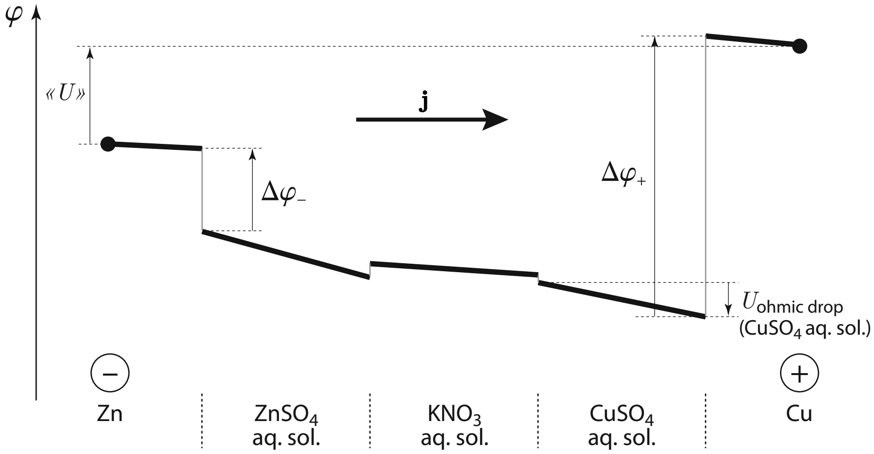

Figure 2.11 - Potential profile in a DANIELL cell working as a power source[37]

To avoid overloading the diagram, only the ohmic drop across the $CuSO_4$ aqueous solution is represented by an arrow.

The diagram shows the profile on the scale of the system with a current flowing through it, whereby copper is the cathode and zinc the anode. In other words, the cell is working as a power source[38]. The voltage between the terminals in this electrochemical cell can

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[35] *Section 2.2.4.2 shows the potential profile in an electrochemical system working either as a power source or as an electrolyser. The differences between the ohmic drops are also highlighted (see figures 2.15 and 2.16).*

[36] *Appendix A.4.1 deals with a more complicated case, in which this relationship no longer holds*

[37] *For a precise definition of «U», refer to note [34].*

[38] *Note (see section 1.4.3) that the current always flows from the positive electrode towards the negative electrode in the circuit part which is out of the power supply device. Figure 2.11 describes the situation inside the electrochemical cell working as a power source where current flows from the negative electrode to the positive electrode. On the other hand, the current flow out of the cell is indeed directed from the positive towards the negative electrode.*

be separated into two, firstly in ohmic drop terms (in the electronic conductors and in the three different ionic conductors) and secondly in interfacial voltage terms (for the electrochemical interfaces, $\Delta\varphi_+$ and $\Delta\varphi_-$, and the two ionic junctions between the solutions)[34]. It will be noted in this diagram that, as in figure 2.1 at open circuit, the various interfacial voltage signs, $\Delta\varphi_+$ and $\Delta\varphi_-$, are arbitrary (shown as positive in this diagram). On the other hand, the sign for potential variations in the conducting volumes (represented in the diagram by negative slopes) tallies logically with the direction of the current, and therefore with the sign for the various ohmic drops, which are here negative. It will also be noted that in power source mode, the direction of the electric field is opposite to what one would expect from the system's polarities.

For a system which starts in equilibrium at open circuit and with negligible ionic junction voltages, the word overpotential usually refers to the difference between the interfacial voltages observed with and without current flow. In connection with the general definition[39], the ohmic drop terms are therefore excluded from overpotential terms. It all comes down to being able to imagine that one can place two references infinitely close to each of the interfaces. The following equation is therefore commonly used:

$$E_+ - E_- = \Delta E_{\text{eq}} + \eta_+ - \eta_- + \sum U_{\text{ohmic drop}}$$

Other systems require more complex descriptions because, even at open circuit, the conducting volumes are not necessarily equipotential. The voltage expression with no current is not simpler than the corresponding expression for when a current is flowing through[40]. However, if the ohmic drop at open circuit can be disregarded, just as much as to what degree the sum of the ionic junction voltages evolves when a current flows, then we can write the following simplified equation:

$$E_+ - E_- = E_+(I = 0) - E_-(I = 0) + \pi_+ - \pi_- + \sum U_{\text{ohmic drop}}$$

Subsequently, this chapter will only describe situations of this type. Notably, what will not be touched upon are electrochemical systems in which the ionic junction voltages undergo large changes when there is a current flow.

From a practical point of view, it is often useful to bring in a reference electrode to separate the overall voltage between the system's terminals. The reference electrode splits the cell into two parts, allowing one to distinguish between the contributions at both extremities. However, one must keep in mind the fact that if the various ohmic drops are significant in value, then the spatial position of the reference electrode has an impact on the experimental values of the voltages being measured.

◤ Returning to the example of the DANIELL cell (figure 2.11), two types of potential measurements can be compared, when the reference electrode is dipped either into the $CuSO_4$ aqueous solution or in $ZnSO_4$ aqueous solution. As shown in the diagram in figure 2.12, the first case gives a measurement for the potential of the positive electrode ($E_{\text{Cu}} - E_{\text{Ref 1}}$) with an ohmic drop contribution that is smaller than that of the negative

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[39] Refer to section 1.5.2.

[40] For instance, in an open-circuit system not in equilibrium, such as a metal undergoing corrosion, the current density is not strictly zero at any point in the electrolyte. Even if the overall current is zero, the electrolyte and the electrodes are not necessarily equipotential and therefore the ohmic drop terms may not necessarily be zero in open-circuit conditions.

electrode ($E_{\text{Zn}} - E_{\text{Ref 1}}$). In the second case (with Ref 2), the measure of the potential of the negative electrode will be closest to its interfacial voltage.

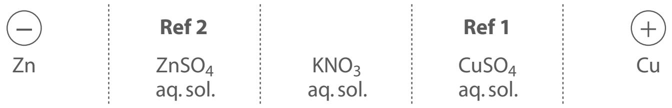

Figure 2.12 - Different positions for a reference electrode in a DANIELL cell

2.2.4 - OHMIC DROP IN A CONDUCTING MEDIUM

The sum of ohmic drops across each conducting medium represents a part of the overall voltage between the terminals in an electrochemical cell. The precise size of that share depends on the system in question. The aim here is to evaluate these terms by focusing on simple cases.

2.2.4.1 - OHM'S LAW AND THE OHMIC DROP

In certain experimental conditions the diffusion layers occupy only a small part of the total volume of each conducting medium. Therefore, as far as conduction modes are concerned, the quasi-totality of the volume of each conducting medium presents a case of pure migration [41]. In other instances, when a supporting electrolyte [42] is present and if the overall current and migration current can be considered as equal, then once again it is simple to define the potential and calculate the ohmic drop, even if the diffusion layers are thick. We can then consider that the current density of each charge carrier is proportional to the electric field [43].

It is the local expression of OHM's law:

$$\mathbf{j} = -\left(\sum_i \sigma_i\right)\mathbf{grad}\,\varphi = \sigma\,\mathbf{E} = \frac{1}{\rho}\,\mathbf{E}$$

with:

$\mathbf{j}$	the current density, with the modulus in	[A m^{-2}]
σ_i	the electric conductivity due to species i	[S m^{-1}]
σ	the electric conductivity of the medium	[S m^{-1}]
$\mathbf{E}$	the electric field, with the modulus in	[V m^{-1}]
ρ	the electric resistivity of the medium	[Ω m]

In any conducting medium, outside the diffusion layers, there is a constant electric conductivity for each charge carrier [44]. By integrating the local expression of OHM's law

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[41] When convection occurs, the overall convection current density is zero (see section 4.2.1.5). Therefore, when expressing the overall current density in a zone where diffusion can be disregarded, only the migration terms are to be taken into consideration.

[42] Sections 2.2.1.1 and 2.2.4.4 as well as appendix A.4.1 all give a definition of a supporting electrolyte, and explore some of the properties which are directly linked to its presence.

[43] Refer to section 4.2.1 which describes the macroscopic laws of conduction, and in particular, migration terms.

[44] The various concentrations are homogeneous outside the diffusion layers. The conductivity is also constant in the corresponding volume, since it is only dependent on these concentrations (for an isothermal system, see sections 2.2.4.3 and 4.2.2).

taking into account the system's geometry, one obtains the ohmic drop across the medium ($U = RI$, in absolute value).

For instance, the potential profile is linear in the case of a cylindrical homogeneous conductor with a length ℓ and a normal cross section of area S, as represented in figure 2.13. The system's geometry is called unidirectional, which means that the equipotential surfaces are planes and the current lines are straight[45].

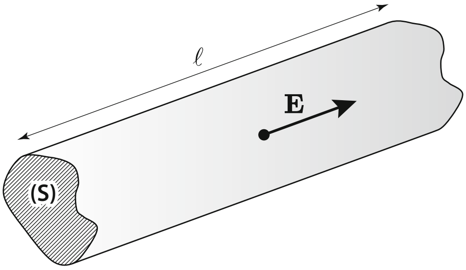

Figure 2.13 - Diagram of a conducting volume with a unidirectional geometry

The resistance of the electrolyte volume, R, and the potential difference, U, between two sections positioned at a distance equal to ℓ are:

$$R = \frac{\rho\,\ell}{S} = \frac{\ell}{\sigma\,S} \quad \text{and} \quad U = \frac{\rho\,\ell}{S}\,I = \frac{\ell}{\sigma}\,j$$

with:

R	the resistance of the electrolyte volume	[Ω]
ρ	the electric resistivity	[Ω m]
σ	the electric conductivity	[S m^{-1}]
ℓ	the length of the cylinder	[m]
S	the surface area	[m^2]
U	the potential difference	[V]
I	the current	[A]
j	the current density modulus	[A m^{-2}]

◤ When fixing an order of magnitude for the ohmic drop in an electrochemical cell, let us consider a cylindrical electrochemical cell where two electrodes with identical geometry are positioned 5 cm apart. It is assumed that the thickness of the diffusion layers will be small enough to guarantee that the only significant quantity is the ohmic drop in the bulk electrolyte. During electrolysis, a current with a density of 7 mA cm^{-2} flows through the cell (same area for the electrodes, therefore the same current density). The electrolyte contains sulphuric acid with a concentration of 0.5 mol L^{-1}, which acts as a supporting electrolyte and therefore sets the solution's conductivity at a value of $\sigma = 43\ \mathrm{S\,m^{-1}} = 0.43\ \mathrm{S\,cm^{-1}}$.

In this cell with unidirectional geometry the ohmic drop is given by the following equation:

$$U = \frac{\rho\,\ell}{S}\,I = \frac{\ell}{\sigma}\,j$$

hence the ohmic drop is 81 mV.

---

[45] *The first step when studying electrochemical engineering often involves determining how the current lines and equipotential surfaces are distributed. In this first step, the only phenomenon taken into account is migration in the electrolyte given the cell geometry. In this case we commonly refer to the primary distribution of the current. The geometry in question here, which is an example of unidirectional geometry, was selected on the grounds that it is very simple. Obviously, it does not fit all the different types of experimental device.*

This value is rather high, although the solution used is highly concentrated. One can spot the great influence of the distance between the electrodes.

To determine the various orders of magnitude, one can calculate that the ohmic drop across a metallic sample with identical geometry, and with a conductivity of $\sigma = 5\times10^7$ S m^{-1} $= 5\times10^5$ S cm^{-1}, would be equal to 0.1 µV. In most electrochemical systems the ohmic drop is found mainly in the electrolyte. However, this is not a hard and fast rule. For example, in certain industrial plants where aluminium is produced[46], the current density is about 1 A cm^{-2}, the mean voltage is about 4.3 V, including an ohmic drop of 2.4 V. This ohmic drop is divided up into 1.7 V in the electrolyte and 0.7 V in the electrodes (aluminium, carbon, etc.), as well as the current leads and the connections between adjacent cells (an industrial installation is made up of many cells connected in series).

2.2.4.2 - MOVEMENT DIRECTION VIA MIGRATION

In the case of migration, negatively charged species (electrons, anions) and positively charged species (electron holes, cations) move in opposite directions: positive charges migrate in the same direction as that of the electric field and negative charges move in the opposite direction. Yet the corresponding current densities always have the same direction as that of the electric field, as illustrated in figure 2.14.

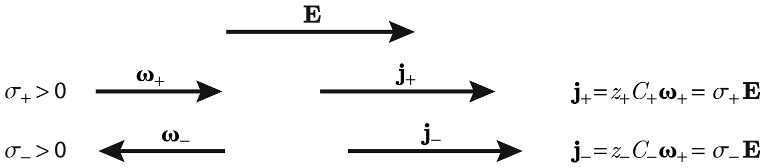

Figure 2.14 - Diagram showing the movement of charge carriers in an electric field: $\boldsymbol{\omega}_i$, velocity, and $\mathbf{j}_i$, current density of species i

The conductivity of each type of charge carrier (as well as the overall electric conductivity) is always positive. Therefore when considering any conducting material, including mixed conductors, one has:

$$\sigma = \underbrace{\sigma_{\text{electrons}} + \sigma_{\text{holes}}}_{\sigma_{\text{electronic}}} + \underbrace{\sigma_{\text{anions}} + \sigma_{\text{cations}}}_{\sigma_{\text{ionic}}}$$

It is important to underline the fact that in such a simple example of pure migration, the direction in which the ions move is unequivocally linked to the direction of the current density. Cations move in the same direction as the current density and anions move in the opposite direction. The following sentence expresses these characteristics, with the merit of being easy to remember and applicable for both a power source and an electrolyser.

Anions migrate towards the anode, cations migrate towards the cathode.

This result can be generalised to fit most electrochemical systems: the sufficient condition is that the migration current densities are in the same direction as the total current density[47].

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

[47] *Section 4.2.1.5 gives an example which lays out in detail the link between the overall current density and migration current density.*

One should avoid oversimplifying and focusing exclusively on an electrostatic viewpoint by only looking at the polarities of the electrodes. Nor should one jump to the conclusion that cations are attracted and therefore migrate towards the electrode with negative polarity. In a cell which works as a power source, the cations migrate towards the cathode, which is the positive electrode in the system. The great error here would be to take into consideration the overall potential difference between the two electrodes (merely focusing on the polarities), whereas the electric field that governs the migration process is the one found in the electrolyte, that is having already excluded the two interfacial zones. This aspect has been illustrated previously in figure 2.11, showing the potential profile in a DANIELL cell in the power source mode, as well as by the following simpler example where power source and electrolyser modes are compared in a system with no ionic junction.

In other respects, one must carefully keep in mind the fact that migration is nothing more than just one amongst other transport modes. Just because a cation migrates towards the cathode, this does not mean that it cannot react at the anode[48]. In the latter case, the effect of the convection and diffusion of the cation pushes it in the opposite way to that of migration[49].

◤ A lithium battery is an example of an electrochemical chain with no ionic junction which can be considered to be in equilibrium at open circuit:

$$\mathrm{Li} \mid \text{organic solution of LiTFSI} \mid \mathrm{Li_xMnO_2}$$

The organic electrolyte is a solution in an organic solvent of Li^+ cations and bis-(trifluoromethanesulfonyl)imide anions denoted by $TFSI^-$.

- The diagrams in figure 2.15 represent the potential profile on the scale of the system, either when it is at open circuit or when a current is flowing through it in the power source mode (or discharge mode): here lithium metal, which constitutes the negative electrode, is the anode.

  As in figures 2.1 and 2.11, the signs for $\Delta\varphi_+(I=0)$ and $\Delta\varphi_-(I=0)$ are chosen at random. Each of the diagrams are set with the same given potential at a random point in the electrolyte, whether it be in the system at open circuit or in the same system with a current flowing through it. To give an example, this random point might be where a reference electrode could be placed. On the other hand, the sign of the potential variation in the conducting volumes (corresponding to the various ohmic drops and represented in the diagram by straight-lined slopes) follows the direction of the current flow.

  The diagrams highlight the following general relationships[50]:

$$\Delta\varphi_- - \Delta\varphi_-(I=0) = \eta_- = \eta_{\mathrm{an}} > 0$$
$$\Delta\varphi_+ - \Delta\varphi_+(I=0) = \eta_+ = \eta_{\mathrm{cat}} < 0$$

  We therefore end up with a decrease in the overall voltage, $U < U(I=0)$, for a system working as a power source.

---

[48] *Section 1.2.1 has already shown that a cation can act as either oxidant or reductor in a redox couple.*

[49] *Systems where the migration and diffusion fluxes directions are different are presented in qualitative terms in section 4.3.1.5.*

[50] *These general relationships can be illustrated in a different way by using the current-potential curves to spot the working point of an electrochemical system, as described in sections 2.4.3 and 2.4.4.*

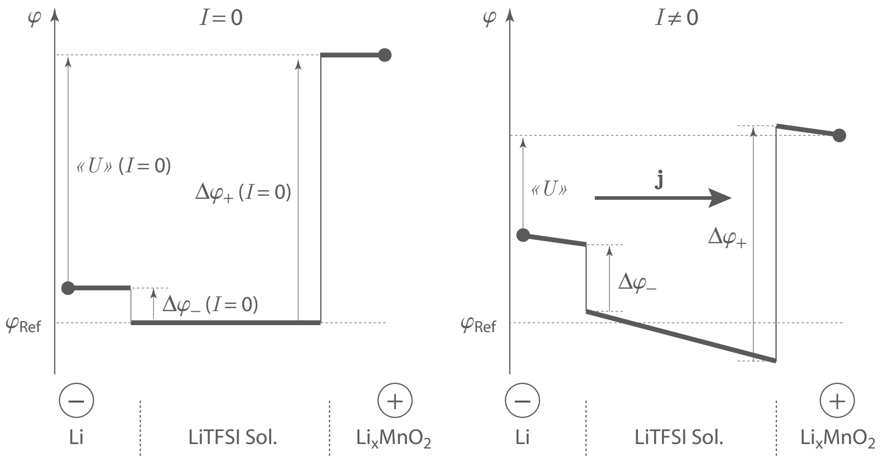

Figure 2.15 - Comparison of the potential profiles in a system in equilibrium with the same system working as a power source[51]

- The second diagram in figure 2.16 corresponds to the same system, which is however in electrolyser mode (or recharging battery mode): the lithium negative electrode is the cathode.

