In this chapter, the basics of electrochemical sensing and sensors are described. As is the case with physical sensors in the electrical domain, the retrieved information can be represented by a voltage, a current or an impedance, as shown in Figure 9.1.

For chemical sensors based on electrochemical measuring principles, this subdivision turns out to be a fundamental one because different means of (ionic) mass transport are involved. Information represented by a voltage, a current or an impedance is retrieved by potentiometric sensors, by amperometric sensors or by electrolyte conductivity sensors, respectively.

This determines the outline of this chapter: a section defining some fundamentals is followed by three sections: Potentiometry, Amperometry and Electrolyte Conductivity.

9.1 SOME FUNDAMENTALS AND DEFINITIONS

In this section, several repeatedly used terms are defined [1].
- An electrolyte is a liquid solution through which charge is carried by the movement of ions.
• An electrode is a piece of metal (or semi conductor) through which charge is carried by electronic movement.
• An electrochemical cell is most generally defined as two electrodes separated by an electrolyte.
• The cell potential is the difference in potential across the electrodes of an electrochemical cell.

In an electrochemical cell, often two independent half-reactions take place, each representing the chemical changes at one of two electrolyte/electrode interfaces. Most of the time, we are only interested in one of these two reactions and the electrode at which this occurs is called the working electrode. The remaining electrode is called the reference electrode and is standardized by keeping the concentrations of the species involved in this half-reaction constant. (Nb: the reference electrode is used in potentiometry. For amperometry, another electrode, called the counter electrode, is required. The precise way of using the reference- and counter electrode is beyond the scope of this chapter.) An internationally accepted reference is the normal hydrogen electrode (NHE) where H₂ gas at one atmosphere pressure passes a platinum wire via a hollow tube in a solution with pH=0. All these definitions are visualized in Figure 9.2.

![Figure 9.2 Visualization of the concept of an electrochemical cell.](image)

### 9.2 POTENTIOMETRY

Since the reference electrode has a constant makeup, its potential is fixed. Therefore, any changes in the electrochemical cell are ascribed to the working electrode. We say that we observe or control the potential of the working electrode with respect to the reference, and that is equivalent to observing or controlling the energy of the electrons within the working electrode [1]. By driving the electrode to
more negative potentials the energy of the electrons is raised, and they will eventually reach a level high enough to occupy vacant states on species in the electrolyte. In this case, a flow of electrons from electrode to solution (a reduction current) occurs, resulting in a chemical reaction called reduction. A few examples of reduction reactions, illustrated in Figure 9.3a and b, are

$$\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+} \quad (9.1)$$

occurring, e.g., at an inert Pt electrode; both Fe$$^{x+}$$ ions remain dissolved in the electrolyte, and

$$\text{Ag}^+ + e \rightarrow \text{Ag} \quad (9.2)$$

occurring at a silver electrode, now getting thicker from the deposited silver ions.

Similarly, the energy of the electrons can be lowered by imposing a more positive potential, and at some point electrons on solutes in the electrolyte will find a more favourable energy on the electrode and will transfer there. Their flow, from solution to electrode, is an oxidation current. Some examples of oxidation reactions, illustrated in Figure 9.3c and d, are

$$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e \quad (9.3)$$

occurring, e.g., at a Pt electrode; both Fe$$^{x+}$$ ions remain dissolved in the electrolyte, and

$$\text{Ag} \rightarrow \text{Ag}^+ + e \quad (9.4)$$
occurring at a silver electrode, now getting thinner because of the dissolving silver ions.

It is obvious that (9.1) and (9.2) as well as (9.3) and (9.4) represent identical chemical reactions, only evolving in different directions. This is an interesting observation: lowering an electrode potential causes a reduction current, e.g., according to (9.1) and increasing the potential of this electrode causes the flow of the current to reverse its direction, resulting in an oxidation current, according to (9.3). Obviously, there must exist an electrode potential for which the (net) current is zero! Now what is this potential and how is it related to the chemical reaction of (9.1) and (9.3) and the concentrations of the species involved? This relation between the concentration of chemical species, participating in a redox reaction (= a reaction involving the reduction or oxidation of species) is found by Nernst1.

Let us first generalize (9.1) into:

\[ \text{ox} + n\,e \rightleftharpoons \text{red} \tag{9.5} \]

where \( n \) is the number of electrons involved in the redox reaction. In case there is neither oxidation nor reduction current, (9.5) represents a true equilibrium as indicated by the double arrow. Let us assume that this equilibrium occurs at electrode potential \( E \) (always with respect to the potential of the reference electrode, being 0 Volt per definition for a NHE). If we would force the electrode to a potential \( E' \), we would have to use an amount of work to oxidize (if \( E' > E \)) \( n \) mol of red into ox that is equal to

\[ n(E' - E)F = \text{[VC/mol]} \times \text{[J/mol]} \tag{9.6} \]

in which \( F \) equals Faraday's constant2, expressing the amount of Coulomb3 that is present in one mole of electrons: \( 1.6022 \times 10^{-19} \times 6.0220 \times 10^{23} = 96484 \) C/mol. The ratio of the concentrations of red and ox ions in that case is derived from Boltzmann4 statistics, stating that

\[ e^{-\alpha/RT} \tag{9.7} \]

equals the fraction of species (in moles) having an extra energy of at least \( \alpha \). \( RT \) [J/mol] is the product of the gas constant \( R \) (= 8.314 J/(mol K)) and temperature \( T \).

