

ELECTROCHEMISTRY

THE BASICS, WITH EXAMPLES

1 - BASIC NOTIONS

1.1 - INTRODUCTION

1.1.1 - ETYMOLOGY

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

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

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

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

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

[1] These notions are defined in section 1.2.

[2] These notions are defined in section 1.3.

[3] These notions are defined in section 1.5.

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

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

The cell is represented below:



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

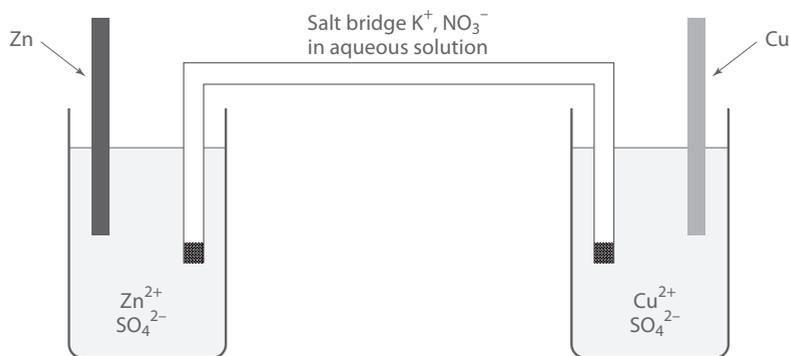
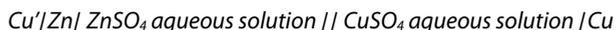


Figure 1.4 - Diagram of a DANIELL cell

1.4.1.2 - THE POLARITY OF THE ELECTRODES

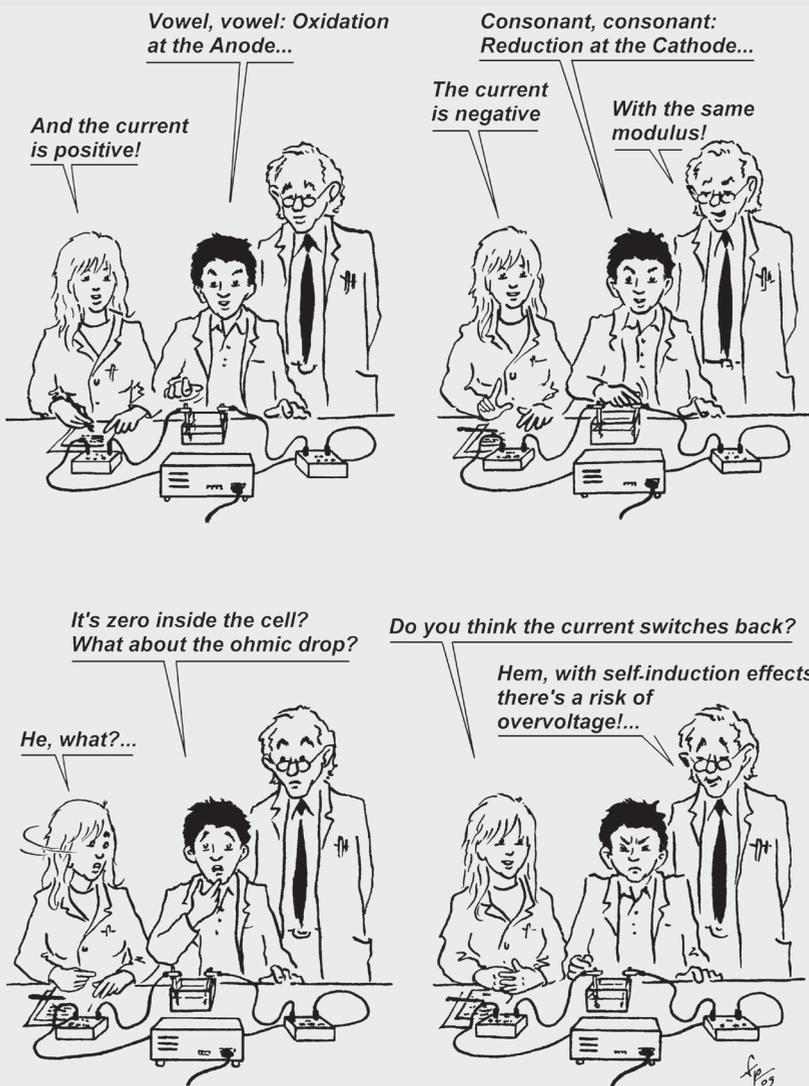
The voltage of an electrochemical cell, denoted by U , is the potential difference between the two terminals of the cell; it is expressed in volts (V)^[48]. The notation U is not systematically used in scientific literature, but here it has been chosen in preference to the notation E which is also frequently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