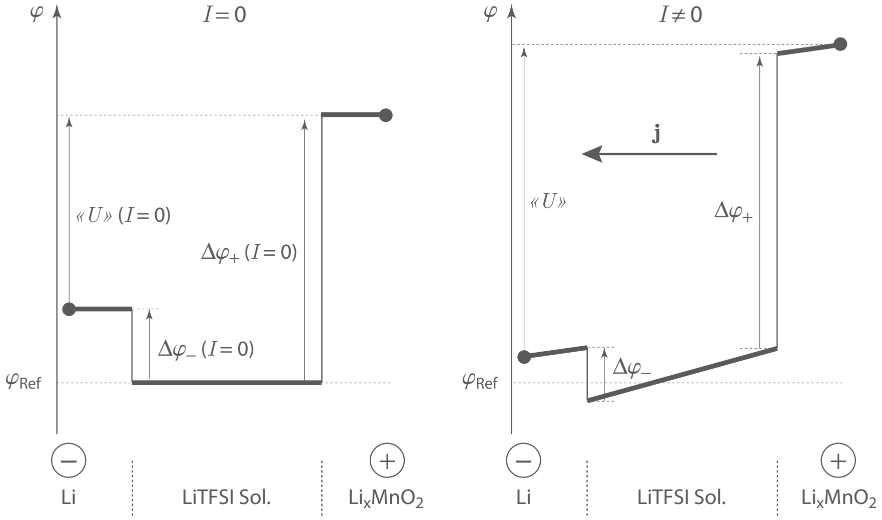

Figure 2.16 - Comparison of the potential profiles in a system in equilibrium with the same system working as an electrolyser[51]

In this second case, the diagrams highlight the following general relationships[48]:

$$\Delta\varphi_- - \Delta\varphi_-(I=0) = \eta_- = \eta_{\text{cat}} < 0$$

$$\Delta\varphi_+ - \Delta\varphi_+(I=0) = \eta_+ = \eta_{\text{an}} < 0$$

We therefore end up with an increase in the overall voltage, $U > U(I=0)$, for a device working as an electrolyser.

---

[51] *The voltage «U» is the voltage between the cell terminals, up to a constant: see note [34] of section 2.2.3.*

In connection with the sign of the ohmic drops, let us highlight the fact that when in power source mode, the ohmic drop decreases the output voltage of the cell. Yet when in electrolyser mode it leads to an increase in the voltage, which must be imposed so as to trigger the reaction(s). In both cases ohmic drops cause energy losses, in the form of heat loss (JOULE effect).

2.2.4.3 - MOLAR CONDUCTIVITIES AND TRANSPORT NUMBERS

The electrical conductivity in conductors is a function of their charge carrier number per unit volume. The relationship between conductivity and concentration is not necessarily a simple function[52]. Nevertheless the molar conductivity of each type of charge carrier can be defined by the following equation:

$$\lambda_i = \frac{\sigma_i}{C_i} \quad \text{or} \quad \sigma_i = \lambda_i C_i$$

with:

with:	λ_i	the molar conductivity of charge carrier i	[S m^2 mol^{-1}]
	σ_i	the electric conductivity of charge carrier i	[S m^{-1}]
	C_i	the concentration in charge carrier i	[mol m^{-3}]

λ_i is, as σ_i, a positive quantity (see figure 2.14).

For a solution with a solute concentration C, the molar conductivity, $\Lambda = \sigma / C$, is also defined. For a solute $A_{p_+}B_{p_-}$, the ionic concentrations are:

$$C_+ = p_+ C \quad \text{and} \quad C_- = p_- C$$

hence, since $\sigma = \sigma_+ + \sigma_-$,

$$\Lambda = p_+ \lambda_+ + p_- \lambda_-$$

If the only significant transport mode is migration[53], then the fraction of the current which is transported by a species i, i.e., the latter species' contribution to the overall conductivity, is expressed by a quantity called the transport number of i. This is defined by the following:

$$t_i = \frac{I_i}{I} = \frac{j_i}{j} = \frac{\sigma_i}{\sigma}$$

with

$$\sum_i t_i = 1$$

Generally, this notion of transport number is used when the only transport mode that is to be considered is migration. Since all the current densities are parallel and have the same direction (that of the electric field, see figure 2.14), then the transport number values are between 0 and 1.

---

[52] *Section 4.2.2.5 describes how the relationship between conductivity and concentration is, for instance, rather complicated for concentrated solutions*

[53] *The general definition for transport numbers in the case where diffusion, migration and convection are all simultaneously involved in mass transport is given in section 4.1.1.3 and illustrated in appendix A.4.1.*

When dealing with all the various types of conducting media, the total conductivity is the quantity that is easiest to measure. If one wants to distinguish between the different contributions of the various charge carriers then this requires a set of complementary transport number measurements which are often more complex in experimental terms.

The level of conductivity in a decimolar aqueous solution of calcium nitrate, $Ca(NO_3)_2$, which is a strong electrolyte, is measured as $\sigma = 26.2$ mS cm^{-1} at 25 °C. Assuming that the molar conductivity is unrelated to the concentrations, we are able to calculate the molar conductivity of the electrolyte, that of the calcium ions and the transport numbers of the two types of ions present in the solution (with data provided in scientific literature, see table 4.2 in section 4.2.2.4):

$$\lambda_{NO_3^-} = \lambda^\circ_{NO_3^-} = 7.14\times10^{-3}\ \mathrm{S\,m^2\,mol^{-1}}$$

$$\sigma = 26.2\ \mathrm{mS\,cm^{-1}} = 2.62\ \mathrm{S\,m^{-1}}$$

$$\begin{cases} [NO_3^-] = 2C = 0.2\ \mathrm{mol\,L^{-1}} = 200\ \mathrm{mol\,m^{-3}} \\ [Ca^{2+}] = C = 0.1\ \mathrm{mol\,L^{-1}} = 100\ \mathrm{mol\,m^{-3}} \end{cases}$$

$$\sigma = \lambda_{NO_3^-}[NO_3^-] + \lambda_{Ca^{2+}}[Ca^{2+}] = (2\,\lambda_{NO_3^-} + \lambda_{Ca^{2+}})C = \Lambda C$$

hence $$\Lambda = 26.2\times10^{-3}\ \mathrm{S\,m^2\,mol^{-1}}$$

and $$\lambda_{Ca^{2+}} = 11.9\times10^{-3}\ \mathrm{S\,m^2\,mol^{-1}}$$

Often, data tables which are drawn up for solutions still take into account the values of the so-called equivalent conductivity λ_{eq}. For example, in the case of Ca^{2+} one finds:

$$\lambda_{\frac{1}{2}Ca^{2+}} = \frac{1}{2}\lambda_{Ca^{2+}} = \lambda_{eq} = 5.96\times10^{-3}\ \mathrm{S\ m^2\ mol^{-1}}$$

However, the notion of equivalent, which tends to disappear, will not be used here, because it will only confuse the issue.

As for transport numbers, the following ratio is determined:

$$t_{NO_3^-} = \frac{\sigma_{NO_3^-}}{\sigma} = \frac{\lambda_{NO_3^-}}{\lambda_{NO_3^-} + \frac{1}{2}\lambda_{Ca^{2+}}} \quad \text{and} \quad t_{Ca^{2+}} = 1 - t_{NO_3^-}$$

$$t_{NO_3^-} = 0.545 \quad \text{and} \quad t_{Ca^{2+}} = 0.455$$

2.2.4.4 - THE SUPPORTING ELECTROLYTE

Now let's imagine that one introduces into an ionically conducting medium a strong electrolyte in high concentration in comparison to the concentration level of other ions in the medium (a factor of 100 is generally considered to be sufficient). Here we observe how the quasi-totality of the migration current is due to this electrolyte. This is what is called a supporting electrolyte. Usually, the supporting electrolyte is made up of non-electroactive ions, and plays no part in the faradic phenomena (redox reactions) at the interfaces. On the other hand, it does contribute to the current flow in the electrolyte volume and possibly to the capacitive current at the interfaces.

The effects of introducing a supporting electrolyte can be highlighted by numerical calculations involving transport numbers and conductivities in two different solutions:

- an aqueous solution containing silver nitrate with a concentration of 10^{-3} mol L^{-1},

- an aqueous solution containing silver nitrate with a concentration of 10^{-3} mol L^{-1} and potassium nitrate with a concentration of 0.1 mol L^{-1}.

To find the different values of molar conductivity at infinite dilution one can refer to the relevant literature (see table 4.2, section 4.2.2.4). For the purposes of simplicity, we will assume here that the molar conductivities are unrelated to the concentrations:

$$\begin{aligned} \lambda_{NO_3^-} &= \lambda°_{NO_3^-} = 7.14\times10^{-3}\ \mathrm{S\ m^2\ mol^{-1}} \\ \lambda_{Ag^+} &= \lambda°_{Ag^+} = 6.19\times10^{-3}\ \mathrm{S\ m^2\ mol^{-1}} \\ \lambda_{K^+} &= \lambda°_{K^+} = 7.35\times10^{-3}\ \mathrm{S\ m^2\ mol^{-1}} \end{aligned}$$

- silver nitrate solution:

$$[Ag^+] = [NO_3^-] = 10^{-3}\ \mathrm{mol\ L^{-1}} = 1\ \mathrm{mol\ m^{-3}}$$

The solution's conductivity is calculated using the following equation:

$$\sigma = \lambda_{NO_3^-}\,[NO_3^-] + \lambda_{Ag^+}\,[Ag^+] = (\lambda_{NO_3^-} + \lambda_{Ag^+})\,[Ag^+]$$

hence $\sigma = 13.3\times10^{-3}\ \mathrm{S\ m^{-1}} = 1.33\times10^{-4}\ \mathrm{S\ cm^{-1}}$

The transport numbers of the two ions are equal to:

$$\begin{cases} t_{Ag^+} = \dfrac{\sigma_{Ag^+}}{\sigma} = \dfrac{\lambda_{Ag^+}}{\lambda_{NO_3^-} + \lambda_{Ag^+}} = 0.46 \\[2ex] t_{NO_3^-} = \dfrac{\sigma_{NO_3^-}}{\sigma} = \dfrac{\lambda_{NO_3^-}}{\lambda_{NO_3^-} + \lambda_{Ag^+}} = 0.54 \end{cases}$$

- silver and potassium nitrate solution:

$$\begin{cases} [Ag^+] = 10^{-3}\ \mathrm{mol\ L^{-1}} = 1\ \mathrm{mol\ m^{-3}} \\ [K^+] = 0.1\ \mathrm{mol\ L^{-1}} = 100\ \mathrm{mol\ m^{-3}} \\ [NO_3^-] = 0.1 + 10^{-3} \approx 0.101\ \mathrm{mol\ L^{-1}} = 101\ \mathrm{mol\ m^{-3}} \end{cases}$$

The solution's conductivity is calculated using the following equation:

$$\sigma = \lambda_{NO_3^-}\,[NO_3^-] + \lambda_{Ag^+}\,[Ag^+] + \lambda_{K^+}\,[K^+] \approx (\lambda_{NO_3^-} + \lambda_{K^+})\,[K^+]$$

hence $\sigma = 14.6\times10^{-1}\ \mathrm{S\ m^{-1}} = 1.46\times10^{-2}\ \mathrm{S\ cm^{-1}}$

This value is about 100 times higher than in the last solution. Moreover, it gives the following transport numbers:

$$\begin{cases} t_{Ag^+} = \dfrac{\sigma_{Ag^+}}{\sigma} = \dfrac{10^{-3}\ \lambda_{Ag^+}}{10^{-3}\,\lambda_{Ag^+} + 0{,}1\ \lambda_{NO_3^-} + 0{,}1\ \lambda_{K^+}} \approx 0.004 \\[2ex] t_{K^+} = \dfrac{\sigma_{K^+}}{\sigma} = \dfrac{0{,}1\ \lambda_{K^+}}{10^{-3}\,\lambda_{Ag^+} + 0{,}1\ \lambda_{NO_3^-} + 0{,}1\ \lambda_{K^+}} \approx 0.49 \\[2ex] t_{NO_3^-} = \dfrac{\sigma_{NO_3^-}}{\sigma} = \dfrac{0{,}1\ \lambda_{NO_3^-}}{10^{-3}\,\lambda_{Ag^+} + 0{,}1\ \lambda_{NO_3^-} + 0{,}1\ \lambda_{K^+}} \approx 0.51 \end{cases}$$

We will keep in mind that here in this second case, when a supporting electrolyte KNO_3 is present, then the solution's conductivity is much higher, and that:

$$t_{Ag^+} \ll t_{K^+} \quad \text{and} \quad t_{Ag^+} \ll t_{NO_3^-}$$

Adding a supporting electrolyte, whenever possible (that is to say, in liquid electrolytes), only serves a purpose in a certain range of applications. For example, being able to disregard the contribution made by electroactive species in the migration transport, often makes easier the use of experimental data, for instance in analytical applications. Adding a supporting electrolyte also increases the electrolyte's overall conductivity. However, in many industrial applications, there is a sufficiently large amount of electroactive species to ensure that the electrolyte has a good level of conductivity, all of which generally does away with the need for an additional compound. This is particularly key for example when the weight of the overall system is seen as an important criterion as in applications for batteries in portable electronic devices.

2.3 - THE SHAPE OF THE CURRENT-POTENTIAL CURVES

In the description given outlining electrochemical systems in which a current flows, key parameters include the variations of the anodic and cathodic polarisations (or overpotentials if applicable) as a function of current and time. These relationships are generally represented in the form of current-potential curves of an electrode, $I = f(E)$, where E is the voltage between the electrode in question and a reference electrode[54]. The experimental results can also be presented in the form of current density-potential curves. However, when the study concerns the whole electrochemical system and is not just focused on the working electrode, it is best to keep the current-potential representation[55].

Generally speaking, these characteristics are time-dependent. Here, we will only look at the steady-state current-potential curves, so called because they are obtained in steady-state conditions. However the shapes presented remain valid in qualitative terms at all times. Moreover, the voltage that is accessible in experimental conditions includes an ohmic drop term between the electrode in question and the reference electrode. However, this simplified description will not take into account this ohmic drop. Yet this type of curve, once corrected for the ohmic drop, can be determined in most cases in experimental conditions. Here we will discuss their shape in qualitative terms but not the detail of the curves[56].

The current-potential curves reflect the kinetic behaviour of redox systems since they indicate the changes in current, and therefore also indicate the changes in the reaction rate for different values of the potential. The word kinetic is very broad and includes the

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[54] *Some books also call these curves polarisation curves, especially those which choose to represent the potential as a function of the current. The* EVANS *diagrams, depicting the use of currents in corrosion, provide an example of such a type of representation. In this document, we will only choose to use the current-potential representation which is quite a natural choice if the data are recorded using potentiostatic techniques.*

[55] *Sections 2.4.2 to 2.4.5 describe various examples that illustrate the importance of using current-potential curves when discussing the operating conditions in electrochemical systems. This choice is explained by the fact that, contrary to current density, the current remains constant in all sections of the system, as presented in section 1.4.1.3.*

[56] *Quantitative analytic expressions of these curves are given for simple redox systems in section 4.3.3.*

whole phenomena leading to the current flow. In electrochemistry, the two main types of phenomena involved are frequently distinguished using the expressions ' mass transport kinetics ' and ' redox reaction kinetics '[57]. Sections 2.3.2 and 2.3.3 describe the main impact of both types of kinetic phenomena on the shape of the current-potential curves.

2.3.1 - GENERAL CHARACTERISTICS

2.3.1.1 - POLARISATION SIGN

The polarisation sign depends on each particular situation encountered. Drawing an analogy with mechanical systems can help one understand certain rules about this sign. Whilst an object moves spontaneously from an initial velocity in an environment where it is only subject to friction force, then the mechanical energy decreases. Therefore, to maintain a given speed, a supplement is needed to compensate for the energy that is dissipated by the friction force. To cause a current to flow in an electrochemical chain operating as an electrolyser, that is to say, in order to produce a given reaction rate, an additional electric energy supply is needed due to electric polarisations. One can argue that electric polarisations play a role that matches that of the force in brakes, namely friction. They must be overcome in order to impose a given rate, in other words a given current. This extra energy supply is reduced to heat in the electrochemical system, as in the JOULE effect.

To sum up, given the chosen convention for the current sign[58], the following relationships are generally true:

$$\pi_+ \, I_+ > 0 \quad \text{and} \quad \pi_- \, I_- > 0$$

and similarly $$\pi_{\text{an}} \, I_{\text{an}} > 0 \quad \text{and} \quad \pi_{\text{cat}} \, I_{\text{cat}} > 0$$

Remember that anode polarisation is positive whilst cathode polarisation is negative.