In our case, the species obtain this extra energy by the increased electrode potential. Now, the new ratio in red and ox concentrations can be expressed by substituting the amount of extra work given by (9.6) into (9.7), defining this ratio:

\[ \left( \frac{[\text{ox}]}{[\text{red}]} \right)_{\text{new}} = e^{-n(E-E)F/RT} \tag{9.8} \]

---

1 Walter Nernst (1864 – 1941), German physical chemist, winner of the Nobel prize in Chemistry in 1920.
2 Michael Faraday, 1791 – 1867, British physicist
3 Charles Augustin Coulomb, 1736 – 1806, French physicist and mathematician
4 Ludwig Boltzmann, 1844 – 1906, Austrian theoretical physicist
where \([\text{species}]\) represents the concentration of the species in \(\text{mol/dm}^3\). It will be no surprise, suggesting that this identity was already valid for the original equilibrium situation of (9.5) with the assumed electrode potential \(E\). In that case with non-existent \(E' (=0)\), (9.8) becomes

\[
\left( \frac{[\text{ox}]}{[\text{red}]} \right)_{\text{original}} = e^{nFRT} \tag{9.9}
\]

or

\[
E = \frac{RT}{nF} \ln \left( \frac{[\text{ox}]}{[\text{red}]} \right) \tag{9.10}
\]

dropping the subscript 'original'. This assumed concentration dependent electrode potential \(E\) has to be added to the standard potential of an electrode, \(E^0\), being the experimentally determined electrode potential under standard conditions for a specific red/ox couple (These standard conditions are: unity concentrations of 1 \(\text{mol/dm}^3\), at 101.3 \(\text{kPa}\) and \(T=298 \text{ K}\)). The values of \(E^0\) are different for each red/ox couple and can be found in tables.

In conclusion, we derived Nernst Law for any electrochemical reaction of the form \(\text{ox} + ne \rightleftharpoons \text{red}\) being

\[
E_{\text{Nernst}} = E^0 + \frac{RT}{nF} \ln \left( \frac{[\text{ox}]}{[\text{red}]} \right) \quad \text{or} \quad E_{\text{Nernst}} = E^0 + \frac{2.303 \cdot RT}{nF} \log \left( \frac{[\text{ox}]}{[\text{red}]} \right) \tag{9.11}
\]

By definition, a red or ox species, present in solid form or in gaseous form at atmospheric pressure gets unity (=1) concentration.

This important equation (9.11) is the basis of potentiometry, i.e., measuring the electrode potential with respect to a reference electrode as a function of the concentration of some chemical species in the electrolyte at (almost) zero current.

**Example 9.1 From electrode potential to concentration**

A silver electrode is immersed in an aqueous solution containing \(\text{AgNO}_3\). AgNO\(_3\) dissolves easily in water. The potential of that electrode is 0.70 \(\text{V}\), measured with respect to a Normal Hydrogen reference Electrode at room temperature. What is the concentration of \(\text{Ag}^+\), present in the solution?

The standard electrode potential of the redox reaction \(\text{Ag}^+ + e \rightleftharpoons \text{Ag}\) is \(E^0 = 0.80 \text{ V}\) (as tabled in many textbooks, e.g., in [1]). Now substituting the relevant parameters in eq. 9.11 yields:

\[
0.70 = 0.80 + \frac{2.303 \cdot 8.314 \cdot 298}{96484} \cdot \log \left[ \frac{[\text{Ag}^+]}{[1]} \right],
\]

or \([\text{Ag}^+]\]=\(2.0 \cdot 10^{-2} \text{ mol/dm}^3\) or 20 \(\text{mM}\), being 20 milliMolar, meaning \(2.0 \cdot 10^{-2} \text{ mol/dm}^3\).
Many types of electrodes exist, each requiring a detailed description, not given in this introductory chapter. All potentiometric electrodes, however, can be grouped according to their kind, as summarized in Table 9.1.

Basically, the concentration of a certain ion can be determined by measuring the electrode potential with respect to a reference electrode and using Nernst Law, but only in case one specific redox couple is present in the solution, like the examples mentioned in Table 9.1 for redox electrodes or electrodes of the first or second kind. When more redox couples are present, some mixed potential results, which does not represent the concentration of one specific ion. In all these cases extra membranes have to be engineered and added to the electrode in order to obtain specific information of the concentration of just one ionic species. This results in the last type of electrodes, mentioned in Table 9.1: the Ion Selective Electrodes (ISE).