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



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

SIGN CONVENTION FOR CURRENT



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

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

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

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):

$$E_{\text{eq}} = E^{\circ}_{\text{app MnO}_2/\text{LiMnO}_2} + \frac{RT}{\mathcal{F}} \ln \frac{1-y}{y}$$

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

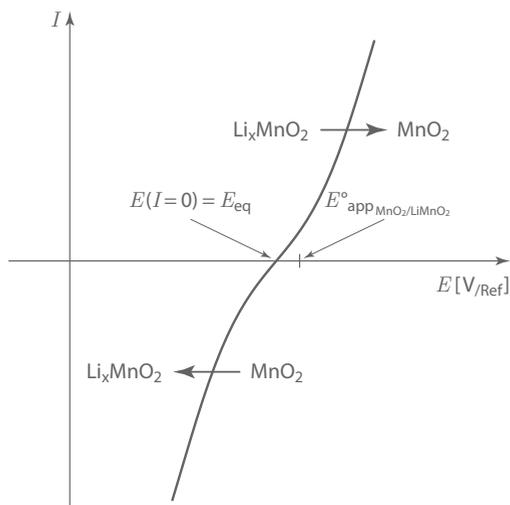


Figure 2.22 - Current-potential curve of a manganese oxide electrode in an organic solution containing Li^+ ions

- ▶ 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

[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.

3 - THERMODYNAMIC FEATURES

A state of equilibrium can be defined in any system where the intensive variables (pressure, temperature, concentration, etc.) remain constant over time. In this chapter we will describe the state of equilibrium in an electrochemical system and give examples of conditions in which equilibrium can be observed^[1]. In fact, the state of equilibrium is not always necessarily observed, since it cannot always be reached on the time scale of the experiment.

When a system is in equilibrium there is no movement of species on the macroscopic scale, resulting in a zero current. However, when the current is zero this does not necessarily mean that the system is in equilibrium, since a compensation of charge fluxes of different carriers can occur. This is the case when the interfacial open-circuit potential is a mixed potential^[2] or for a liquid junction, a salt bridge, in an electrochemical system at open circuit^[3].

3.1 - CONCEPTS OF POTENTIAL

The term potential is used frequently in different fields of physics and chemistry. It always refers to the energy per unit quantity related to the matter in question (number, mass, charge, etc.). Here we are particularly interested in electric and chemical energies. Therefore we will speak on the one hand in terms of electric potential: by using the quantity of charge (in C) as a quantity parameter, the electric potential is expressed in volts ($V = J C^{-1}$). On the other hand, by using the amount of substance (in mol) as a quantity parameter, the chemical potential is expressed in $J mol^{-1}$.

In a material these potentials are macroscopic, and represent an average across a large volume compared to atomic sizes (higher than a few tens of nm^3).

[1] As presented in section 2.1, an electrochemical system is defined as being isolated without any possibility of exchanging energy or matter with the surroundings. To make a different comparison to that in section 2.1, imagine an apple on a table. One can say it is in equilibrium, yet if the table is removed, then its equilibrium state is its new position on the ground. In the same way, all isolated electrochemical systems have an equilibrium state, yet this state is often very different after a current has been allowed to flow through an electric load, in other words once the system has functioned as a power source.

[2] Section 2.4.1 outlines this type of behaviour, which can be seen at an interface that is at open circuit however not in equilibrium.

[3] As described in qualitative terms in section 2.1.1, when there is a salt bridge or a liquid junction through a porous membrane, it takes an extremely long time to reach a state of equilibrium where a perfect mix of solutions is achieved. Generally a quasi-steady state is observed at open circuit (i.e., at zero current) where the molar fluxes are low but not zero (see appendix A.1.1).

It is a very quick process to write the thermodynamic equilibrium of a reactive interface if you are using electrochemical potentials. The equation that emerges shows the difference in GALVANI potentials at the interface in equilibrium. Different examples are studied below.

- ▶ Let us first study the simplest interfacial reaction, i.e., the exchange of one species between two phases. One has to distinguish whether the exchanged particle is charged or not. First let us look at the exchange of molecules M , as shown in figure 3.5.



Figure 3.5 - Exchange equilibrium of a molecule at an interface water | oil

For instance, this example relates to the equilibrium found between two solutions containing alcohol in water and alcohol in oil.