The current-potential curves are therefore often monotonous and with a positive slope (following the sign conventions chosen in this document), however this is not an absolute rule[59]. In this book we will limit ourselves to monotonous curves.

It is important not to confuse the concepts of the polarity and the polarisation of an electrode. There is no necessary connection between the signs of these two quantities. Thus during electrolysis, the positive electrode is the anode and its polarisation is positive. In other words, its potential, when a current is flowing, is higher than when it is measured without a current. Yet when the system is working as a power source, then the

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[57] *Section 4.3.2.1 gives a thorough, qualitative description of the phenomena that are involved when current flows through an electrochemical system*

[58] *The current sign convention used in electrochemistry is presented in detail in section 1.4.1.3.*

[59] *For example, when a metal surface is passivated due to an insulating layer forming (oxide, hydroxide, etc.) then there is a blockage in the redox reaction. The current then decreases sharply. This phenomenon can be observed when drawing a curve $I(E)$ in the potentiostatic mode. In intensiostatic mode, the potential suddenly jumps towards a value where a new redox reaction occurs.*

positive electrode is the cathode and its polarisation is negative. In the latter situation, the fact that there is a current flowing implies that one is only able to retrieve a reduced part of the electric energy, due to the electric polarisations in the system.

If both two species of a redox couple Ox/Red are present, then the current-potential curve takes on the shape as shown in figure 2.17. In this type of representation, the use of an arrow enables us to identify the polarisation at a given working point. The sign for polarisation is positive if the arrow points in the same direction as the potential axis, as shown in figure 2.17, and negative if the arrow points in the opposite direction. By convention, on a current-potential curve the two elements of the redox couple which are responsible for the current, are indicated as well as an arrow specifying the direction of the reaction (oxidation direction for a positive current). Given the direction of the potentials axis (increasing potential to the right), the reduced species (Red) of the couple is placed on the left and the oxidised species (Ox) on the right. This corresponds to a similar representation in predominance diagrams, which are used for instance for acido-basic equilibria[60]. When following common electrochemical conventions, one must therefore always represent the reactions by using an arrow to the right for positive currents (oxidation) and an arrow to the left for negative currents (reduction).

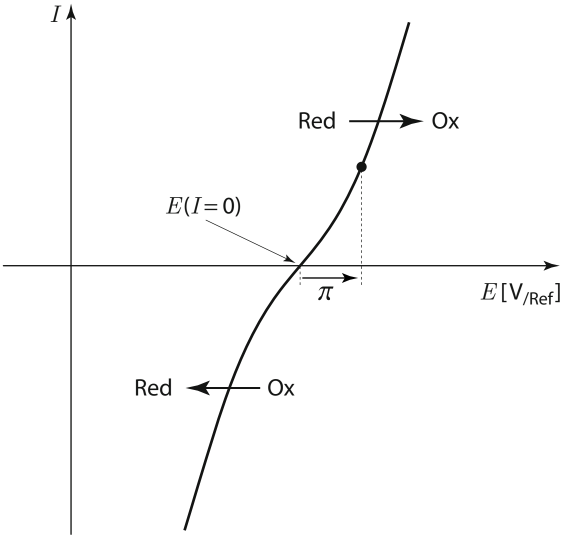

Figure 2.17 - Current-potential curve of an electrode when both elements of a redox couple are present

In the particular case in point here, the two elements of a single redox couple are present and therefore the open-circuit potential corresponds to the equilibrium potential given by the NERNST law that is applied to that couple. In this case, we can use the term of overpotential instead of polarisation.

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[60] *In fact an analogy can be made between the NERNST law for the potential of a redox couple and the law which expresses the pH of a solution based on the pK_a and the respective concentrations of the two forms of an acido-basic couple.*

2.3.1.2 - STEADY-STATE CURVES

If only one species of the couple is present in the system studied, then the shape of the current-potential curve is different from that shown in figure 2.17 and the open-circuit potential cannot be defined simply by this species alone. In particular, the NERNST law can no longer be applied. The activity of one of the species of the redox couple is zero, therefore giving no value for the equilibrium potential. On the other hand, insofar as we are only representing steady-state current-potential curves here, if a species is absent in the initial system, then this remains the case throughout the experiment. Therefore this species cannot contribute to the faradic current. Only one part of the curve is seen in this case, and can be either anodic or cathodic depending on the situation. For example, if we look at the interface between a copper electrode and a large volume of aqueous electrolyte devoid of Cu^{2+} ions, then the steady reduction of the Cu^{2+}/Cu redox couple is not possible. The corresponding current-potential curve is therefore situated entirely in the anodic zone corresponding to copper oxidation, as shown in figure 2.18.

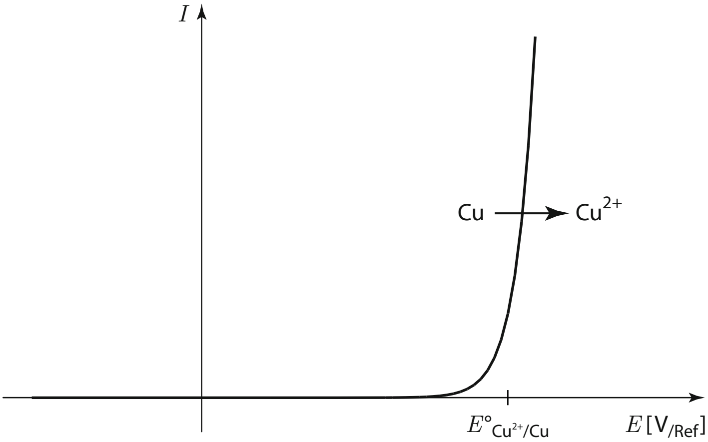

Figure 2.18 - Current-potential curve when only one element of the redox couple is present
Example of a copper electrode dipped in an aqueous solution containing no Cu^{2+} ions.

In this system, which is actually quasi-steady[61], Cu^{2+} ions are produced when one measures a point corresponding to a non-zero current on the anodic branch. There can be a high concentration of these ions in the diffusion layer next to the working electrode (copper). However, given how large the volume of the electrolyte, the amount of Cu^{2+}ions produced during this measuring process is very low. Therefore in practice, when examining the operating conditions at lower potentials, where a reduction of Cu^{2+} ions would be expected, no steady-state current can be found. This is because the Cu^{2+} ions previously produced are extremely diluted in the overall volume of the electrolyte and are no longer in the diffusion layer[62].

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[61] *Section 1.6.4 focuses on the notion of strictly steady systems.*

[62] *This particular characteristic of current-potential curves is linked to the steady character, which is chosen for this description. In transient experiments such as voltammetry, using a copper electrode with no Cu^{2+} ions in the solution, one would see a reduction current during the reverse scan of the*

Another important point, as far as the steady-state current-potential curves are concerned, is the position on the potential axis of the branch plotted, which in the example above is anodic. As previously underlined, no equilibrium potential can be spotted because the open-circuit potential cannot be defined by the NERNST law. However, it is quite useful to have the thermodynamic constant associated with the redox couple in question, which in this case is the standard potential [63] $E°(Cu^{2+}/Cu)$, because this enables one to position the current-potential curve, i.e., the potential zone where the current undergoes sharp variations (see figures 2.18 above and 2.21 in section 2.3.2.2) [64]. Our aim here is to plot and use the shapes of the curves rather than to estimate their precise mathematical expression or any potential values to the mV.

If a current flows through a system for a long time, then one generally witnesses a variation in the chemical composition of the medium. Such a system is no longer steady, unlike the system presented in the example above. Then one observes a current which corresponds to a species that is produced at the electrode but which was not present in the electrolyte from the start. This is illustrated in figure 2.20 in section 2.3.2.1.

2.3.2 - ROLE OF MASS TRANSPORT KINETICS

2.3.2.1 - LIMITING CURRENT

When mass transport kinetics interferes, the steady-state current-potential curves show a limiting current for the redox process, which brings into play this mass transport. The limiting current is shown on a current-potential curve as a horizontal plateau. It is often also called a limiting diffusion current. It is dependent on the mass transport parameters (migration, diffusion and convection) and is, with a few exceptions [65], proportional to the concentration of the consumed species, because their mass transport limits the reaction rate and therefore the current flow [66].

Let us return to the example of the interface between a copper electrode and an aqueous electrolyte now containing Cu^{2+} ions. With both elements of the Cu^{2+}/Cu couple present, the two branches of the current-potential curve are then observed. For a cathodic working point, Cu^{2+} ions must be carried to the cathode to be reduced. As shown in figure 2.19, a reduction limiting current is observed, with a value proportional to the Cu^{2+} concentration in the bulk solution.

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voltammogram (which is also a current-potential curve). The Cu^{2+} ions produced by the oxidation of the copper electrode during the direct scan are still partly present at the interface during the reverse scan.

[63] *Generally, the value to consider here is the apparent standard potential when it is relevant (see section 2.1.2.2 with, for instance, the IO_3^-/I^- couple in a buffered medium).*

[64] *This property applies for rapid systems. The changes of current-potential curves are discussed in section 2.3.3, when the kinetics of the redox reactions interferes.*

[65] *Such exceptions are found for example in the case of electrolytes with both members of a given redox couple in conditions where their migration cannot be disregarded (an absence or too small a quantity of supporting electrolyte).*

[66] *Section 4.3.3.1 outlines the quantitative laws linking the limiting current to the concentration in consumed species in simple systems.*

On the other hand, the shape of the current-potential curve is different in the oxidation branch because metallic copper is not concerned by any mass transport phenomenon, since copper is always present at the interface. The zone where the current undergoes large variations is close to the open-circuit potential, which is, in this case, equal to the equilibrium potential of the system. The latter, which can be calculated using the NERNST law, is shifted slightly from the standard potential. To give an order of magnitude for a concentration in Cu^{2+} ions equal to 10^{-3} mol L^{-1}, there is the following:

$$\begin{aligned} E_{\mathrm{eq}} &= E^\circ_{\mathrm{Cu^{2+}/Cu}} + \frac{0.06}{2}\log\left(a_{\mathrm{Cu^{2+}}}\right) \\ &\approx E^\circ_{\mathrm{Cu^{2+}/Cu}} + \frac{0.06}{2}\log\left[\mathrm{Cu^{2+}}\right] = E^\circ_{\mathrm{Cu^{2+}/Cu}} - 90\,\mathrm{mV} \end{aligned}$$

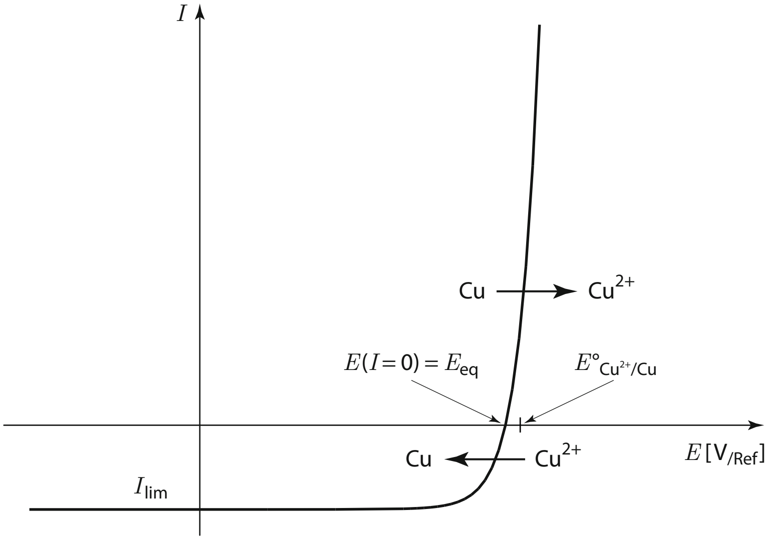

Figure 2.19 - Current-potential curve of a copper electrode in an acidic aqueous solution containing Cu^{2+} ions

In another kind of experiment, starting with no Cu^{2+} ions in an aqueous solution, the limiting current can be used to follow the reaction progress during an electrolysis with a copper anode. This example is detailled in the next page and illustrated in figure 2.20.

There is another particular case concerning limiting currents where certain electroactive species are found in very large quantities compared to the other electroactive species studied (for example, the solvent in systems with electrolyte solutions). Since the limiting currents are proportional to the corresponding concentrations in solution, the plateau resulting from the mass transport limitation for these couples is much larger (in absolute value) than that of the other redox couples in the system. These large limiting currents are hardly visible and the current increases very sharply (in absolute value) on the scale of the current-potential curves. The definition of the electrochemical window of a system is based on these characteristics. The term solvent window is also used, even if this constitutes a misnomer when the corresponding reaction involves either the supporting electrolyte or the electrode itself (see section 2.3.6).

Take the example of electrolysis being carried out in an electrochemical system, with copper oxidation as the anodic reaction in a non-renewed solution, which at the outset contained no Cu^{2+} ions. If we draw a quick steady-state current-potential curve at different times throughout the electrolysis process, then we can trace the electrolysis progress by measuring the limiting reduction current, which indicates the concentration of Cu^{2+} ions generated. The time required to draw each current-potential curve is very small compared to the electrolysis duration and the system can be considered in a quasi-steady state during this short time period. The system is no longer steady on the time scale of the electrolysis process as shown by the difference between the two current-potential curves in figure 2.20.

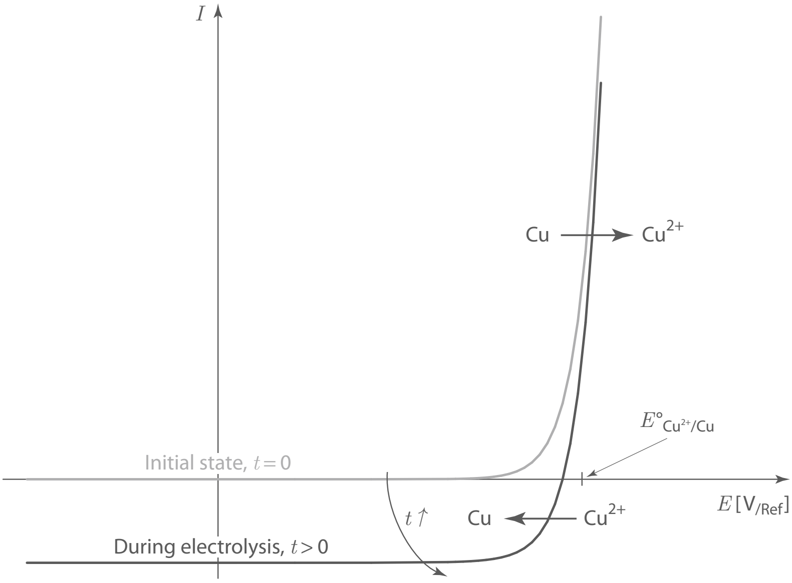

Figure 2.20 - Example of a copper electrode dipped in an aqueous solution containing initially no Cu^{2+} ions: changes during oxidation

2.3.2.2 - HALF-WAVE POTENTIAL

Even though the aim of this presentation is not to outline quantitative relationships, it is nonetheless interesting to know a property which characteristically emerges when these curves are described in quantitative terms[67]. It is indeed possible to show that for simple redox systems with very close transport parameters (in the example below, the diffusion coefficients of the two ions of the Fe^{3+}/Fe^{2+} couples are taken as equal) the value of the current for the standard potential[68] is equal to half the sum of the limiting currents (see figure 4.26 in section 4.3.3.2). In other words, the half-wave potential, $E_{1/2}$, and the standard potential are identical. When systems contain both elements of a redox couple at the outset, then this particular detail has little impact on how the current-potential curves are plotted in qualitative terms, since the NERNST law allows one

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[67] *Quantitative analytic expressions for these curves are given for simple redox systems in section 4.3.3.*

[68] *More generally speaking, the value to consider here is the apparent standard potential, when it applies.*

to spot the open-circuit potential. Yet in the opposite case, when only one species of a redox couple is present, then on the contrary this becomes a highly relevant detail in helping to correctly draw the shape of the current-potential curves. Take the example of the current-potential curve of a platinum electrode dipped in an aqueous solution containing Fe^{2+} ions and no Fe^{3+} ions, as shown in figure 2.21.

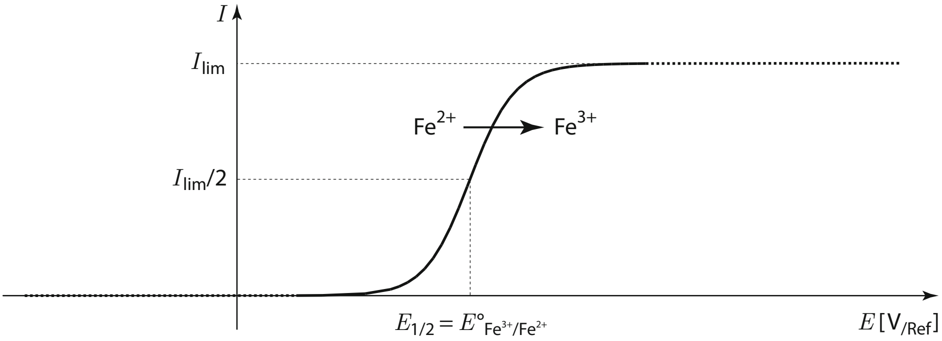


Figure 2.21 - Current-potential curve of a platinum electrode dipped in an acidic aqueous solution containing Fe^{2+} ions

Given that Fe^{2+} is the only electroactive species, only the anodic branch is observed in a limited potential range. This branch presents a limiting current that is proportional to the Fe^{2+} concentration in the bulk solution. In this case (no Fe^{3+} in the bulk electrolyte) it is not possible to spot the equilibrium potential of the redox couple. However, if one wishes to correctly situate the potential zone where the current sees sharp variations, then it is adequate to know that the half-wave potential is close to the standard potential of this couple.