Some examples:

\[
\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}, \quad E_{\text{Nernst}} = 0.77 + \frac{RT}{F} \ln \left( \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right), \quad \text{at Pt electrode, redox type;}
\]

\[
\text{Pb}^{2+} + 2e \rightarrow \text{Pb}, \quad E_{\text{Nernst}} = -0.13 + \frac{RT}{2F} \ln \left( [\text{Pb}^{2+}] \right), \quad \text{at Pb electrode, first kind;}
\]

\[
\text{Cl}_2 + 2e \rightarrow 2\text{Cl}^-, \quad E_{\text{Nernst}} = 1.36 + \frac{RT}{2F} \ln \left( \frac{[\text{Cl}_2]}{[\text{Cl}^-]} \right) = 1.36 - \frac{RT}{F} \ln \left( [\text{Cl}^-] \right), \quad \text{at Pt electrode, redox type.}
\]

Basic instrumentation for the measuring of the electrode potential with respect to the reference electrode only consists of a good voltmeter with a very high input impedance ($>>1\, \text{M} \Omega$), or an impedance transformer (a ‘follower’) with a high input impedance ($>>1\, \text{M} \Omega$) and a simple voltmeter. The main concern for the electronic part of the sensor system is to avoid noise, caused by the high source impedance of the electrochemical cell.

When measuring properly, the three given examples yield the following electrode potentials when the Fe$^{3+}$, the Pb$^{2+}$ and the Cl$^-$ concentration, respectively, is varied (see Figure 9.4). Remember that species present in solid form or in gaseous form at atmospheric pressure get unity concentration (=1) in the Nernst equation, which is here the case for the Pb and the Cl$_2$ concentration. Also, it is

<table>
<thead>
<tr>
<th>Electrode type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redox</td>
<td>Pt electrode in Fe$^{3+}$/Fe$^{2+}$-containing solution</td>
</tr>
<tr>
<td>First kind</td>
<td>Pb electrode in Pb$^{2+}$-containing solution</td>
</tr>
<tr>
<td>Second kind</td>
<td>Ag/AgCl electrode in Cl$^-$-containing solution</td>
</tr>
<tr>
<td>Membrane or ISE</td>
<td>Electrode in which a potential difference occurs across a membrane</td>
</tr>
<tr>
<td>Selective Electrode</td>
<td>(on top of the electrode); pH glass electrode, NO$_3^-$ electrode</td>
</tr>
</tbody>
</table>
assumed that the Fe\(^{3+}\)-concentration is varied at constant Fe\(^{2+}\)-concentration in Figure 9.4.

9.3 AMPEROMETRY

Amperometry\(^5\) is a technique of determining the concentration of an electro-active species via the electrical current that occurs due to the electrochemical reaction of that species at an electrode. Consider a possible redox reaction, e.g.,

\[
Ag^+ + e \rightleftharpoons Ag \tag{9.12}
\]

at a silver electrode in an electrolyte, containing Ag\(^+\)-ions.

When we now apply a potential step to the Ag-electrode in negative direction (lowering the electrode potential with respect to some reference electrode), it is already explained in Section 9.2 that a reduction current will occur (as shown in Figure 9.3b) resulting in a reduction reaction of the equilibrium reaction (9.12):

\[
Ag^+ + e \rightarrow Ag \tag{9.13}
\]

What is happening, is that silver ions from the electrolyte are now reduced to silver atoms and are deposited at the silver electrode, growing thicker. Due to this process, there are less Ag\(^+\)-ions near the electrode surface than in the bulk of the solution, causing a gradient in Ag\(^+\)-concentration; from the bulk (higher concentration) to the electrode (lower concentration). Such a gradient causes mass transport by diffusion: movement of a species under the influence of a concentration gradient.

As a result of this mass transport, the Ag\(^+\)-ions reach the electrode surface at a certain rate (= number of ions per second) and are subsequently reduced to Ag atoms. When we now express the number of ions in moles and normalize this rate

---

\(^5\) after André Marie Ampère, 1775 – 1836, French physicist and mathematician
per unit area, then the so-called flux of Ag\(^{+}\)-ions, \(J_{Ag^{+}}\), in mol/(m\(^2\)s) is obtained. Clearly, from (9.13), this flux of silver ions at the electrode surface is related to the reducing current, \(i_{red}\), through the electrode. This current can be easily expressed in the flux of Ag\(^{+}\)-ions, \(J_{Ag^{+}}\), by multiplying this flux with the actual electrode area \(A\) and Faraday’s constant \(F\):

\[
i_{red} = -J_{Ag^{+}}A\cdot F \quad [C/s] = [A]
\]

(9.14)

All this is schematically shown in Figure 9.5 in a simplified representation.

Figure 9.5 Impression of the flux caused by the concentration gradient resulting from the reduction of Ag\(^{+}\)-ions at the electrode.

Now let us summarize and generalize. The following general reduction reaction occurs at an electrode with a suitable potential:

\[
ox + ne \rightarrow \text{red}
\]

(9.15)

The depletion of ox at the electrode surface causes a concentration gradient of ox, leading to mass transport by diffusion. This results in a flux of ox, \(J_{ox}\) that is related to the reduction current, \(i_{red}\), through the electrode with area \(A\) according to

\[
i_{red} = -nFAJ_{ox} \quad \text{or} \quad J_{ox} = -\frac{i_{red}}{nFA}
\]

(9.16)

(9.16) is called Faraday’s Law stating that the amount of species involved in the redox reaction, transported by the flux in the electrolyte, is proportional to the amount of charge, transported through the electrode (=electrical current).