The surface reaction is the following:

$$M_{\alpha} \rightleftharpoons M_{\beta}$$

The thermodynamic equilibrium results in the following equation:

$$\Delta_r \tilde{G} = \tilde{\mu}_{M_{\beta}} - \tilde{\mu}_{M_{\alpha}} = 0$$

or

$$\tilde{\mu}_{M_{\beta}} = \tilde{\mu}_{M_{\alpha}}$$

and since it is a molecule (neutral species):

$$\mu_{M_{\beta}} = \mu_{M_{\alpha}}$$

- ▶ Secondly, let us now consider the exchange of one particular charged species, assuming that it is the only reactive phenomenon at the interface. This is the case, for example, of an AgCl solid crystal in equilibrium with an aqueous solution containing Ag^+ ions, as shown in figure 3.6.

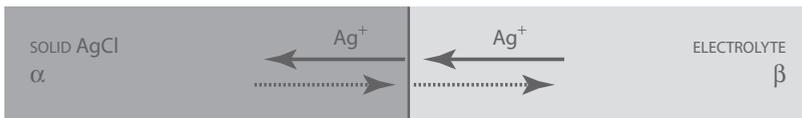


Figure 3.6 - Exchange equilibrium of Ag^+ ions between a crystal of AgCl and an aqueous solution

The surface reaction is the following:

$$\text{Ag}^+_{\alpha} \rightleftharpoons \text{Ag}^+_{\beta}$$

The thermodynamic equilibrium results in the following equation:

$$\Delta_r \tilde{G} = \tilde{\mu}_{\text{Ag}^+_{\beta}} - \tilde{\mu}_{\text{Ag}^+_{\alpha}} = 0$$

or, since Ag^+ is a cation:

$$\mu_{\text{Ag}^+_{\beta}} + \mathcal{F} \varphi_{\beta} = \mu_{\text{Ag}^+_{\alpha}} + \mathcal{F} \varphi_{\alpha}$$

The difference in GALVANI potentials between the two phases is therefore:

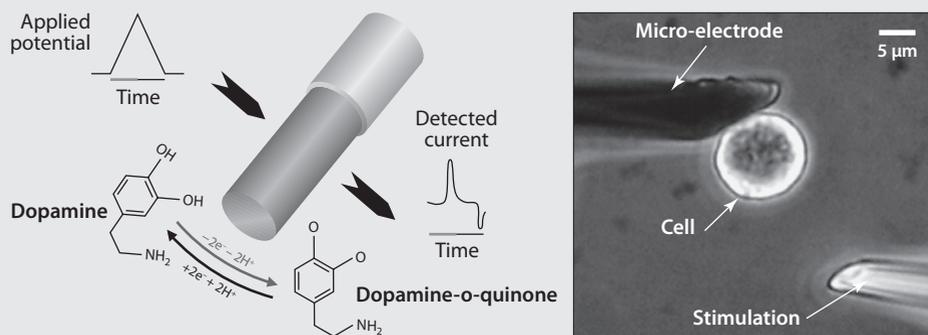
$$\varphi_{\beta} - \varphi_{\alpha} = \frac{1}{\mathcal{F}} (\mu_{\text{Ag}^+_{\alpha}} - \mu_{\text{Ag}^+_{\beta}})$$

ELECTROCHEMISTRY AND NEUROBIOLOGY

*Document written with the kind collaboration of S. ARBAULT,
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Electrochemistry made its first contribution to biology and medicine with the works of L. CLARK in the early 1950's. He came up with the first electrochemical sensor based on an amperometric method in order to measure out dissolved oxygen in water, especially in biological fluids. It was only after the early 1970's that on the back of this type of device, other electrochemical biosensors were developed (specifically for detecting glucose, or chemical neurotransmitters). In the case of neurobiology, these developments reflected the need to understand how mechanisms worked for the chemical transmission of neuronal information, a field of study which has been in evidence since the late 1960's.

Moreover, the 1970's marked the development of new electrochemical tools, including microelectrodes. These tools quickly found a new field of applications: *in vivo* measurements. Indeed, if you take the case of carbon fibers measuring from 5 to 30 μm in diameter, you can see how microelectrodes share the same dimensions as living cells. They therefore have a slightly invasive effect when inserted into cellular tissue. Fundamental studies have also demonstrated how during analysis the time constants offered by microelectrodes are significantly lower than those offered by conventional millimetre electrodes. When a very high voltammetry scanning rate is applied (several hundreds of volts per second) it is possible to study transient phenomena in the range of milliseconds. Several research groups have developed this type of analysis using carbon microelectrodes to understand the mechanisms behind how dopamine, a major neurotransmitter in the central nervous system, is released. The studies which were pioneered on slices of rodent brain were then able to be carried out *in vivo* on the brains of anaesthetized animals.