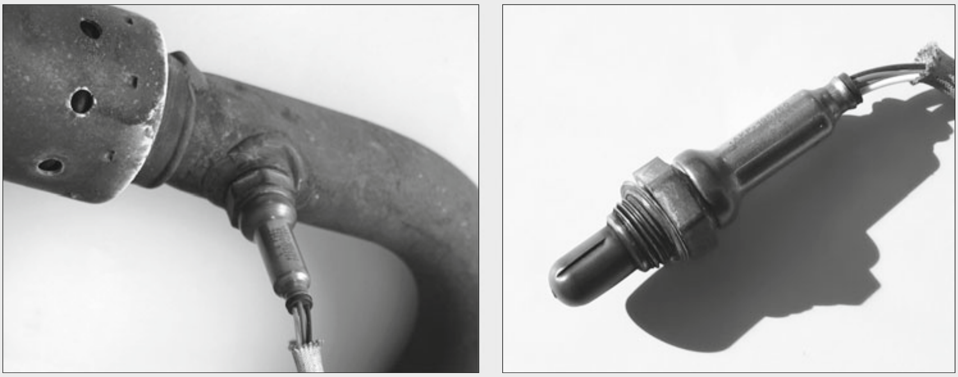
The value of the couple's standard potential (or apparent potential when it applies) is what enables one to position the potential range where the current varies greatly, assuming that one is only interested in the shape of the current-potential curves and provided that the kinetics of the redox reactions does not interfere (see section 2.3.3). One must not forget that when the concept of apparent standard potential becomes relevant, then it has to be taken into account to locate the portions of current-potential in relation to each other. For example, in a very basic medium, the characteristics of the various couples may or may not depend on the pH of the system, and consequently the order of the apparent standard potentials can be reversed in relation to the order in highly acidic medium.

This reasoning, based on the value of half-wave potentials, leads to a qualitative but rigorous drawing of current-potential curves. This line of reasoning is in contrast with common habits found in scientific literature, especially in the field of corrosion. In this area, when drawing the current-potential curve shape in an example where only one redox species is present, one takes into consideration an arbitrary and low concentration of the missing species, most often 10^{-6} mol L^{-1} (but why not 10^{-7} mol L^{-1} or 10^{-9} mol L^{-1}?) as present, meaning that the equilibrium potential can be calculated using the NERNST law. It is not valid to take this value for the open-circuit potential.

REGULATING OF FUEL ENGINES

Document written with the kind collaboration of J. FOULETIER,
professor at Joseph Fourier University of Grenoble, in France

The ‘ lambda ’ sensor is used to monitor internal combustion engines. It is shaped like a candle and placed in the vehicle exhaust pipe at the outlet of the cylinder head. It is a potentiometric type of sensor using a closed-bottom ceramic tube. Several million examples of this type of sensor are produced every year.



Photograph of a lambda sensor extracted from a car after use

The type of solid electrolyte used is yttria-stabilised zirconia ($ZrO_2 - Y_2O_3$, 8% molar), and conducts with O^{2-} oxide ions. Both the interior and exterior surfaces of the tube are coated with platinum paint, and constitute the electrodes. The reference electrode of the cell is the oxygen in the air in contact with the inside wall of the tube. The external surface of the tube is in contact with the exhaust gases. The measuring electrode is protected by a metal cover and a porous oxide layer.

The electrochemical chain is: O_2(air),Pt | $O^{2-}_{\text{solid electrolyte}}$ | Pt,O_2(gas).

If the electrode were in equilibrium, the NERNST law would give the accurate partial pressure of oxygen in the analysed gases which is fixed by the mixture of combustion products. In fact, the exhaust gases are not in equilibrium, and therefore the device merely serves to indicate any oxygen excess or lack in the fuel mixture at the carburettor outlet. To prevent the measuring electrode from being contaminated, it is imperative that the fuel used is lead-free.

The term ‘lambda’ indicates that the sensor is designed to operate at the stoichiometric point, which has an air/fuel ratio equal to 14.5. The transition from a ‘rich’ mixture in fuel (therefore meaning poor in oxygen) to a ‘poor’ mixture, or indeed the opposite transition, entails a shift in the signal delivered by the sensor which is over 500 mV. Such a variation is sufficient for the sensor (which itself is placed in a feedback loop) to provide adequate control of the carburettor operation.

To finish, similar other sensors using stabilised zirconia are also developed to measure the partial pressure of oxygen to be found in gases (air, and waste gas) or in molten metals (in metallurgy). However, these sensors have a reference electrode made of a metal which is mixed with its oxide inside the zirconia tube.

2.3.3 - ROLE OF REDOX REACTION KINETICS

The redox reactions kinetics also plays a part in shaping the current-potential curves. Assume[69] that the main impact is the change seen in the potential zones which relate to the rising parts of the curve, themselves corresponding to the redox couple. Therefore, for the two limiting cases concerning the kinetics of redox reactions, most often referred to as fast and slow couples[70], we find the following:

- for fast couples, the kinetics of the redox reaction, in other words the electron transfer step, has no impact on the current-potential curve. Moreover this curve shows significant current variations around the half-wave potential, in other words around the standard potential. This case applies to all the examples seen so far;

Consider the interface between an organic solvent containing Li^+ ions and the solid phase Li_xMnO_2 (manganese oxide which is a lithium insertion material). The system is in thermodynamic equilibrium when no current flows through it. The equilibrium potential is generally close to the standard apparent potential (see insertion isotherm in section 2.1.2.2):

$$E_{\text{eq}} = E^\circ_{\text{app}_{MnO_2/LiMnO_2}} + \frac{RT}{\mathcal{F}} \ln \frac{1-y}{y}$$

The shape of the current-potential curve is presented in figure 2.22.

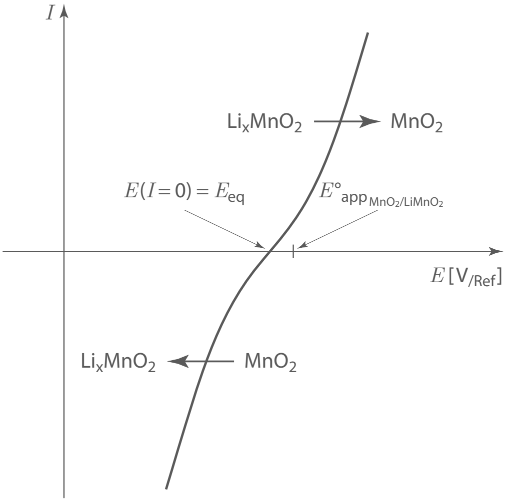


Figure 2.22 - Current-potential curve of a manganese oxide electrode in an organic solution containing Li^+ ions

- for slow couples, however, the kinetics of the redox reaction has a strong influence on the characteristics of the current-potential curve. This curve shows a significant potential difference between the anodic and cathodic branches when both species of

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[69] *Section 4.3.3 gives quantitative analytic expressions of these curves for simple redox systems as a function of various kinetic and thermodynamic parameters.*

[70] *Section 4.3.2.6 gives a precise definition of the terms fast and slow, which characterise the charge transfer kinetics of simple redox systems.*

the couple are present in the bulk of the electrolyte or electrode. In the anodic branch, large current variations are found around a potential called the anodic half-wave potential, $E_{1/2_{an}}$, which is higher than the thermodynamic standard potential[71]. The difference between the anodic half-wave potential and the standard potential of the couple in question increases as the kinetics of the redox reaction slows down. The cathodic branch shows similar behaviour, with a cathodic half-wave potential that is algebraically lower than the standard potential. All things being equal, if you take the example of a redox couple involving a simple mechanism and two species, it gives a change in current-potential curves as appears in figure 2.23, when the kinetics of the redox reaction varies. The cathodic and anodic half-wave potentials are indicated for the very slow system of curve **d**[72].

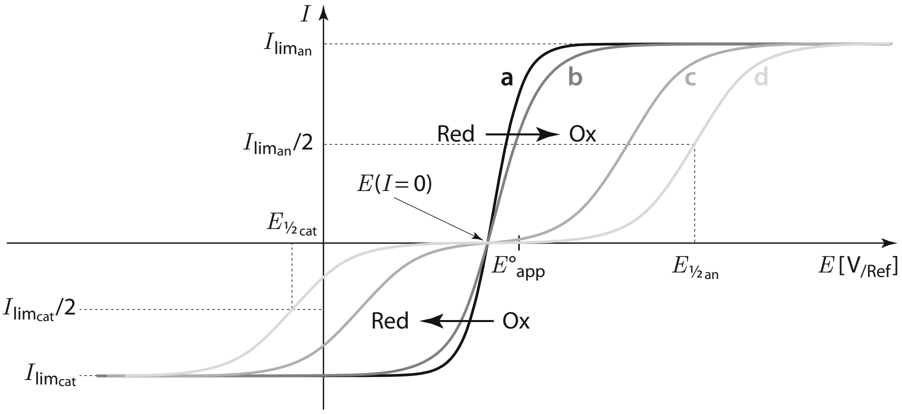

Figure 2.23 - Current-potential curve of an electrode containing both elements of a redox couple present for systems with different redox kinetics
***a** - very fast; **b** - fast; **c** - slow; **d** - very slow*

Certain documents refer to the difference between the half-wave potential and the equilibrium potential as an activation overpotential[73]. This terminology is not used here because it is rarely possible to distinguish the various contributions to a system's overpotential in unambiguous terms[74].

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[71] *Generally speaking, the value to consider is that of the apparent standard potential when it applies. Section 4.3.3.3 gives a precise definition of the anodic and cathodic half-wave potentials for slow systems and the relationship with the system's kinetic parameters.*

[72] *When establishing a method for determining redox kinetics, one can consider using the value of the slope of the current-potential curve for the open-circuit potential. However, it is impossible to assign a specific slope value to a fast couple because this slope is highly dependent on the limiting anodic and cathodic currents. To approach this issue from a quantitative point of view, one can start from the expression of the polarisation resistance around the equilibrium potential (see section 4.3.3.4).*

[73] *This derives from the notions of activation energy and activated complex (see section 4.3.2.3). It therefore refers to the influence of the redox half-reaction kinetics. The term activation polarisation can also be found, yet it is even less suitable if the system at open circuit is not in equilibrium.*

[74] *This question is approached from a more precise quantitative angle for simple systems in section 4.3.3.4.*

The kinetics of redox reactions naturally depends on the couple in question but may also depend on the electrode where the reaction is occurring, even if this electrode does not play an explicit role in the overall redox reaction (it then intervenes in the mechanism). This is the case for instance in the reduction of protons in acidic medium. Here, the characteristics vary depending on the nature of the electrode where the reaction is occurring (e.g., platinum or mercury, see figure 2.31 in section 2.3.6).

2.3.4 - ADDITIVITY OF FARADIC CURRENTS OR CURRENT DENSITIES

Remember that faradic currents are additive: if several electroactive species react at a given interface, the overall current density is the sum of the corresponding current densities. In simple cases, the overall current-potential curve at an interface is therefore obtained by adding the individual current-potential curves of each electroactive species. It must be emphasised that the curve resulting from this sum is the only curve that is accessible through experiments. The situation becomes more complicated when the interface is not uniform as is often the case in corrosion[75]. Here we will limit ourselves to simple cases.

For any given system, one can predict the shape of the current-potential curve of an interface by carrying out the following steps:

- make a list of the electroactive species actually present in the system at the interface in question, paying attention not to forget the solvent or the electrode material when they are not inert. Any species that are present in only trace amounts in the medium will not be considered in this qualitative reasoning, except in specific cases. For example, if you consider the shape of the current-potential curve for a copper electrode (see figure 2.18), even though the copper electrode used contains traces of another electroactive element, it is represented by taking into account the material as if it were pure;
- list all the possible redox couples relating to each species identified. In particular one must remember that for aqueous solution, water is involved in two redox couples[76]: $O_2/H_2O,OH^-$ and $H^+,H_2O/H_2$;
- position the standard potentials (apparent standard potentials when it applies[77]) for each of these couples;
- represent the current-potential curves of each electroactive system by positioning them using the standard potential (to see how this positioning is done refer to sections 2.3.2 et 2.3.3);
- finally, for each potential value, sum up the currents of all the curves previously drawn. The resulting curve is the only one accessible in an experiment.

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[75] *In corrosion phenomena, the same interface can frequently present both anodic and cathodic zones.*

[76] *The terms used to denote both the water redox couples presented in section 2.1.2.3 correspond with the terms used to write these two same couples in acidic or basic media.*

[77] *The concept of apparent standard potential, defined in section 2.1.2.2 (and 2.1.2.3 for water couples), can be useful when one or several chemical species written in the redox half-reaction are found in very large quantities compared to the other. This is often the case for instance for redox couples in very acidic or very basic solutions.*

For a given potential, the construction of the overall current-potential curve from the different contributions of each electroactive species allows to view the concept of faradic yield as shown below.

Consider the interface between an inert platinum electrode and a deaerated aqueous electrolyte (that is, without any dissolved oxygen left) containing H^+ ions ($pH = 2$) and Ni^{2+} ions. This example picks up again on the system previously chosen to illustrate the concept of faradic yield (see section 2.2.2.3). The shape of the overall current-potential curve is shown in figure 2.24 with a dashed and dotted line[78].

If we are only interested in the cathodic branch of the curve, then the relevant electroactive species are protons and Ni^{2+} ions. The grey lines represent the current-potential curves that would be seen if only one reducible species were present. Each branch is situated in the zone which corresponds to its apparent standard potential:

$$E^\circ_{Ni^{2+}/Ni} = -0.23\ V_{/SHE} \quad \text{and} \quad E^\circ_{app_{H^+,H_2O/H_2}} = -0.12\ V_{/SHE}$$

The overall current-potential curve (represented by a dashed and dotted line) is the sum of the two grey curves. As for the working point shown in figure 2.24, the current required for the reduction of Ni^{2+} ions, I_1 represents about 25% of the overall current, $I = I_1 + I_2$. This therefore means that the faradic yield for hydrogen production by reduction is equal to about 75%.

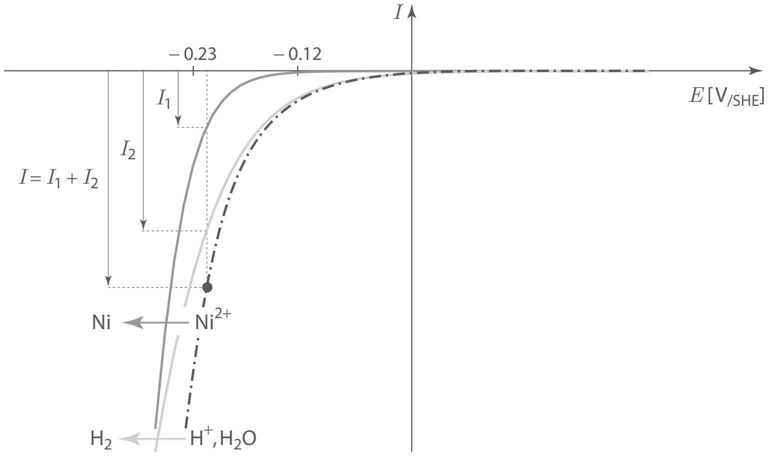

Figure 2.24 - Current-potential curve of a platinum electrode in an acidic solution containing Ni^{2+} ions

2.3.5 - WATER REDOX COUPLES

As already emphasised, the water redox couples play a particularly important role in all electrochemical systems involving an aqueous electrolyte. The corresponding current-potential curves are rather complex, notably because water autoprotolysis occurs[79]. However some qualitative characteristics can be retained, especially for very acidic or

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[78] *Remember that figure 2.24 does not represent experimental data. It is merely a simplified shape illustrating the various principles involved.*

[79] *Appendix A.2.1 focuses in detail on the shape of current-potential curves of the $H^+,H_2O/H_2$ couple, which is supposed to be fast, thus justifying the results stated here.*

very basic media in the case of fast redox reactions[80]. In these conditions, one can say that the apparent standard potential is what defines the position of the current-potential curves in qualitative terms.