**Example 9.2 From current to flux**

An electric reducing current of 10 \(\mu\)A passes a silver electrode, immersed in an aqueous solution containing plenty of AgNO\(_3\) (easily dissolving in water). The electrode area in contact with the solution is 1 mm\(^2\). What is the flux of Ag\(^{+}\) ions, \(J_{Ag^{+}}\), that reaches the electrode and how many silver ions are reduced to silver per second?
Using eq. 9.16 yields: \( J_{Ag^+} = \frac{10 \cdot 10^{-6}}{1.96484 \cdot 1.1 \cdot 10^{-6}} = 1.04 \cdot 10^{-4} \text{ mol/m}^2\text{s} \). In 1 s on a 1 mm\(^2\) electrode, \( J_{Ag^+} \cdot 1 \cdot \text{A} \cdot N_A = 1.04 \cdot 10^{-4} \cdot 1 \cdot 10^{-6} \cdot 6.022 \cdot 10^{23} = 6.24 \cdot 10^{13} \text{ Ag}^+ \) ions are being reduced.

Now how can we relate the measured \( i_{\text{red}} \) to the original concentration of ox in (9.15)? In first approximation, this can be derived and expressed quite easily: \( i_{\text{red}} \) can be measured and is via (9.16) related to the flux \( J_{ox} \). The driving 'force' for \( J_{ox} \) is the concentration gradient of ox near the electrode, so we only have to find an expression for this gradient. For that, Figure 9.6 is used, being a more strict visualization of Figure 9.5.

![Figure 9.6 Illustration of the flux \( J_{ox} \) caused by the gradient \( \frac{\partial C_{ox}}{\partial x} \), present in the diffusion layer with thickness \( \delta_0 \).](image)

The flux \( J_{ox} \) is linearly related to the concentration gradient via a proportionality constant, \( D_{ox} \), and only one-dimensional diffusion is considered:

\[
J_{ox} = -D_{ox} \frac{\partial C_{ox}(x)}{\partial x} \text{ [mol/m}^2\text{s]} \tag{9.17}
\]

The minus sign is obvious from Figure 9.6. \( D_{ox} \) is the diffusion coefficient, the ease with which the ox particles travel through the electrolyte, and is expressed in m\(^2\)/s. Combining (9.16) and (9.17) yields an expression relating the measured current \( i_{\text{red}} \) to the concentration gradient:

\[
i_{\text{red}} = -nJ_{ox}AF = nFAD_{ox} \frac{\partial C_{ox}(x)}{\partial x} \text{ [A]} \tag{9.18}
\]

Equation (9.18) is generally valid and is called Fick's first law of diffusion\(^6\).

Now, we make a few assumptions in order to find a simple analytical expression for the gradient.

1. The slope of the gradient, \( \frac{\partial C_{ox}}{\partial x} \), is linear, as drawn in Figure 9.6.

\(^6\) Adolf Eugene Fick, 1831 – 1879, German physiologist, mathematician and physicist
2. The thickness of the layer in which diffusion takes place is fixed, $\delta_0$ in Figure 9.6.
3. The potential of the electrode is such, that $C_{ox}(x=0) = 0$, i.e., the concentration of ox at the electrode surface drops to zero.

In that case, (9.18) becomes

$$i_{red, \text{limiting}} = nFAD_{ox} \frac{(C_{ox}(\text{bulk}) - C_{ox}(x = 0))}{\delta_0} = \frac{nFAD_{ox}}{\delta_0} C_{ox}(\text{bulk}) \quad (9.19)$$

This is an important equation. It expresses the so-called limiting current for a given species at a certain concentration. It is called 'limiting', because a larger current for the specific reduction reaction of (9.15) is not possible at a fixed bulk concentration $C_{ox}(\text{bulk})$: $J_{ox}$ is at its maximum value. Note from (9.19), that apart from the variable to be measured, $C_{ox}(\text{bulk})$, the diffusion coefficient $D_{ox}$ also determines the limiting current. This value can be found in appropriate tables, or the curve $i_{red} = f(C_{ox}(\text{bulk}))$ can be experimentally determined once with known concentrations of $C_{ox}$, i.e., the sensor can be calibrated. Obviously, a curve like in Figure 9.7 will then be the result.

![Graph](image)

Figure 9.7 Illustration of the relation between the limiting current and the bulk concentration.

An example of a successful amperometric sensor that is based on the relatively simple equation (9.19), is the oxygen sensor (O$_2$-sensor) as introduced by Clark. An electrochemical cell, consisting of a Pt disk working electrode and a Ag ring counter electrode in an inner electrolyte solution, as shown in Figure 9.8a and b, is closed by a thin O$_2$-permeable membrane.