The principle of detecting dopamine at the surface of a carbon fiber microelectrode and the view under a microscope of a detection experiment carried out on a single cell

On the left, dopamine detection: reprinted from *Trends Anal. Chem.*, **22**, PHILLIPS P.E.M. and WIGHTMAN R.M., *Critical guidelines for validation of the selectivity of in-vivo chemical microsensors*, 509-514, © 2003, with permission from Elsevier; On the right, microelectrode: AMATORE C., ARBAULT S., BONIFAS I., BOURET Y., ERARD M. and GUILLE M.: *Dynamics of full fusion during vesicula exocytotic events: release of adrenaline by chromaffin cells*. *ChemPhysChem*. 2003. **4**. 147-154. © Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission)

4 - CURRENT FLOW: A NON-EQUILIBRIUM PROCESS

The purpose of this chapter is to provide the tools to describe the relationships between voltage and current, in quantitative terms, as a function of time in electrochemical systems.

When a current flows through a system, movements of at least one type of charged species are observed on the macroscopic scale. Consequently the system is in a non-equilibrium state.

4.1 - MASS BALANCES

Once the relationship has been defined between the current and the quantities characterizing mass transport, then one can write mass balances in volume and at the interfaces to describe the electrochemical systems in which a current flows in quantitative terms.

4.1.1 - DEFINITIONS FOR THE MACROSCOPIC QUANTITIES RELATED TO THE CURRENT

Since all elementary charged species have a mass, then by definition the notion of current is related to the notion of overall mass transport.

4.1.1.1 - MOLAR FLUX

Any movement of substance, whether relating to a charged species or not, can be quantified by the amount of substance (mol) flowing through a surface per time unit. This represents the molar flux or flow rate (mol s^{-1}). Here we define an associated local macroscopic quantity: the molar flux density which depends on the position. This value is an average taken around the point in question, and calculated for a large volume when compared to atomic dimensions (greater than tens of nm^3)^[1]. The latter is defined in relation to the amount of species i , dn_i , flowing through a surface of elementary area dS during an elementary time interval dt . It is a vector, \mathbf{N}_i , which is collinear with the local velocity of the species in question, and which is oriented in the same direction (see the development below). Its modulus is given by the following equation:

$$\|\mathbf{N}_i\| = \frac{1}{dS} \frac{dn_i}{dt}$$

[1] Many authors in the field of electrochemistry wrongly omit the term density when using the term molar flux, whereas it is indeed a matter of molar flux density. This may lead to misunderstanding since the terms flux and flow rate are synonyms in many other scientific domains, yet in this context they have different meanings.

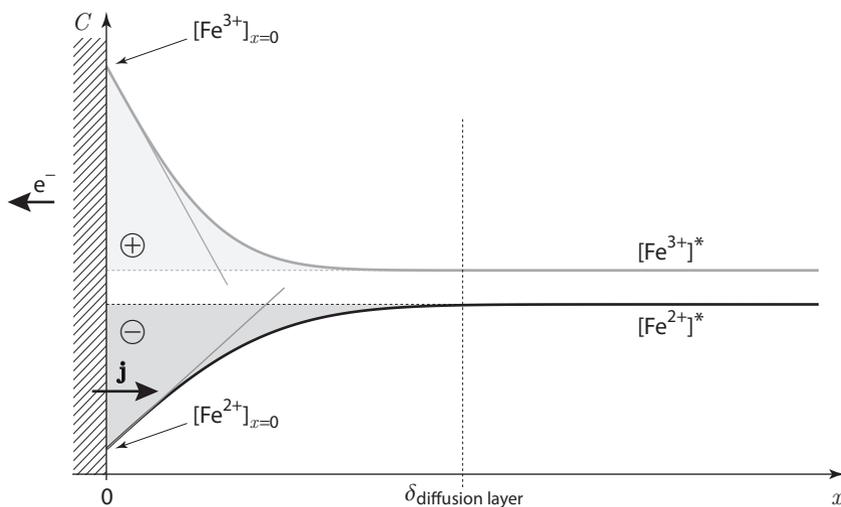


Figure 4.15 - Concentration profiles of Fe^{3+} ions (grey) and Fe^{2+} ions (black) during oxidation
 $[\text{Fe}^{2+}]_{x=0}$ and $[\text{Fe}^{3+}]_{x=0}$: interfacial concentrations,
 $[\text{Fe}^{2+}]^*$ and $[\text{Fe}^{3+}]^*$: bulk concentrations, far from the interface.