For example, let us consider the interface between a very acidic aqueous electrolyte ($pH = 1$), containing neither dioxygen nor dihydrogen dissolved species, and a platinum electrode which is inert in this electrolyte. The only electroactive species present in the bulk electrolyte are protons and water. The corresponding redox couples are $O_2/H_2O,OH^-$ and $H^+,H_2O/H_2$. The shape of the current-potential curve (represented in figure 2.25 with a dashed and dotted line) is the sum of the contributions of each couple (grey curves). These couples are supposed to be fast, and the values of the apparent standard potentials are:

$$E^\circ{}_{\text{app}_{H^+,\,H_2O/H_2}} = -\,0.06\ \text{V}_{/\text{SHE}} \quad \text{and} \quad E^\circ{}_{\text{app}_{O_2/H_2O,OH^-}} = +\,1.17\ \text{V}_{/\text{SHE}}$$

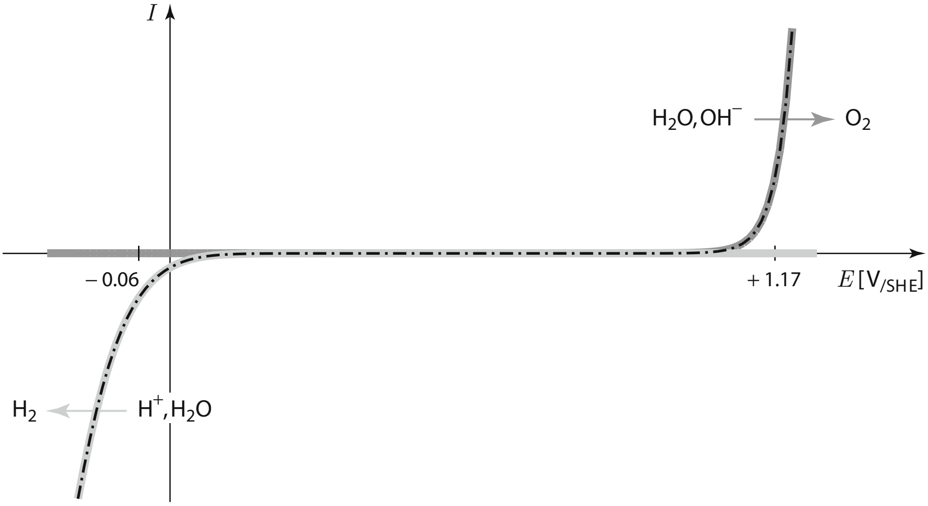

Figure 2.25 - Current-potential curve of a platinum electrode in an acidic aqueous solution

Since there are large quantities of both water and protons, no limiting current plateau can be seen (in the usual current ranges) which would be explained by a limited supply rate of water or protons at the interface. This current-potential curve shows the position of the electrochemical window in this system (see section 2.3.6).

Exactly the same type of current-potential curve would be found for a very basic solution. The only difference in this case would be the values of the apparent standard potential. Here again no limiting current is observed. However, when the pH values become less extreme, the shape of the curve changes and can become quite complex (see appendix A.2.1) as illustrated by the two examples discussed below (figures 2.26 and 2.27).

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[80] *Here one can refer to figure 2.28 that gives an example where the redox reactions kinetics plays a role. It is worth recalling that the current-potential curves in the figures presented in this document are not experimental results but simplified representations to explain the various phenomena involved.*

- Consider the example of an inert platinum electrode and a deaerated electrolyte (with no dissolved dioxygen) containing H^+ ions ($pH=3$) and involving redox couples that are considered to be fast. In these conditions, with a limited amount of protons, a limiting proton reduction current appears in the cathodic domain. However, given the specific characteristics of the water redox couples, H_2O can also be reduced in a second potential zone. Consequently, there is no limiting current plateau in this second zone, as shown in figure 2.26.

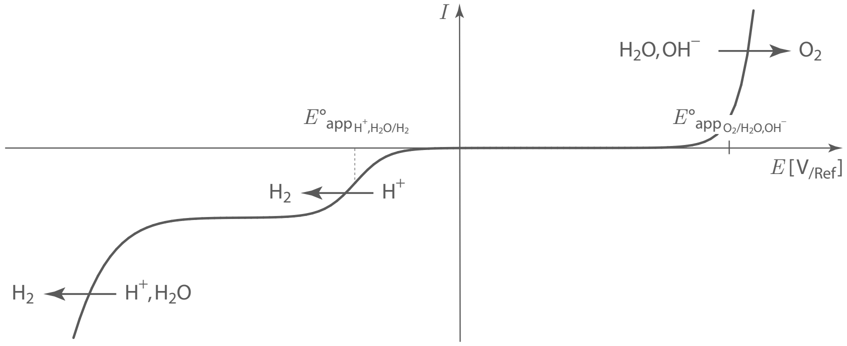

Figure 2.26 - Current-potential curve of a platinum electrode in a deaerated aqueous solution at $pH = 3$

- The behaviour is entirely symmetrical in moderately basic solutions ($pH=11$ for example). The corresponding current-potential curve displays two anodic zones relating to the single $O_2/H_2O,OH^-$ couple, as shown in figure 2.27.

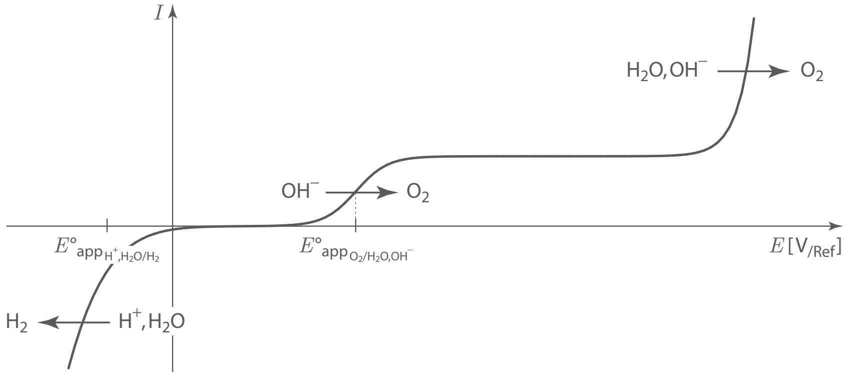

Figure 2.27 - Current-potential curve of a platinum electrode in a deaerated aqueous solution at $pH = 11$

In addition, reactions that produce gaseous dihydrogen (or dioxygen) *via* the reduction (or oxidation) of an aqueous solution are quite complex. The characteristics and even the mechanisms involved differ greatly depending on the nature of the electrode. These reactions are studied extensively, especially in the development of fuel cells whose performance is lowered by any kinetic limitation due to these couples. One of the main limitations faced by fuel cells at moderate temperatures, such as the PEMFC, is the dioxygen reduction reaction[81].

---

[81] *PEMFC: Proton Exchange Membrane Fuel Cell.*

Let us return to the more conventional examples of dioxygen and dihydrogen production, which most of the time form the electrochemical window bounds for electrochemical systems with aqueous electrolytes. Depending on the mechanisms involved, these couples can lead the current-potential curves to take on very different shapes. The simplest case of kinetic limitation can be found when both reactants have slow kinetics, which causes the typical shift in the current-potential curve. This curve shows a common shift towards the potentials that are lower than the apparent standard potential in the case of dihydrogen release, and towards higher potentials in the case of oxygen release. This is typically observed in the current-potential curve for a boron-doped diamond electrode in an acidic solution, as shown in figure 2.28. In the case of these specific redox reactions, given that no limiting currents are defined, then one cannot use the half-wave potentials, which are no longer defined. One then has to resort to the more relative concept of ' effective reaction potential '[82].

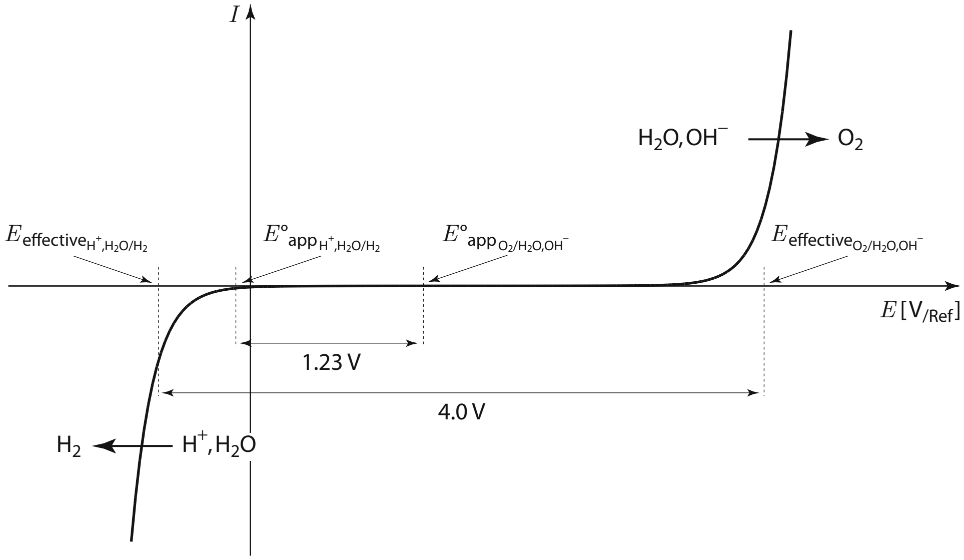

Figure 2.28 - Current-potential curve for a boron-doped diamond electrode in an acidic aqueous solution

We can finally note that, even when no limiting current can be observed as in the case of dihydrogen or dioxygen production, one can still frequently observe a limiting reduction diffusion current (see figure 2.29). This relates to the reduction of dissolved oxygen in the case where the electrolyte has not been correctly deaerated. Indeed, air is made up of about 20% dioxygen and 80% dinitrogen. The solution can only be properly de-oxygenated by bubbling an inert gas through it (most often dinitrogen or argon) if the bubbling phase lasts at least ten minutes or so and if an inert gas atmosphere is maintained above the solution.

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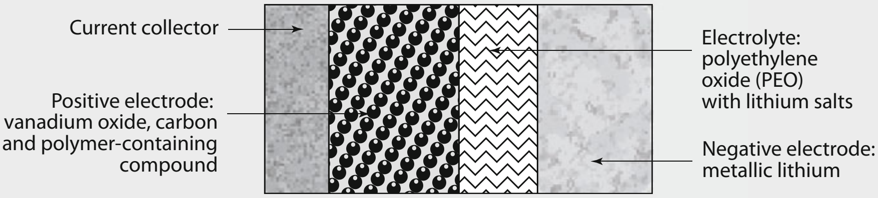
[82] This ' effective reaction potential ' is defined as the potential corresponding to a given current value or current density value taken as reference, and with a typical value of 1 mA cm^{-2}.

ENERGY STORAGE: THE LI-METAL-POLYMER (LMP) BATTERIES

Document written with the kind collaboration of K. GIRARD,
R&D engineer for the company Batscap based in Quimper, France

A secondary battery works on the basis of having two redox couples with different redox potentials. The two electrodes are separated by an electrolyte which is an electronic insulator as well as an ionic conductor. Lithium is a particularly interesting material because it is the lightest of the metals (0.534 g cm^{-3}) and the best at reducing making it an ideal negative electrode material. In the case of lithium-ion batteries, it is only used in its ionic form. The positive and negative electrodes are made up of insertion materials, where lithium ions are inserted in both discharge and charge modes respectively.

In LMP batteries, the negative electrode is a lithium-metal foil, meaning that it enjoys the full range of benefits offered by this material. Another peculiarity of the LMP batteries is the fact that the electrolyte used is a polymer-based solid film. Its main advantages include increased safety (no risk of explosion) and improved processing ability. Its main drawback is low conductivity which means that operations have to be carried out at a temperature between 60 and 80 °C.

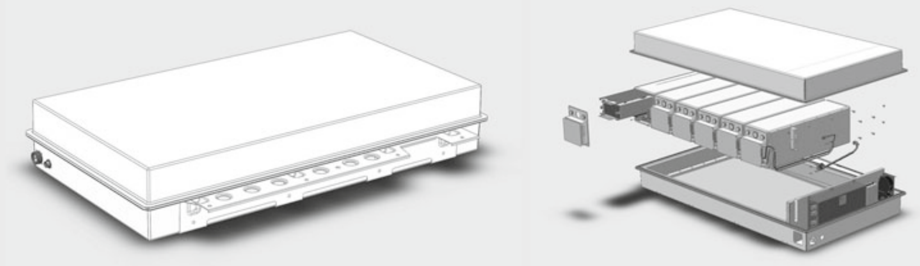


Presentation of the film components in a LMP battery *(© Batscap)*

On discharge:

$$z\,\mathrm{Li} \rightarrow z\,\mathrm{Li}^+ + z\,e^-$$
$$\mathrm{Li}_{x-z}\mathrm{VO}_y + z\,\mathrm{Li}^+ + z\,e^- \rightarrow \mathrm{Li}_x\mathrm{VO}_y$$

This means that a particularly high energy density can be reached, measuring about 100 Wh/kg for a 30 kWh pack. The various electrochemical phenomena at play in the batteries being operated, such as electron transfer or diffusion, limit the power density to around 200 W/kg in discharge for the same battery pack. The LMP's main application is the fully-electric vehicle, for which it works as an energy reservoir. When linked to a supercapacitor, which is a kind of power reservoir, it can provide the ideal performance for use in electric vehicles.



Presentation of a LMP Battery pack of 30 kWh *(photo Batscap)*

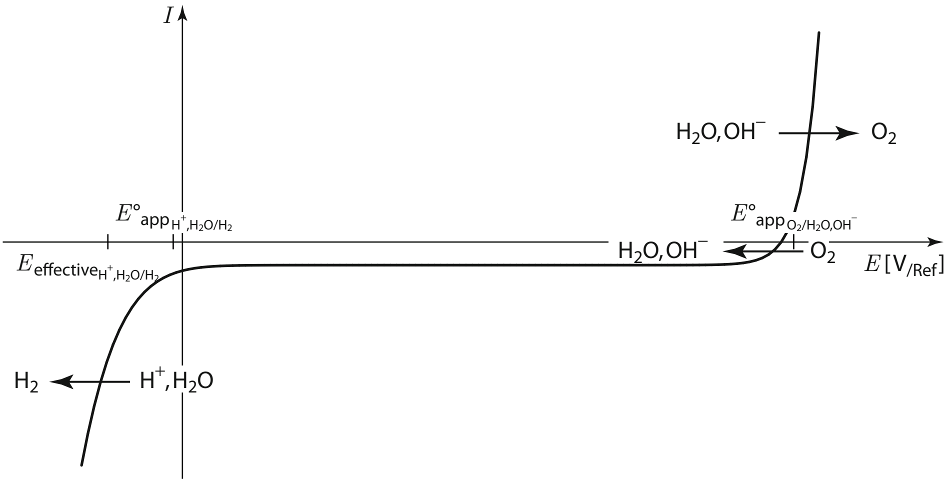


Figure 2.29 - Current-potential curve of a platinum electrode in a non deaerated acidic aqueous solution

The degree to which dioxygen contributes to the current-potential curve often remains negligible, since the concentration level of dissolved dioxygen is quite low with a typical value of 3×10^{-4} mol L^{-1} at usual air pressures. The value for the diffusion limiting current in the case of dissolved dioxygen reduction is therefore around 1 mA cm^{-2} for systems with usual forced convection [83].

2.3.6 - ELECTROCHEMICAL WINDOW

In any electrochemical system the currents created by the redox reactions of the solvent or supporting electrolyte join to combine with the other phenomena, as illustrated in the example below. Figure 2.30 shows the shape of the current-potential curve of a platinum electrode in an acidic solution ($pH = 1$) containing Fe^{2+} ions with a concentration of 10^{-3} mol L^{-1}. The current-potential curve (indicated by a black dashed and dotted line) is the sum of the grey curves corresponding to the Fe^{2+} ions (see figure 2.21) and to the water couples (see figure 2.25).

In practice, when studying a system, it is recommended to first examine the characteristics without yet introducing the electroactive species that is studied. As a result one obtains the current-potential curve of the solvent, possibly with a supporting electrolyte present. This all comes down to drawing a background current-potential curve for the forthcoming measurements, which generally displays a potential window with very low currents. The potential window between the values where the current undergoes a sharp increase is commonly called the ' electrochemical window ' (or sometimes ' solvent window ' even if it corresponds more frequently to the redox stability window of the solvent with a supporting electrolyte). It refers to the system's kinetic stability window,

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[83] *This value corresponds to an RDE experiment, for example, with a rotating speed of about 500 rpm and therefore a diffusion layer thickness of about 30 µm.*

and can be wider than the thermodynamic stability window if the solvent decomposition reactions (or possibly those of the supporting electrolyte) are slow. It provides the potential window that opens up the opportunity to making various experimental studies possible. In fact, in the medium in question, one cannot study any electroactive species with a current-potential curve that is beyond this range. In that instance one would then merely measure the overall current, the majority of which is derived from the solvent, which in itself would completely hide the contribution of the compound added. Figure 2.31 collects together the electrochemical windows of a few systems, giving orders of magnitude. Obviously these values depend on what choices are made for the maximal current/current densities authorized.