---

7 Leland C. Clark, medical biologist, developed the heart-lung machine and invented the Clark Oxygen Electrode
The Pt working electrode is kept at a potential of –0.7 V versus the Ag/AgCl electrode functioning as counter as well as reference electrode. Oxygen can arrive at this working electrode when it travels through the membrane (slowly, due to the low diffusion coefficient of O₂ in the membrane) and the thin layer of electrolyte (fast, due to the high diffusion coefficient of O₂ in water). At the electrode, the oxygen will immediately and completely be reduced at –0.7 V according to

\[
O_2 + 4e^- + 4H^+ \rightarrow 2H_2O
\]

Due to the difference in diffusion coefficient in the membrane and the electrolyte, and the fact that the electrolyte film is even thinner than the membrane, it is reasonable to assume, that the O₂-concentration gradient (determining the flux and the reduction current, according to (9.19)) is only present in the membrane and is virtually absent in the thin electrolyte film, as schematically shown in Figure 9.9.

Figure 9.8 The amperometric oxygen sensor: the Clark electrode; a) cross-sectional view of the total cell; b) a detailed view of the top, showing the membrane and the working and counter electrode.
This makes the Clark electrode successful: the carefully engineered membrane fixes the thickness \( \delta_0 \) in which the O\(_2\)-gradient is present. Figure 9.10a shows the importance of choosing the correct potential of the Pt working electrode. When the potential is too negative, other interfering redox reactions start to occur, resulting in an increased current. When the potential is not negative enough, not all O\(_2\) is completely reduced, causing a partial collapse of the current. The Clark electrode must operate, therefore, at a potential in the plateau region of the current. Only then the measured current truly represents the limiting current according to (9.19). By now, it should be clear that this limiting current increases for higher O\(_2\)-concentrations, as shown in Figure 9.10b.

Equation (9.19) is not generally valid because of the assumptions we had to make in order to derive (9.19) from (9.18). The weakest assumption is number 2, that of the assumed constant diffusion layer thickness \( \delta_0 \). In reality the thickness of
this layer increases in time, making δ a function of time: δ(t). What happens, is schematically shown in Figure 9.11.

Clearly, the slope of the concentration profile

$$\frac{\partial C_{ox}(x)}{\partial x} = \frac{\left(C_{ox}(bulk) - C_{ox}(x = 0)\right)}{\delta(t)}, \text{ with } C_{ox}(x=0)=0$$  \hspace{1cm} (9.20)

decreases for increasing t, because δ(t) increases. Consequently, according to (9.18) and (9.19) the flux and thus the measured current decreases with time, as shown in Figure 9.12.

Unfortunately, there is no longer one constant limiting current for each bulk concentration anymore. Assumption number 1 under (9.18), stating that \(\partial C_{ox}/\partial x\) is thought to be linear is also not true in reality, but the error thus introduced is only a constant factor of \(2/\sqrt{\pi}\) (ca. 13%). The real, curved concentration profile is shown in Figure 9.13 together with the assumed linear profile.

In order to get rid of the errors, introduced by the assumptions, we need a more rigorous description. For that, some extra mathematics is required, starting with the equation that describes the conservation of matter: the continuity equation:

$$\frac{\partial C_{ox}(x,t)}{\partial t} = -\frac{\partial J_{ox}(x,t)}{\partial x}$$  \hspace{1cm} (9.21)
This equation represents the change in concentration per second being equal to the change in flux per meter; [mol/(s m^3)] and can easily be illustrated with Figure 9.14. The change in concentration at x (in compartment Δx) can only be caused by the difference in flux into and flux out of this compartment:

\[
\frac{\partial C_{\alpha x}(x,t)}{\partial t} = \frac{J_{\alpha x}(x,t) - J_{\alpha x}(x + \Delta x,t)}{\Delta x}
\]

Letting Δx approach zero results in (9.21). Note that \( \frac{\partial J_{\alpha x}(x,t)}{\partial x} \) has dimensions of mol/(m^3 s), being a change in concentration per unit time, as required. Combining (9.17) and (9.21) yields Fick’s second law of diffusion:

\[
\frac{\partial C_{\alpha x}(x,t)}{\partial t} = D_{\alpha x} \left( \frac{\partial^2 C_{\alpha x}(x,t)}{\partial x^2} \right)
\]

(9.22)
If we now presume a planar electrode (e.g., a platinum disk at \(x=0\)) and an unstirred solution \([1]\), we can calculate the diffusion-limited current, \(i_{\text{red}}\), using eq. 9.22 and the following boundary conditions:

\[
C_{\text{ox}}(x,t = 0) = C_{\text{ox}}(\text{bulk}) \tag{9.23}
\]

\[
\lim_{x \to \infty} C_{\text{ox}}(x,t) = C_{\text{ox}}(\text{bulk}) \tag{9.24}
\]

\[
C_{\text{ox}}(x = 0,t) = 0 \quad \text{(for } t > 0\text{)} \tag{9.25}
\]

The initial condition (9.23) merely expresses the homogeneity of the solution before the experiment starts at \(t=0\), and the semi-infinite condition (9.24) is an assertion that regions sufficiently distant from the electrode are unperturbed by the experiment. The third condition, (9.25), expresses the surface condition after the (negative, reducing) potential step, resulting in sudden, complete depletion of ox-particles at the electrode surface.