The charge balance of the electroactive species in the diffusion layer shows a change in charge distribution. This would also be the case even if the diffusion coefficients were identical. In the example illustrated in figure 4.15, just as in any oxidation half-reaction, the charge balance for the electroactive species reveals a positive charge excess in the diffusion layer in relation to the bulk of the solution. In this example, it results in a decreasing profile for the sum of $2[\text{Fe}^{2+}] + 3[\text{Fe}^{3+}]$ in the diffusion layer. The electro-neutrality of the solution within the diffusion layer still applies. This means that the other non-electroactive ions (belonging to the supporting electrolyte or the counter-ions if no supporting electrolyte) compensate for these charge modifications in the diffusion layer caused by the redox reaction. For these non-electroactive species, the concentration profiles also present variations in the diffusion layer^[50].

Let us return to the example of an oxidation reaction occurring at the interface between a platinum electrode and an aqueous solution containing ferrous and ferric nitrates with a KNO_3 supporting electrolyte. To simplify, we assume that all the ionic diffusion coefficients are close to each other. We have already dealt with the concentration profiles of the electroactive species. However, the concentration profiles of non-electroactive species, which are rarely touched upon because they are often not a subject of great interest, are not flat. We should however keep in mind that although the diffusion fluxes share the same order of magnitude as electroactive species, their relative variations appear to be negligible because these non-electroactive species are much more concentrated. The two approaches outlined below enable one to determine in qualitative terms the shapes of the concentration profiles of the non-electroactive species K^+ and NO_3^- .

in steady or quasi-steady state conditions. In this instance, the significance of the surface lying between the steady-state profile and the initial profile is more complex to interpret. A simple example is explored in appendix A.4.2.

[50] In addition to the next example, one can also refer to the example outlined in appendix A.4.1.

4.4.1.2 - OBTAINING NON-ZERO-CURRENT STEADY STATES

For such a type of closed electrochemical cell with no convection, it is possible to obtain a non-zero-current steady state (in the strictest sense of the term as regards the electrolyte) if all the electroactive species present in the electrolyte have the same stoichiometries in both electrode redox reactions. The average composition of the electrolyte does not change over time, as illustrated in the example in figure 4.36 which shows concentration profiles for a chronopotentiometry with a fast and nernstian redox system in the presence of a supporting electrolyte with no convection^[78].

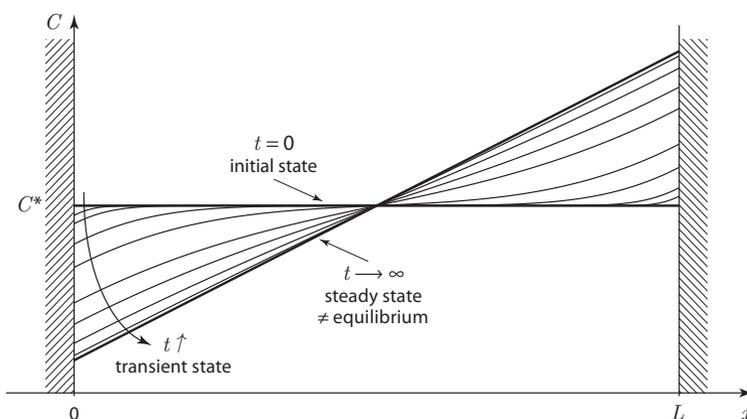
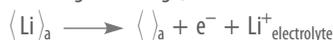


Figure 4.36 - Concentration profile in chronopotentiometry

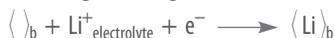
Here again, in this system without convection, the composition throughout the electrolyte is non-homogeneous, with the diffusion phenomena occupying the entire volume after a transient period.