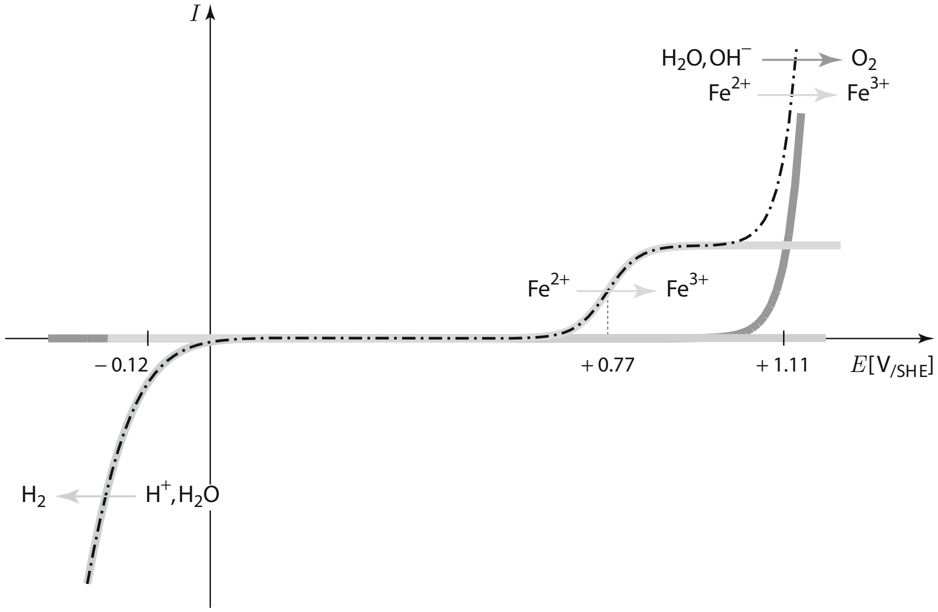
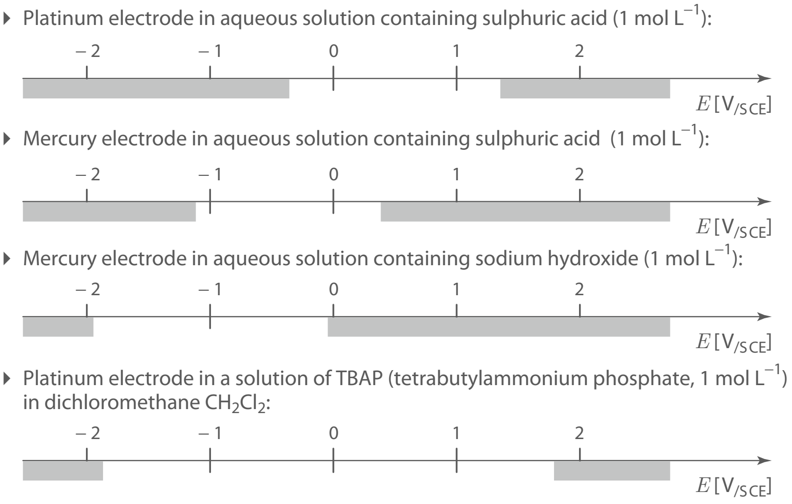


Figure 2.30 - Current-potential curve of a platinum electrode in an acidic aqueous solution containing Fe^{2+} ions

The electrochemical window of a system is highly dependent on the composition of the electrolyte and on the nature of the electrode. This is illustrated below through four different examples: aqueous or organic electrolyte and platinum or mercury electrode. In the latter case, the limiting oxidation reaction is that of mercury oxidation, therefore the term solvent window would be misused. The limits for the potential ranges shown in figure 2.31 are estimated through experimentation for current density values of 10 µA cm^{-2}.

This figure highlights the following in particular:

- organic electrolytes have a redox stability window that is often wider than that of the aqueous electrolytes;
- mercury has the particular effect of considerably slowing down the rate of proton reduction in aqueous solutions. This property is used to advantage in several analytical techniques found in electrochemistry which are particularly effective for analysing trace metal ions, although obviously less used due to the toxicity of mercury. All analytical techniques using mercury are grouped under the term polarography.



- Platinum electrode in aqueous solution containing sulphuric acid (1 mol L^{-1}):
- Mercury electrode in aqueous solution containing sulphuric acid (1 mol L^{-1}):
- Mercury electrode in aqueous solution containing sodium hydroxide (1 mol L^{-1}):
- Platinum electrode in a solution of TBAP (tetrabutylammonium phosphate, 1 mol L^{-1}) in dichloromethane CH_2Cl_2:

Figure 2.31 - Electrochemical windows of four different systems

2.4 - PREDICTING REACTIONS

One can use current-potential curves, whether qualitative or quantitative, as a particularly powerful tool in understanding and/or predicting the reactions occurring in various situations, as well as for accounting for the corresponding working points (U, I).

2.4.1 - SPONTANEOUS EVOLUTION OF A SYSTEM AT OPEN CIRCUIT

The first example discussed here involves predicting reactions occurring in a system with no current. Remember that such a system may or may not be in equilibrium. When describing an entire electrochemical system at open circuit, one usually considers what is occurring at each of the two interfaces as two separate entities. Here we will therefore focus on only one current-potential curve, in other words, one single interface.

Drawing a current-potential curve enables one to identify the processes occurring at open circuit. Indeed, the open-circuit working point (which is located at the intersection between the current-potential curve and the potentials axis) always corresponds to the sum of two opposite currents for oxidation and reduction. Three main scenarios can be distinguished.

- The interface in question is in thermodynamic equilibrium. For this to occur requires the two species of the couple to be present. In these conditions, the open-circuit potential is equal to the potential determined by the NERNST law applied to this redox couple. Figure 2.32 shows how the overall current-potential curve can theoretically be divided down into two contributions, one anodic and the other cathodic. This figure picks up on the example given of the interface between an organic electrolyte containing Li^+ ions and solid Li_xMnO_2 (refer back to figure 2.22). At open circuit, the overall current, which is zero, is the sum of two exactly opposite currents as indicated in the figure by the symbol //. The common absolute value of these currents indicates the rate of the redox kinetics, since it characterises the number of events occurring per unit time in opposite directions, which lead to the equilibrium state without involving any overall chemical transformation. If the couple in question is very slow, then the theoretical value of the open-circuit potential is still defined by the NERNST law. However, because the slope of the current-potential curve is very low, this potential can be significantly affected by small perturbations, with only a slow return to equilibrium. For instance, very low current flow or traces of another species can both make a significant change in the open-circuit potential of such a system.

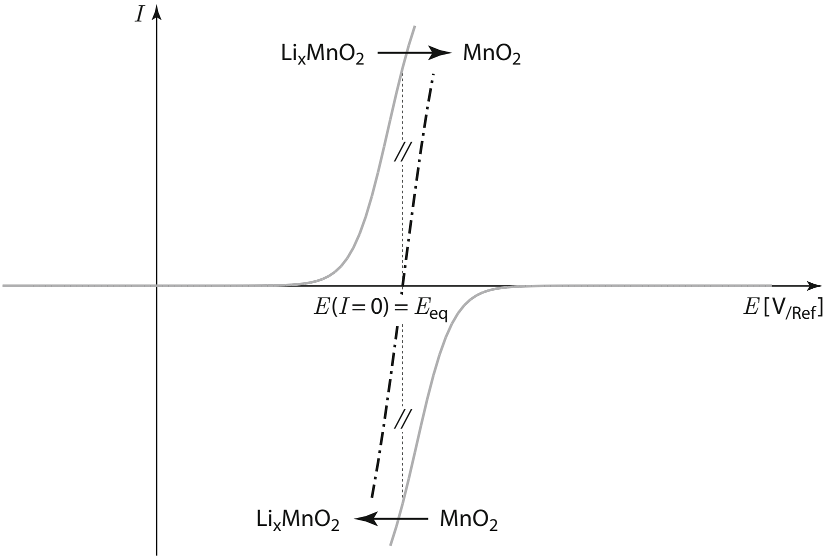


Figure 2.32 - Current-potential curve of a manganese oxide electrode in an organic solution containing Li^+ ions

- The interface in question is not in thermodynamic equilibrium. For this to occur at least two different redox couples must be responsible for the value of the open-circuit potential. The overall zero current then corresponds to a chemical balance which is not null. This is the case for instance in corrosion. The open-circuit condition is not in equilibrium and the system changes with time. The open-circuit potential, which is not given by the NERNST law, depends on the properties of at least two redox couples: in this instance one often refers to the term ‘ mixed potential ’.

For example, in the case of a copper foil immersed in an acidic solution (with no Cu^{2+} ions at the outset) which has not been deaerated, dioxygen can be reduced. The resulting current-potential curve, which is shown by a dashed and dotted line in figure 2.33, is the sum of the three grey curves which relate to the three couples (supposedly fast) present in the system: Cu^{2+}/Cu, $H^+,H_2O/H_2$ and $O_2/H_2O,OH^-$. It is important to emphasise again that the resulting curve shown by a dashed and dotted line is the only one accessible through experiments. As far as the open-circuit potential is concerned, the overall current-potential curve for such a simple system is the sum of the copper oxidation current and the dioxygen reduction current. This accounts for the corrosion of the copper foil, as shown in the following:

$$\begin{array}{c} 4\,H^+ + 4\,e^- + O_2 \longrightarrow 2\,H_2O \\ Cu \longrightarrow Cu^{2+} + 2\,e^- \\ \hline O_2 + 4\,H^+ + 2\,Cu \longrightarrow 2\,H_2O + 2\,Cu^{2+} \end{array}$$

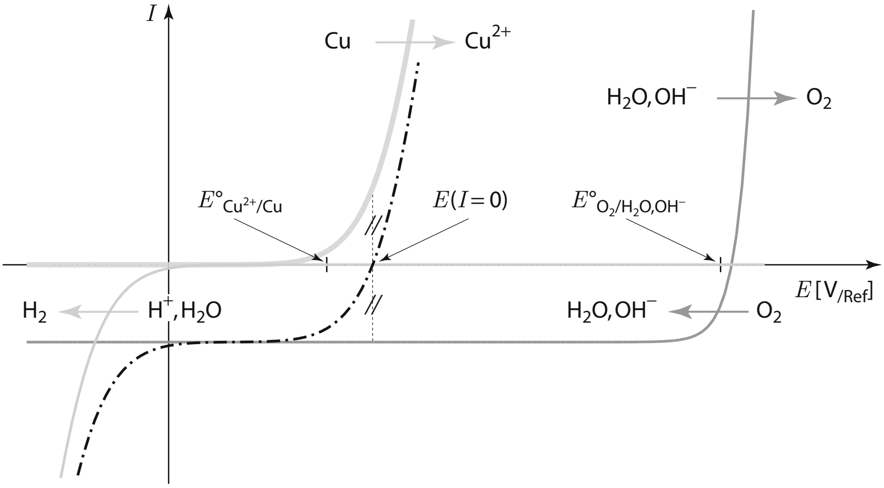


***Figure 2.33** - Current-potential curve of a copper electrode in an acidic aqueous solution containing dissolved dioxygen*

The copper oxidation current at the open-circuit potential is called the corrosion current, and it characterises the metal's corrosion rate. The open-circuit potential, also called corrosion potential, is situated between the standard potentials of the two redox couples involved. There is no simple equation to link these values: more particularly there is no reason why the corrosion potential should be the average of both standard potentials, as illustrated in figure 2.33.

- The interface is not in thermodynamic equilibrium and the properties of the redox couples involved are such that the overall chemical reaction which expresses this situation progresses extremely slowly. If the time scale is not too large then the system undergoes practically no change. However rigorously speaking, this system is not in thermodynamic equilibrium. In particular, the open-circuit potential is a mixed potential which does not depend exclusively on thermodynamic data. Consequently traces of another species may significantly change its value.

◤ Let us look back at the example of an acidic aqueous electrolyte containing neither dioxygen nor dihydrogen in solution and a platinum electrode which is inert in this medium. The only electroactive species here are water and protons, and the redox couples involved are $O_2/H_2O,OH^-$ and $H^+,H_2O/H_2$. The shape of the current-potential curve is represented in figure 2.34 (the same as figure 2.25): the dashed and dotted line corresponds to the overall curve.

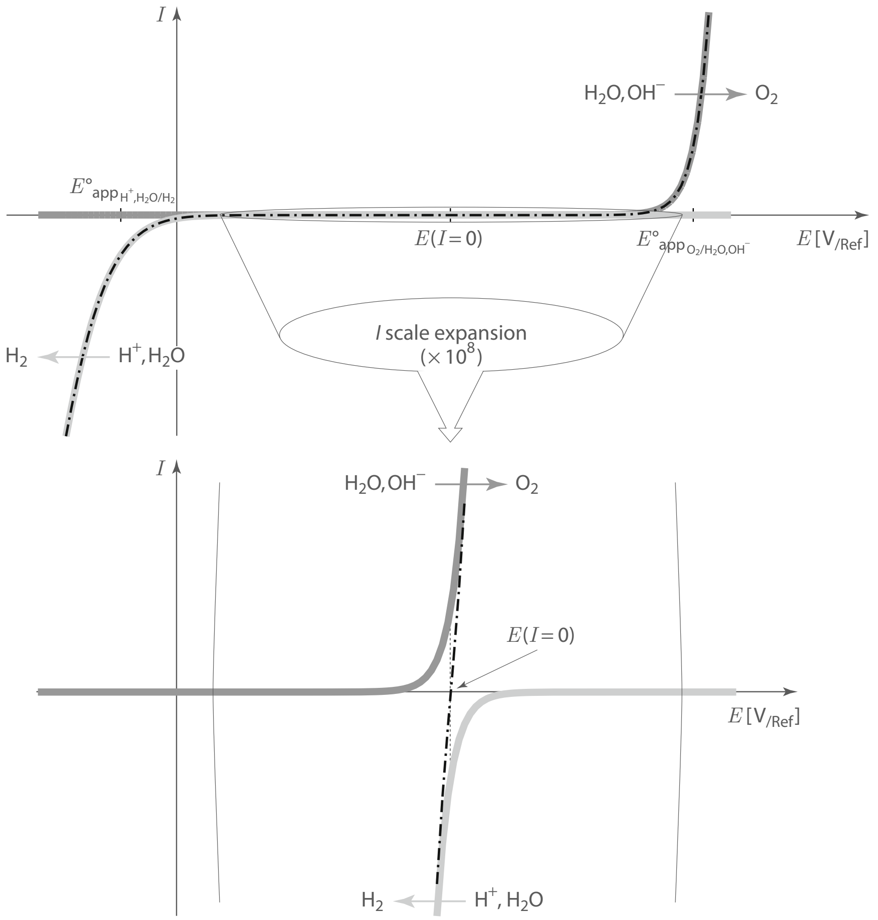


Figure 2.34 - Current-potential curve of a platinum electrode in a deaerated acidic aqueous solution

At open circuit the system is not in thermodynamic equilibrium, however the reaction occurring, namely the following:

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

progresses extremely slowly.

The mixed potential measured at open circuit depends on the thermodynamic and kinetic parameters of the couples $O_2/H_2O,OH^-$ and $H^+,H_2O/H_2$ at the interface studied (platinum in this example). It is situated between the two apparent standard potentials of the two water couples.

In these experimental conditions the open-circuit potential is generally unstable. This can be explained by the slope of the current-potential curve which is extremely low in this potential zone. Traces of an electroactive species in this potential zone would significantly modify the value of the open-circuit potential. ◢

2.4.2 - WORKING POINTS OF A WHOLE ELECTROCHEMICAL SYSTEM

The following description is confined to simple systems in which both electrodes can be considered chemically independent. The products generated at a given electrode do not intervene at the other electrode. This is a scenario that is frequently encountered, and to illustrate, here are a few experimental examples given below:

- during a microelectrolysis experiment, as frequently seen in analytical electrochemistry,
- in numerous battery types involving redox species in solid phase,
- in an electrolyser, where a membrane which is situated between the two electrodes separates an anodic compartment from a cathodic compartment with *a priori* different compositions.

One frequently encounters more complex cases where one cannot consider the phenomena at the two electrodes as independent[84]. When products resulting from one electrode intervene at the other electrode, then this amounts to an ionic short circuit. One also refers to an electrochemical shuttle.

The working point of the whole system, i.e., the (U,I) couple, corresponds to two points (found on the current-potential curve (E,I) of each electrode) such that the values of the current are equal in absolute value (see figure 2.35, dotted vertical lines). Operating such an electrochemical system involves having a point in the oxidation branch and a point in the reduction branch at two different electrodes. Moreover, if there is a difference between the surfaces of the two electrodes, care must be taken to consider the equality of the absolute current values and not that of the current densities[85].

It is important to distinguish between the different situations at the cathode and at the anode because the species involved are not necessarily the same. For instance, one could represent the current-potential curves at the cathode and at the anode using two different colours. Since the issue of drawing the shape of each current-potential curve has been laid out in the previous section, here we will merely focus on their use in the overall system.

By way of example, figure 2.35 illustrates the shapes of the current-potential curves for each interface in the lithium Li/Li_xMnO_2 battery. The redox reactions involved include the Li_xMnO_2 insertion reaction and the redox half-reaction of the Li^+/Li couple. Each of these two curves has been represented in its entirety (anodic and cathodic branches), as both of them would be obtained independently of one another. At open circuit, the whole system is in thermodynamic equilibrium. The working point of the whole system represented in figure 2.35 corresponds to the electrolyser mode or to a charging battery[86]. Bear in mind that in a recharging setup the anode is the positive electrode (Li_xMnO_2) and the cathode is the negative electrode (lithium metal). This diagram shows again the polarisation signs previously introduced in section 2.3.1. The working points indicated here correspond to an anodic overpotential which is positive and to a negative cathodic overpotential.

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[84] *A few examples of this type are studied in section 4.4.*

[85] *Examples illustrating the influence of the difference between anodic and cathodic surface areas are given in section 1.4.1.3.*

[86] *The example of an electrochemical system in power source mode or in the case of a discharging battery is illustrated later in figure 2.38 in section 2.4.4.*

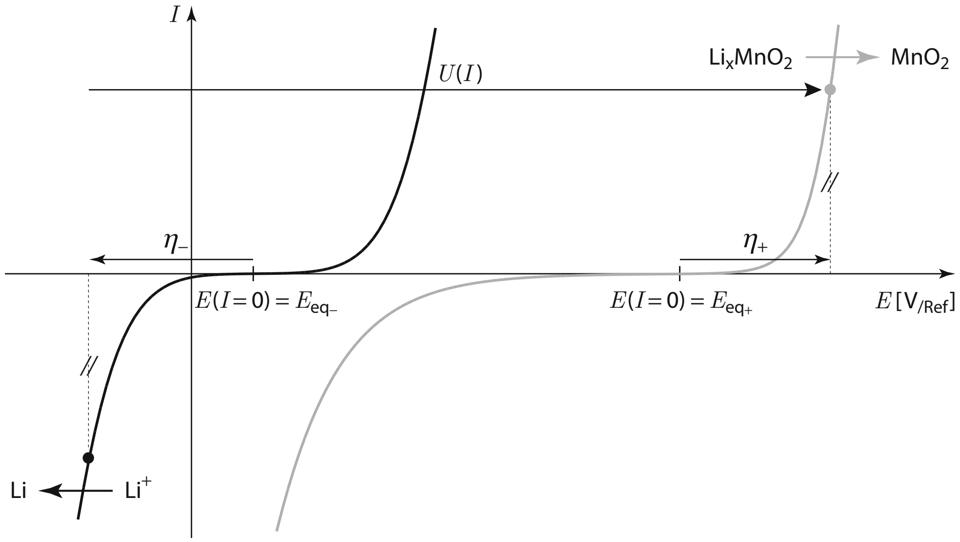

Figure 2.35 - Current-potential curves of the two electrodes with a working point in electrolyser mode (i.e., while the battery is charging)

There is a particular case encountered in systems where two identical electrodes are immersed in the same electrolyte. Both current-potential curves are identical and both electrodes play a symmetrical role. However, unlike when studying open-circuit conditions, as previously, here we must consider both curves, as opposed to just one. In such a system, a particular detail is that the open-circuit condition always corresponds to an overall system voltage equal to zero ($U=0$ or short circuit).