The solution of (9.22), using conditions (9.23)-(9.25) can be obtained after Laplace transformation, resulting in a mathematical expression for \(C_{\text{ox}}(x,t)\). This expression (not given here) can be substituted in (9.23), producing the current-time response by using (9.18):

\[
i(t) = nFAC_{\text{ox}} \frac{D_{\text{ox}}}{\sqrt{\pi t}} \tag{9.26}
\]

which is known as the Cottrell equation\(^8\). As with every equation, having its own name, this is an important one. The meaning and practical use of the Cottrell equation (9.26) for amperometric concentration determination will be illustrated with the following example [3]. In Figure 9.15a several current versus time responses are shown for different concentrations of hydrogen peroxide, \(H_2O_2\). The involved reduction reaction is

\[
H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \tag{9.27}
\]

This reaction, and thus the reduction current as shown in Figure 9.15a occur at a Pt working electrode of 0.5 cm\(^2\) when stepping from 0 to -0.5 V (versus a so-called Ag/AgCl reference electrode).

To show that we are really dealing with the phenomena as predicted by Cottrell, we plot the curves of Figure 9.15a again, but now against \(1/\sqrt{t}\), because (9.26) then predicts straight lines:

\[
\frac{\partial i(t)}{\partial \frac{1}{\sqrt{t}}} = nFAC_{\text{ox}} \frac{D_{\text{ox}}}{\sqrt{\pi t}} C_{\text{ox}} \quad [\text{As}^{1/2}] \tag{9.28}
\]

\(^8\)Frederick Gardner Cottrell, 1877 – 1948, American analytical chemist; the equation was published in 1902
with different slopes for each different $\text{H}_2\text{O}_2$ concentration. Figure 9.15b confirms this prediction. The slopes of these curves are plotted in Figure 9.16, now as a function of the applied $\text{H}_2\text{O}_2$ concentration, giving the calibration curve for this sensor.

From the Cottrell equation, the diffusion coefficient can be determined as a verification:

$$D_\text{H}_2\text{O}_2 = \pi \left( \frac{\text{slope}}{nF} \right)^2 = 1.62 \times 10^{-9} \text{ m}^2/\text{s}$$

which is equal to the theoretical value of $1.6 \times 10^{-9} \text{ m}^2/\text{s}$.

In conclusion: this type of amperometric sensing appears to be a reliable method for the detection of the hydrogen peroxide concentration. This approach can also be applied for other redox couples, present in the solution, as long as they
are alone. However, when other redox-active species are also present, concentration information about one ion specifically can only be obtained by adding a selective membrane to the electrode.

9.4 ELECTROLYTE CONDUCTIVITY

9.4.1 Faradaic and Non-faradaic Processes

Two types of processes occur at electrodes [1]. One kind comprises those just discussed in the previous section, in which charges (i.e., electrons) are transferred across the metal-solution interface. This electron transfer causes oxidation or reduction. Since these reactions are governed by Faraday's law (i.e., the amount of species involved in the redox reaction, transported by the flux in the electrolyte, is proportional to the amount of charge, transported through the electrode (=electrical current), they are called faradaic processes. Electrodes at which faradaic processes occur are sometimes called charge transfer electrodes. Under some conditions a given electrode-solution interface will show a range of potentials where no charge transfer reactions occur because such reactions are thermodynamically or kinetically unfavourable. These processes are called non-faradaic processes. Although charge does not cross the interface under these conditions, external currents can flow (at least transiently) when the potential changes. We discuss now the case of a system where only non-faradaic processes occur: electrolyte conductivity sensing.

Electrolyte Conductivity (EC) sensing nowadays is a well-established and much practiced technique of measuring. After an introduction of the basic concept of EC sensing, the relevant equations to describe conductivity are presented. An additional topic of this section is to treat several options for increasing the reliability of EC sensing.

Electrolyte conductivity (EC) is an expression for the mobility and concentration of ions in an aqueous solution as a result of an electric field [4]. For the determination of EC, a voltage difference must be present between two conducting electrodes, placed in the solution. This difference in potential results in an electric field between the electrodes causing the mobile ions to migrate. The resulting ionic mass transport manifests itself at the conducting electrodes as an electronic current, known or measurable.

Ionic mass transport can take place by three different means, each governed by a different driving force, as indicated in Table 9.2. It will be clear that the only mode of mass transport, involved in EC is migration.