▀ This case is a simplified version of how a lithium battery works^[79]. For example, when a lithium battery has two insertion materials a and b, the electrode phenomena can be written in the following simplified manner:

▶ at the negative electrode (the anode during a discharge):



▶ at the positive electrode (the cathode during a discharge):



Although the two redox couples are not identical, as regards the electrolyte both redox reactions involve a supply or consumption of Li with the same stoichiometry. This applies to a Li-ion battery with two insertion materials or to a Li-polymer battery with Li as the negative electrode and an insertion material at the positive electrode. When a lithium battery is in operation, one must take into account simultaneously the migration and diffusion of the ions in the electrolyte, however, this makes no change in qualitative terms to what has just been illustrated. ▀

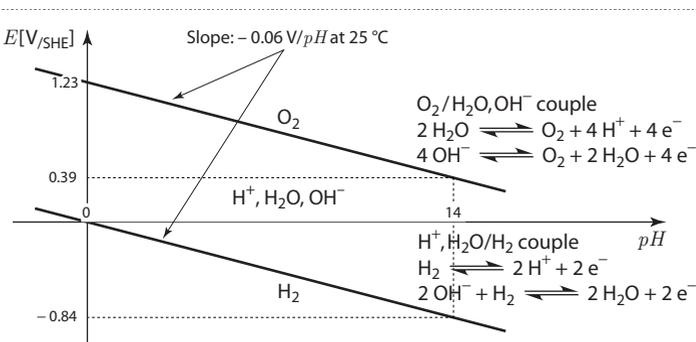
[78] Appendix A.4.1 addresses in detail the characteristics for such a system at steady state, as well as the establishment of that steady state.

[79] These batteries are described in the illustrated board entitled 'Energy storage: the Li-Metal-Polymer (LMP) batteries'. They are often called 'rocking chair batteries' by the specialists when, during operation, the Li^+ ions are de-inserted at one of the interface and simultaneously inserted at the other interface. Lithium is thus tilted from one side to the other during charge or discharge.

2 - SIMPLIFIED DESCRIPTION OF THE ELECTROCHEMICAL SYSTEMS

WHAT NEEDS TO BE KNOWN RESPONSE ELEMENTS

Equilibrium

Writing and using the NERNST law	2.1.2 $E_{/Ref} = E^{\circ}_{/Ref} + \frac{0.06}{v_e} \log \prod_i a_i^{v_i}$ at 25 °C, v_i and v_e algebraic
<i>E/pH</i> diagram of water redox couples	2.1.2 

Current

Main phenomena occurring when a current flows	2.2.1 Transport within the volume: migration, diffusion (diffusion layer), convection At the interfaces: redox or chemical reaction, exchange, accumulation
Writing and using the FARADAY law	2.2.2 $\Delta n_i^{\text{farad}} = \frac{v_i}{v_e} Q^{\text{farad}} = \frac{v_i}{v_e} j^{\text{farad}} S \Delta t$ $\Delta n_i, v_i, v_e, Q$ and j algebraic, $1 \mathcal{F} = N e \approx 96\,500 \text{ C mol}^{-1}$
Defining and using the faradic yield	2.2.2 Faradic yield: proportion of current used for a given half-reaction Additivity of faradic currents if several simultaneous reactions occur at the same interface
Describing the potential profile in an electrochemical system	2.2.3 $U(I \neq 0) = E_+ - E_- = U(I=0) + \pi_+ - \pi_- + \sum U_{\text{ohmic drop}}$ 2.4.3 ▶ system in electrolyser mode: $U(I \neq 0) \geq U(I=0) + U_{\text{ohmic drop}} \geq U(I=0)$ 2.4.4 ▶ system in power source mode: $U_{\text{supplied}} \leq U(I=0) - U_{\text{ohmic drop}} \leq U(I=0)$
Conduction by pure migration: conductivity, transport number	2.2.4 $\mathbf{j} = \sigma \mathbf{E} = \frac{1}{\rho} \mathbf{E}$ or $U = RI$, if σ is homogeneous in the volume $\sigma = \sum_i \sigma_i = \sum_i \lambda_i C_i \quad t_i = \frac{I_i}{I} = \frac{j_i}{j} = \frac{\sigma_i}{\sigma}$ λ_i molar ionic conductivity $\approx 10^{-2} \text{ S m}^2 \text{ mol}^{-1} = 10^2 \text{ S cm}^2 \text{ mol}^{-1}$ in aqueous solution σ_i ionic conductivity $\approx 1 \text{ S m}^{-1}$ for a concentration of about 0.1 mol L^{-1} t_i transport number of species i : $0 < t_i < 1$
Definition of a supporting electrolyte	2.2.4 Non-electroactive ions in much higher concentrations than those of electroactive ions The migration current of electroactive species is then negligible compared to the overall migration current. Moreover, the ohmic drop is most often insignificant in this situation