◤ For instance, a system with two platinum electrodes dipped in an acidic deaerated solution gives the current-potential curves as shown in figure 2.36.

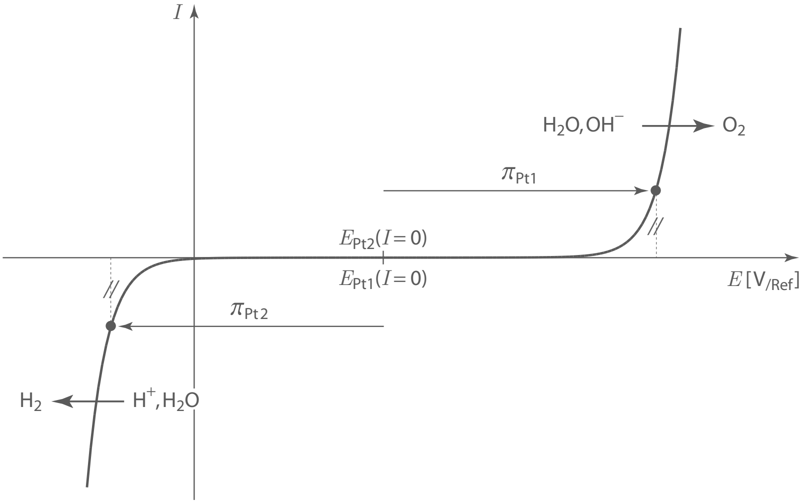

Figure 2.36 - Working point in the electrolyser mode of a cell with two identical platinum electrodes in an acidic deaerated aqueous solution ◢

2.4.3 - PREDICTING REACTIONS IN ELECTROLYSER MODE

Remember that for any electrochemical cell with a current flowing through it, the following equation applies[87]:

$$E_+ - E_- = E_+(I = 0) - E_-(I = 0) + \pi_+ - \pi_- + \sum U_{\text{ohmic drop}}$$

For an electrochemical cell in an electrolysis setup, taking into account the signs of the anodic and cathodic polarisations as well as the positive sign of the ohmic drops, the following is given:

$$\begin{cases} \textit{ANODE} = \textit{positive electrode} + \\ \textit{CATHODE} = \textit{negative electrode} - \\ \pi_+ = \pi_{an} > 0 \quad \textbf{and} \quad \pi_- = \pi_{cat} < 0 \end{cases}$$

with the positive electrode as working electrode, it gives:

$$U(I \neq 0) \geq U(I = 0) + U_{\textit{ohmic drop}} \geq U(I = 0))$$

Starting at open circuit, when the electrolysis current is gradually increased, the voltage imposed across the system also increases in turn and several simultaneous half-reactions may possibly be observed at one electrode (or both of them). Remember that the currents for each half-reaction at the same interface must be added together. This results in faradic yields that are lower than 100%. When it is possible for several reactions to occur at one of the electrodes, the main half-reaction is the one that would lead to the lowest polarisation in absolute value, for the same individual current. When several reactions can be envisaged at both interfaces in the whole system, then the overall reaction which results from the two main half-reactions is the one that requires the lowest imposed voltage.

The main half-reaction usually produces the highest faradic yield for a given working point of an electrode. Current-potential curves, for instance, allow one to define a potential range for each electrode, such that the faradic yield remains close to 100% (see figure 2.37). One must keep in mind that only qualitative reasoning is applied here, as when plotting current-potential curves. One cannot expect these potential ranges to be defined with high precision.

Consider a deaerated acidic aqueous solution containing copper sulphate placed in an electrolytic cell. The two electrodes are copper and platinum respectively. Figure 2.37 outlines the shape of the anodic branch on the current-potential curve of the platinum positive electrode. The cathodic branch for the copper negative electrode is also plotted in this figure. Two working points have been added (round symbols) to indicate an operating point with a low electrolysis current. Two other points (square symbols) define an electrolysis operating point at higher current.

At open circuit the interface with the copper electrode is in thermodynamic equilibrium. However, the interface with the platinum electrode has a mixed potential, and this is defined by adding together the algebraic

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[87] *Refer to sections 1.5.2, 2.2.3, 2.2.4 and 2.3.1 to find the introductions to these notions with their respective signs corresponding to electrolysis.*

currents of both water oxidation and proton reduction. The polarity of each electrode is defined by the experimentally measurable potentials of each electrode *vs* a saturated calomel reference electrode.

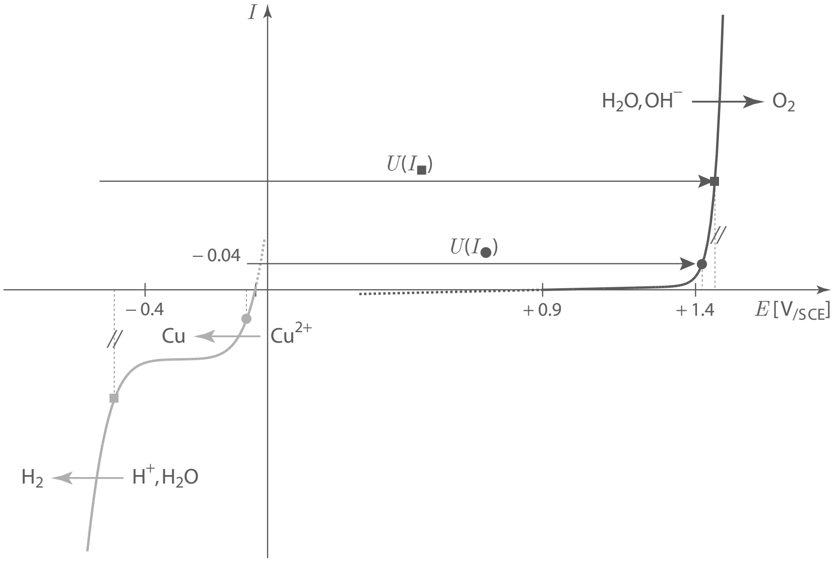

Figure 2.37 - Current-potential curve of a copper electrode (cathodic branch) and of a platinum electrode (anodic branch) in a deaerated acidic aqueous solution containing Cu^{2+} ions

The curves in figure 2.37 show the following values:

$$E_{Cu}(I=0) = -0.04\ V_{/SCE}$$
$$E_{Pt}(I=0) = +0.9\ V_{/SCE}$$

At open circuit, the copper electrode is the negative electrode in the system whereas the platinum electrode is the positive electrode.

The anodic branch at the positive electrode corresponds to a single redox half-reaction, i.e., water oxidation: whatever the working point is, the anodic faradic yield along this branch is 100%. For the current to flow and therefore for electrolysis to occur, the following condition must be fulfilled: $E_{Pt}(I \neq 0) > +1.4\ V_{/SCE}$. This value should be considered as an order of magnitude. In fact, for potentials between 0.9 and 1.4 $V_{/SCE}$, electrolysis occurs, but the current is very low.

The cathodic branch at the negative electrode corresponds to one or two redox half-reactions, depending on the potential zone: the reduction of Cu^{2+} ions and the reduction of protons (or of water). Here for the current to flow and therefore for electrolysis to occur, one must have the following: $E_{Cu}(I \neq 0) < -0.04\ V_{/SCE}$. If the absolute value of the current increases, then the copper electrode potential decreases. When the potential becomes lower than $-0.4\ V_{/SCE}$ (the working point is indicated by squares in figure 2.37) two half-reactions occur simultaneously and the faradic yield of each half-reaction drops lower than 100%.

To give a brief summary, the main overall reaction corresponding, for example, to the operating points indicated by round symbols is the following:

$$2\,H_2O \longrightarrow 4\,H^+ + 4\,e^- + O_2$$
$$Cu^{2+} + 2\,e^- \longrightarrow Cu$$
$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$
$$2\,H_2O + 2\,Cu^{2+} \longrightarrow O_2 + 4\,H^+ + 2\,Cu$$

Such an overall reaction only makes sense if the anodic and cathodic faradic yields are identical and equal to 100%.

While the open-circuit voltage of this electrolysis cell is $0.9 - (-0.04) = +0.94$ V (the platinum electrode is chosen as the working electrode), the minimum electrolysis voltage is about $1.4 - (-0.04) = 1.44$ V. Here we can finally evaluate the maximum electrolysis voltage at which the 100% faradic yield is preserved. If we neglect the polarisation and consider the anodic branch to be quasi-vertical when the current increases, then the electrolysis voltage must be kept lower than $1.4 - (-0.4) = 1.8$ V.

2.4.4 - PREDICTING REACTIONS IN POWER SOURCE MODE

For an electrochemical cell with a current flowing through it in power source mode, considering the signs of the anodic and cathodic polarisations and of the (negative) ohmic drop, the following is given[88]:

$$\begin{cases} \textit{ANODE} = \textit{negative electrode} \; - \\ \textit{CATHODE} = \textit{positive electrode} \; + \\ \pi_+ = \pi_{cat} < 0 \quad \text{and} \quad \pi_- = \pi_{an} > 0 \end{cases}$$

and choosing the positive electrode (here cathode) as working electrode, gives the following:

$$U_{supplied} \leq U(I = 0) - |U_{ohmic\,drop}| \leq U(I = 0)$$

When gradually increasing the current delivered by the power source (though all the while keeping it lower than the short-circuit current, see section 2.4.5), one may observe several half-reactions occurring simultaneously at one or both of the electrodes. As in the previous case, when it is possible for several half-reactions to occur at an interface, then the main half-reaction is the one with the lowest polarisation in absolute value for the same individual current. In power source mode, when several half-reactions can be envisaged at the interfaces, the main overall reaction is the one delivering the highest voltage to the external circuit.

As in electrolysis mode, the main half-reaction usually offers the highest faradic yield. The current-potential curves define a potential range for each electrode such that the faradic yield remains close to 100%, as illustrated in figure 2.38.

Let us consider an electrochemical system with two compartments separated by a membrane or a salt bridge, and whose impact in terms of ohmic drop is disregarded. A zinc electrode is dipped in a dearerated acidic solution in the first compartment. The second compartment contains a silver electrode dipped in a deaerated acidic solution containing Ag^+ and Cu^{2+} ions. Figure 2.38 shows the shape of the cathodic branch of the current-potential curve of the positive silver electrode together with that of the anodic branch of the negative zinc electrode. Two points on the curves (round symbols) define a working point with a low delivered current. Two other points (square symbols) define a working point with a high delivered current.

At open circuit the interface with the silver electrode is in thermodynamic equilibrium. The interface with the zinc electrode has a mixed potential, which is defined by adding the zinc oxidation and proton reduction currents, with the latter reaction characterised as being very slow at the zinc electrode. The polarities of the electrodes in open-circuit conditions are defined by the experimentally measured potentials of each electrode *vs* a saturated calomel reference electrode.

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[88] *Refer to sections 2.2.3, 2.2.4 and 2.3.1 to find the introductions to these notions with their respective signs corresponding to power source mode.*

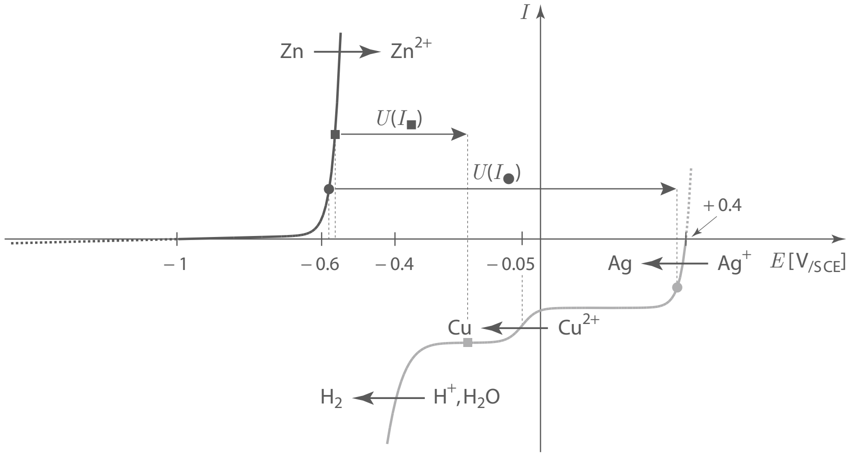


Figure 2.38 - Current-potential curve of a silver electrode (cathodic branch) in a deaerated acidic solution containing Ag^+ and Cu^{2+} ions and of a zinc electrode (anodic branch) in a deaerated acidic solution

The curves in figure 2.38 show the following values:

$$E_{Zn}(I=0) = -1.0\ V_{/SCE}$$

$$E_{Ag}(I=0) = +0.4\ V_{/SCE}$$

At open circuit, zinc is the negative electrode in the system while silver is the positive electrode.

In the potential range plotted, the anodic branch on the negative electrode side corresponds to a single redox half-reaction, i.e., zinc oxidation. The simultaneous oxidation of water would equate to a working point with an extremely large current. One can therefore consider that, regardless of the working point in question, the anodic faradic yield is equal to 100%. For an anodic current to flow, the condition $E_{Zn}(I\neq 0) > -0.6\ V_{/SCE}$ must be fulfilled, and this value should be considered as an order of magnitude. In fact, for potentials between –1.0 and –0.6 $V_{/SCE}$, a spontaneous reaction occurs, but the current is very low. In the following part we will assume that this anodic branch is quasi-vertical.

The cathodic branch on the positive electrode side corresponds to one, two or even three redox half-reactions depending on the potential range considered: the reduction of Ag^+, Cu^{2+} ions, or the reduction of protons (or of water). For a cathodic current to flow, one must have the following: $E_{Ag}(I\neq 0) < +0.4\ V_{/SCE}$. If the current delivered by the electrochemical system increases in absolute value, then the silver electrode potential decreases. When this potential reaches values lower than about –0.05 $V_{/SCE}$, two simultaneous half-reactions occur: the reduction of Ag^+ ions and of Cu^{2+} ions, which are represented by squares in figure 2.38. The faradic yield of the main half-reaction becomes lower than 100%. When the potential gets lower than about –0.4 $V_{/SCE}$ three half-reactions occur simultaneously.

The overall main reaction, corresponding to the working point indicated by round symbols, is expressed as:

$$Zn \longrightarrow Zn^{2+} + 2\,e^-$$

$$Ag^+ + e^- \longrightarrow Ag$$

$$\overline{Zn + 2\,Ag^+ \longrightarrow 2\,Ag + Zn^{2+}}$$

Writing such an overall reaction only makes sense if anodic and cathodic faradic yields are identical and equal to 100%.

While the open-circuit voltage of the cell is 0.4 – (–1.0) = 1.4 V, with the silver electrode chosen as working electrode, the maximum voltage that can be delivered by this system working as power source is about 0.4 – (–0.6) = 1.0 V. The conditions required for preserving faradic yields of 100% equate to a voltage value between – 0.05 – (–0.6) = 0.55 V and 1.0 V.

2.4.5 - VARIOUS WORKING CONDITIONS OF AN ELECTROCHEMICAL SYSTEM

For any given system, one can consider switching from one operating mode to another. When the current-potential curves of both electrodes are monotonous, which tends to be most frequently the case, then three operating zones can be distinguished depending on the values of the current or the voltage across the system. This is outlined in a diagram in figure 2.39, where the main curve represents the various working points (U,I) of the system in question. Beware of the fact that this diagram is not a current-potential curve (E,I), unlike those plotted in the previous sections. On the x-coordinate the voltage U between the two electrodes is represented instead of the potential E of an electrode *vs* a reference electrode. The positive electrode is chosen here as the working electrode in open-circuit conditions: the open-circuit voltage of the system is therefore positive. On the main curve in figure 2.39 the current sign is that of the current flowing through the working electrode. It is positive (respectively negative) when the working electrode is anode (respectively cathode).