<table>
<thead>
<tr>
<th>modes</th>
<th>driving force</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion</td>
<td>difference in concentration, concentration gradient</td>
</tr>
<tr>
<td>migration</td>
<td>difference in electric potential, potential gradient, electric field</td>
</tr>
<tr>
<td>convection</td>
<td>difference in density, stirring</td>
</tr>
</tbody>
</table>
9.4.2 Theoretical background of EC sensing

Relevant equations and definitions[4]

The underlying ionic transport mode of EC is migration. The driving force of migration is a potential gradient, $dV/dx$, or electric field $E$:

$$ E = -\frac{dV}{dx} \text{ [V/m]} \quad (9.29) $$

This electric field imposes an electric force, $F_e$, on every charge particle, i.e., every ion:

$$ F_e = |z_i| q E \text{ [N]} \quad (9.30) $$

with $|z_i|$ the valence of ion $i$, and $q$ the electronic charge. The ion will accelerate until the frictional drag (due to the viscosity of the medium) exactly counterbalances the electric force. Then, the ion travels at a constant velocity, $v$. At this velocity, the ion experiences a frictional or drag force, $F_d$, equal to

$$ F_d = 6 \pi \eta r v \text{ [N]} \quad (9.31) $$

with $\eta$ the viscosity of the medium and $r$ the ionic radius. This situation is depicted in Figure 9.17.

![Figure 9.17](image)

Figure 9.17 The force balance experienced by a charged particle under the influence of an applied electric field, $E$, in a viscous medium, resulting in a constant travelling speed, $v$.

At constant velocity, $F_e = F_d$, and from (9.30) and (9.31) the mobility of the ion $i$, $\mu_i$, is defined:

$$ \mu_i = \frac{v}{E} = \frac{|z_i| q}{6 \pi \eta r} \text{ [m/s per V/m \equiv m^2/(Vs)]} \quad (9.32) $$

The resulting ionic mass transport flux by migration, $J_i$, using (9.29) is

$$ J_i = -\mu_i C_i \frac{dV}{dx} \text{ [mol/(m^2s)]} \quad (9.33) $$

with $C_i$ the concentration of ion $i$ [mol/m^3]. The resulting electronic current density, due to all $n$ ions that are present in the solution is
\[ J = F \frac{dV}{dx} \sum_{i=1}^{n} |z_i| \mu_i C_i \quad [\text{A/m}^2] \quad (9.34) \]

When the electric field \( E = \frac{dV}{dx} \) is linear between two electrode plates with electrode area \( A \) and distance \( \ell \), as depicted in Figure 9.18, the electronic current can be obtained:

\[ i = JA = FA \frac{\Delta V}{\ell} \sum_{i=1}^{n} |z_i| \mu_i C_i \quad [\text{A}] \quad (9.35) \]

with \( \Delta V \) the potential difference that is present between the electrodes.

**Example 9.3 Ion velocity due to migration**

What is the maximum velocity of a silver ion in an aqueous solution migrating between two plan-parallel electrodes placed \( \ell = 1 \text{ mm} \) apart with 0.1 \( V_{\text{RMS}} \) over these electrodes?

The mobility of \( \text{Ag}^+ \) ions is tabulated in text books: \( \mu_{\text{Ag}^+} = 6.43 \times 10^{-8} \text{ m}^2/\text{sV} \) at room temperature. \( V_{\text{electrode}} = 0.1 \text{ V}_{\text{RMS}} \) means \( \Delta V_{\text{electrode}} = 0.141 \text{ V}_{\text{top}} \).

Using eqs. 9.29 and 9.32 the maximum velocity \( v = \mu_{\text{Ag}^+} \cdot E = \mu_{\text{Ag}^+} \cdot \left( \frac{\Delta V_{\text{top}}}{\ell} \right) = 6.43 \times 10^{-8} \times (0.141/1 \times 10^{-3}) = 9.1 \times 10^{-6} \text{ m/s} = 9.1 \mu\text{m/s} \).

Now, the conductance \( G \) can be expressed using (9.35):

\[ G = \frac{1}{R} = \frac{i}{\Delta V} = FA \frac{\sum_{i=1}^{n} |z_i| \mu_i C_i}{\ell} \quad [\text{S}] = [\text{Siemens}] \quad (9.36) \]

with \( R \) is the resistance. The conductance \( G \) is a variable that can be measured, and depends on the type and dimensions of the electrodes. To be independent on these system parameters, the conductivity \( \kappa \) can be defined as

\[ \kappa = \frac{1}{\rho} = Gk \quad [\text{m}^{-1}] \quad (9.37) \]

with \( \rho \) [\text{\Omega m}] the resistivity, and \( k \) [m\(^{-1}\)] the system parameter, called the cell-constant. In the case of two plan-parallel electrodes shown in Figure 9.18 with area \( A \) and distance \( \ell \), \( k = \ell/A \) as can be derived from (9.36) and (9.37). So, from these equations, the expression for the conductivity, \( \kappa \), is

\[ \kappa = F \sum_{i=1}^{n} |z_i| \mu_i C_i \quad [\text{m}^{-1}] \quad (9.38) \]