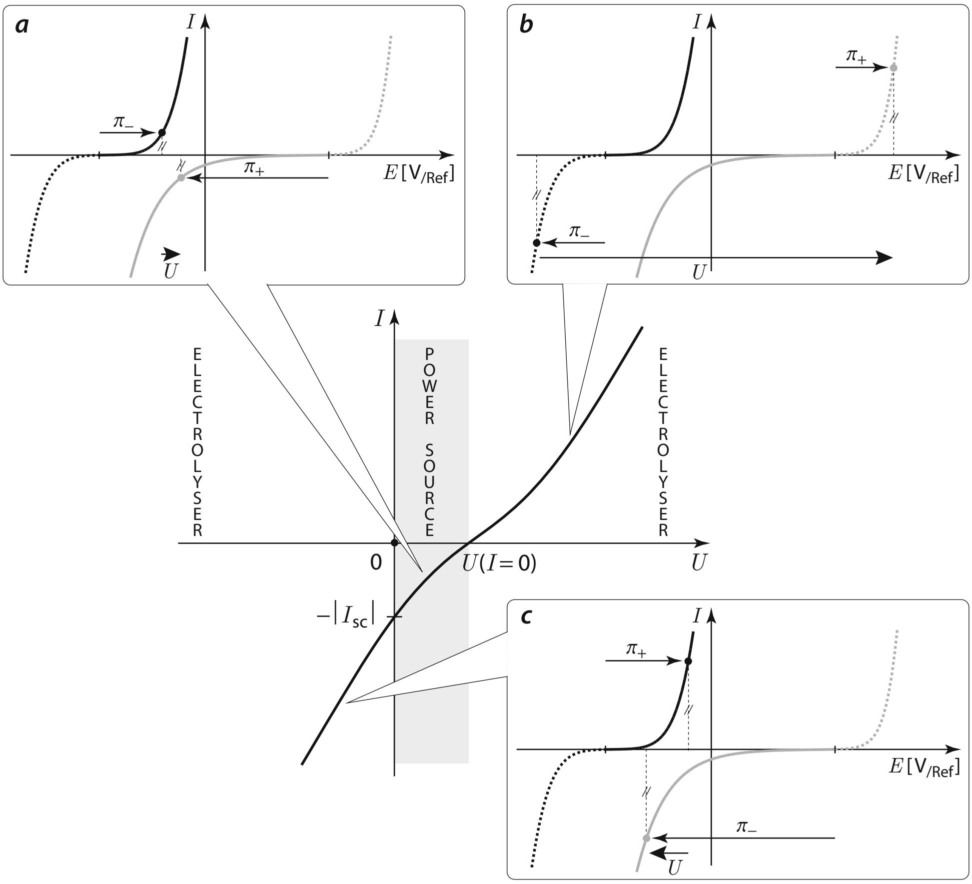


Figure 2.39 - The three working points (U,I) zones of an electrochemical system

In this figure the current-potential curves of each electrode are represented by three medallions, with a working point that is typical of each of the three zones. Medallion ***b***, for instance, refers to figure 2.35 in electrolyser mode. The three possible (U, I) types of operating points are delimited by two particular working points corresponding respectively to open circuit ($U(I=0)$, $I=0$) and to short circuit ($U=0$, $I=-|I_{sc}|$).

Two of the three zones correspond to the usual power source and electrolyser modes. When the system works as a power source, the positive electrode is the cathode [case ***a***, $-|I_{sc}| < I < 0$ and $0 < U < U(I=0)$]. Yet when the system operates as an electrolyser, the positive electrode is the anode [case ***b***, $I > 0$ and $U > U(I=0)$]. The third zone [case ***c***, $I < -|I_{sc}|$ and $U < 0$] provides a more singular case whereby the electrode polarisations are reversed in relation to the open-circuit setup. As long as the working electrode (which switched from positive to negative polarity) is the cathode, then this particular operating mode is possible only on condition that there is a sufficient external energy source used. In this respect, the system works as an electric load. This type of case applies to a battery with several cells in series. If there is a defective cell then it may cause a reversal in polarity, yet all the while the overall battery still functions as a power source. The overall reaction occurring in the defective cell is a forced reaction which is only made possible by the spontaneous reactions occurring in the other cells.

The diagram in figure 2.40 shows the two specific situations which involve open-circuit and short-circuit conditions. Here it can be underlined that the point for $U=0$ corresponds to an ideal short circuit. Therefore, in other words it is achieved using a conductor, meaning that the ohmic drop is insignificant in this setup, which is no easy result to obtain in experimental conditions. It is worth recalling that the curves presented here correspond to systems whose ohmic drop in the electrolyte can be disregarded.

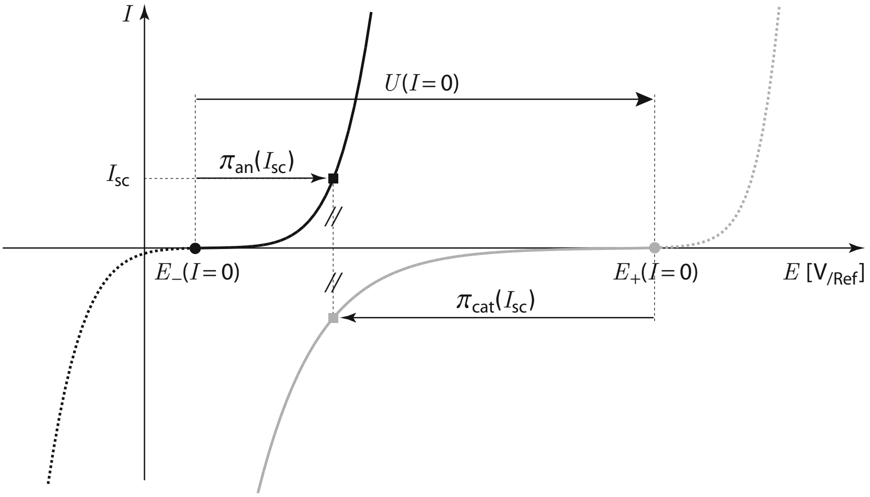


Figure 2.40 - Particular working points (U, I) of an electrochemical system: open circuit (●) short circuit (■)

In systems where two electrodes which are strictly identical are placed in the same electrolyte, the working points in open circuit and short circuit are identical (in other words, the short-circuit current is zero). All the working points here therefore correspond to electrolysis. Both electrodes play perfectly symmetrical roles, and equally symmetrical is the (U,I) curve of the working points of the overall system. Only the role of anode or cathode is swapped between the two electrodes, but the system never works as a power source.

◤ Let us consider the example of an electrolyte and two strictly identical electrodes: the open-circuit voltage is zero, then the corresponding open-circuit and short-circuit points are identical. The two electrodes are indiscernible, and the curve representing the working points is symmetrical, as shown in figure 2.41.

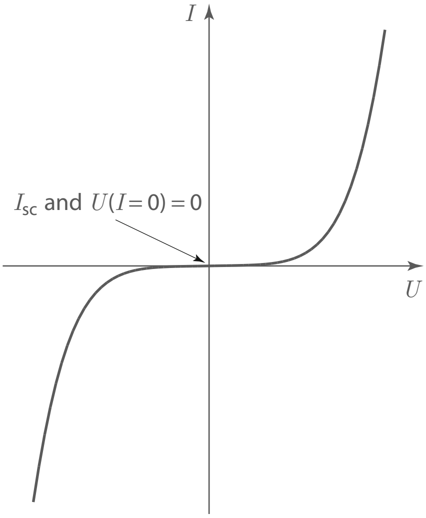


Figure 2.41 - Working points of a system with two identical platinum electrodes in a deaerated acidic aqueous solution ◢

If the active areas of the two interfaces are different, then the two current-potential curves plotted with the current (and not current density) as y-coordinates become distinct again. However, given that the open-circuit voltage is zero, the short-circuit current is zero and all the working points correspond to electrolyser mode (see figure 2.41).

Finally, let us stress the differences between the following:

- a spontaneous redox reaction which corresponds to two half-reactions occurring at the same interface: there is no net current flow. This stems from a situation whereby the two electrodes are short-circuited, a scenario which is usually avoided. Yet it is at the very heart of corrosion phenomena, where anodic and cathodic zones are always found to be in contact, through not in strict short circuit. It is also behind the concept of self-discharge in batteries;
- a spontaneous redox reaction in a discharging battery. The overall result is indeed a spontaneous reaction, but it represents the sum of two half-reactions occurring at two different interfaces (one working as cathode and the other as anode). For the overall reaction to actually occur, the two electrodes must be connected *via* an external circuit which can retrieve electric energy. The idea of electric energy retrieving was impossible in the previous case.

QUESTIONS ON CHAPTER 2

1 - The three mass transport processes are:

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

2 - One studies an interface between cobalt (metal) and an Na^+Cl^- solution in acetonitrile (an organic solvent) where the following reaction occurs:

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

- The interface is reactive true false
- By convention the current sign is positive true false

3 - FARADAY's law expresses, for a redox reaction, the amount of substance transformed as a function of the amount of electric charge which crosses the interface in question. The coefficient of proportionality at the numerator involves:

- the temperature true false
- the FARADAY constant true false
- the number of electrons true false
- the stoichiometric number of the species in question true false

4 - In an industrial aluminium production plant, the main cathodic reaction involves the Al(III)/Al couple with a faradic yield of 90%. The amount of aluminium produced per hour in an electrolysis cell working with a current of 300 000 A is:

10^3 mol 3.4×10^3 mol 3.6×10^3 mol 10^4 mol 3.4×10^6 mol

5 - The overall polarisation of an electrochemical chain can be split into different terms. In a system with no ionic junction, what do you call the term which adds itself to the two interfacial polarisations so as to gain the final overall polarisation value in the electrochemical chain? ....

6 - The concentration of a solution containing a species with a concentration of 0.1 mol L^{-1} is also equal to

100 mol m^{-3} 10^{-4} mol m^{-3} 100 mol cm^{-3} 10^{-4} mol cm^{-3}

7 - Assuming that the molar conductivity of Cu^{2+} ions in aqueous solution is a constant equal to 10 mS m^2 mol^{-1}, then the conductivity value of these same ions in a solution with a concentration of 0.1 mol L^{-1} is:

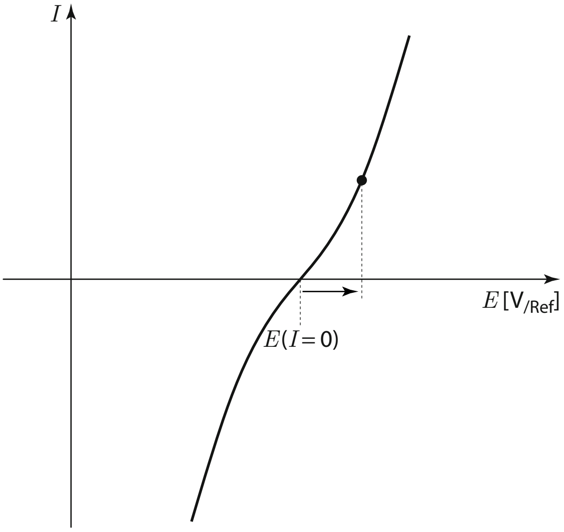
1 S cm^{-1} 10^{-2} S cm^{-1} 1 S m^{-1} 10 S m^{-1}

8 - Adding a supporting electrolyte to an electrochemical system causes, for the electroactive ions, the decrease in:

- their transport number true false
- their ionic conductivity true false

9 - In the following diagram:

- hatch the half-plane corresponding to an anodic operating mode
- indicate the half-reactions occurring in each half-plane with the usual writing conventions, taking the example of the Fe^{3+}/Fe^{2+} couple



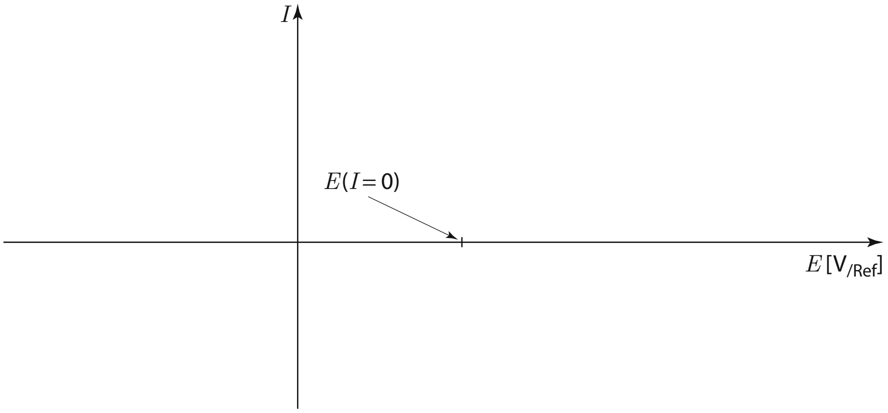
- what does the black arrow represent for the working point which is identified by a black dot?

. . . .

10 - Except in very specific cases, one can predict the signs for each of the two interfacial polarisations in a given system. Therefore, in most cases, one can say that:

- the polarisation of the positive electrode is positive true false
- the polarisation of the anode is positive true false

11 - On the following diagram, draw the shape of the steady-state current-potential curves of three systems with the same open-circuit potential and the same diffusion limiting currents: a fast system (**a**), a slow system (**b**) and a very slow system (**c**).

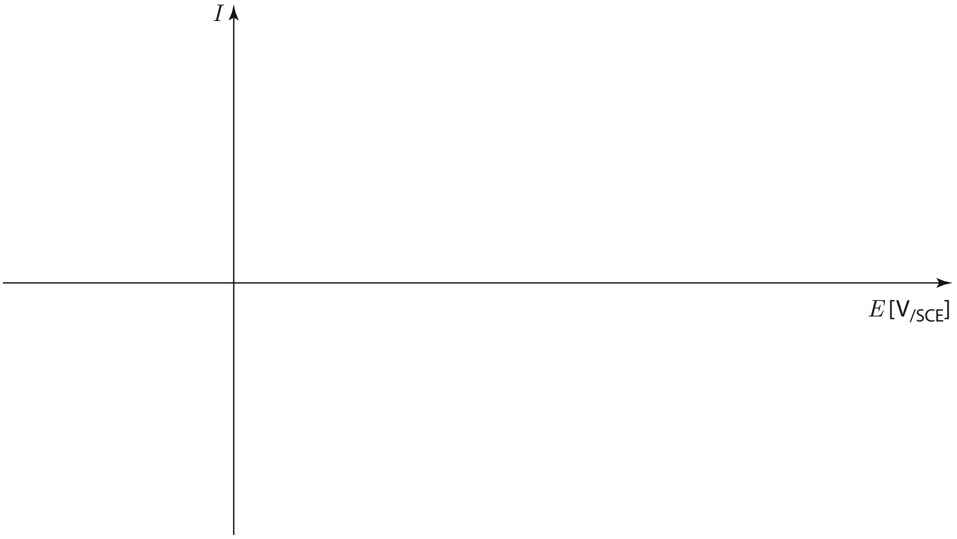


12 - On the following diagram, plot the steady-state current-potential curve of a system containing an inert working electrode dipped in a deaerated acidic aqueous solution ($pH = 0$), with no Fe^{3+} ions and an amount of Fe^{2+} ions befitting the existence of a limiting current. The reference electrode is a saturated calomel electrode. It will be assumed that the electrochemical window is determined by the fast half-reactions of water.

Indicate in the diagram the relevant numerical values of the potentials as well as the half-reactions involved.

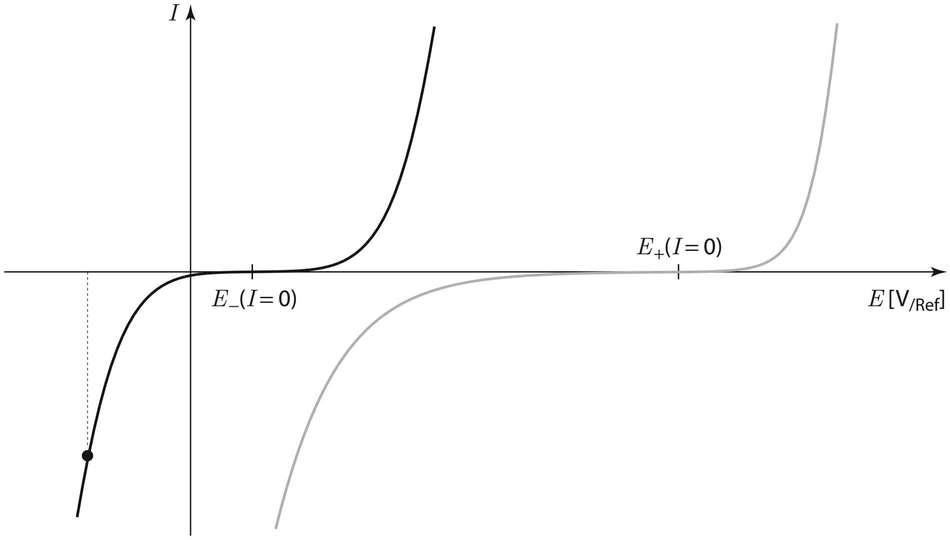
$$E\,(\text{SCE}) = +\,0.24\ \text{V}_{/\text{SHE}} \qquad E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +\,0.77\ \text{V}_{/\text{SHE}}$$

$$E^\circ_{\text{H}^+/\text{H}_2} = 0\ \text{V}_{/\text{SHE}}\ (\text{at } pH = 0) \qquad E^\circ_{\text{O}_2/\text{H}_2\text{O}} = +\,1.23\ \text{V}_{/\text{SHE}}\ (\text{at } pH = 0)$$



13 - Using arrows, complete the following diagram (which represents the steady-state current-potential curves of the two electrodes in a given electrochemical cell) to indicate the following:

- the system's open-circuit voltage, $U(I=0)$
- the polarisation π_- of the negative electrode at the working point indicated by a black dot
- the polarisation π_+ of the positive electrode at the corresponding working point of this electrode (indicate this second dot in the diagram)
- the corresponding working voltage, $U(I\neq 0)$



- the operating mode represented in the diagram corresponds to electrolysis true false