For solutions of simple, pure electrolytes (i.e., one positive and one negative ionic species, like KCl or CaCl\(_2\)) the conductivity can be normalized with respect to its equivalent concentration of positive (or negative) charges, \( C_{\text{eq}} \), from which the equivalent conductivity \( \Lambda_{\text{eq}} \) can be obtained:
\[
\Lambda_{eq} = \frac{\kappa}{C_{eq}} \quad [\Omega^1 m^2/mol \text{ of charge}] \tag{9.39}
\]

with \( C_{eq} = |C| z_i \). From (9.38) and (9.39), \( \Lambda_{eq} \) can be expressed as

\[
\Lambda_{eq} = F (\mu_+ + \mu_-) \tag{9.40}
\]

with \( \mu_+ \), \( \mu_- \) the cationic and anionic mobility, respectively. This equation leads to the definition of equivalent ionic conductivity, \( \lambda_{i,eq} \):

\[
\lambda_{i,eq} = F \mu_i \quad [\Omega^1 m^2/mol \text{ of charge}] \tag{9.41}
\]

Note, that following the same line of reasoning a molar conductivity, \( \Lambda_m \), and a molar ionic conductivity, \( \lambda_{i,m} \), can be defined:

\[
\Lambda_m = \frac{\kappa}{C} \quad [\Omega^1 m^2/mol \text{ of species}] \tag{9.42}
\]

with \( C \) [mol/m³] the concentration of the added species and

\[
\lambda_{i,m} = F \mu_i z_i \quad [\Omega^1 m^2/mol \text{ of species}] \tag{9.43}
\]

**Sensing of EC**

For a proper understanding of practical EC determination, it is necessary to introduce the electrode-solution interface before continuing.
In Figure 9.19 a complete, two-electrode EC sensor is schematically depicted. As explained, a voltage applied over the two electrodes would result in an electric current due to the migrating ions as a result of the electric field that is caused. It will be explained that EC can not be successfully determined by a DC voltage over the electrodes.

**Scenario 1**
The applied DC voltage is that high, that redox reactions at the electrodes will occur and current flows via $R_{\text{diffusion}}$ through the faradaic path of Figure 9.19. Possible reactions in a solution of NaCl in water are, e.g.,:

- at the anode, $+$, $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^{-}$
- at the cathode, $-$, $2\text{H}_2\text{O} + 2\text{e}^{-} \rightarrow 2\text{OH}^- + \text{H}_2$

In this case, however, the concentrations of mobile ions contributing to the EC (Cl$^-$ and OH$^-$, in this example), changes at the proximity of the electrode, giving rise to mass transport by diffusion. Thus, a proper EC determination in which only transport by migration is allowed, is no longer possible.

**Scenario 2**
The applied DC voltage is low enough to avoid any redox reactions. In this case, however, the charge on the conducting electrode that is present due to the applied voltage, will almost immediately be counteracted by an equal amount of ionic charge, of opposite sign, in the solution at the direct proximity of the electrode. Of course, it are these two charges that form the well-known double layer capacitance, also present in Figure 9.19. But now, the potential applied over the electrode, with respect to the solution, will be present over $C_{\text{dl}}$ only: no longer over the solution itself, thus inhibiting any migration due to the absence of the driving force; the electric field.

From this discussion, it may be clear that EC can only be determined properly by applying an AC voltage over the electrode with such an amplitude, that redox processes are avoided, and with such a frequency, that the impedance of $C_{\text{dl}}$ is of the order of, or much smaller than the $R_{\text{dl}}$ to be determined, to allow a practical and precise EC determination.
9.4.3 Extra reliability

Reliability at EC sensing means the unambiguous determination of $R_{el}$ of Figure 9.20.

![Simplified representation of the electrode-solution interface impedance, including the electrolyte resistance, $R_{el}$.](image)

Figure 9.20 Simplified representation of the electrode-solution interface impedance, including the electrolyte resistance, $R_{el}$.

Theoretically, this can be accomplished by carefully taking into account the electrode-solution interface impedance, schematically depicted by $R_{diffusion}$ and $C_{dl}$ of Figure 9.20. This impedance, however, is by no means a constant and ideal element, but varies with the concentration of the electrolyte, its composition, and also with the electrical potential and frequency over the electrode-solution interface. Therefore, a practically more feasible approach is to design the EC sensor in such a way, that the electrode-solution interface impedance influences the total impedance of the sensor (as shown in Figure 9.19) as minimally as possible. Two options are elaborated in the next sub-sections.

Use of Pt-black electrodes

By a proper (electro)chemical treatment, the otherwise shiny surface of a Pt electrode can become black due to the thus obtained cauliflower-like structure. The resulting rough surface can be characterized by its original geometric electrode surface area, $A_{geometric}$ and by its effective surface area, $A_{effective}$, as schematically depicted in Figure 9.21.

![Characterization of Pt-black electrode surfaces](image)

Figure 9.21 a) A Pt-black electrode can be characterized by its geometric electrode area, $A_{geometric}$ and the real area, including the surface area of all micro-structures, $A_{effective}$; b) increasing the roughness of the electrode surface decreases the impedance of the double layer capacitance, leaving the electrolyte resistance unaffected, resulting in a more precise determination of $R_{el}$ at a given measurement frequency.
Remember, that at proper operation, $R_{\text{diffusion}}$ of Figure 9.20 is absent, because only migrational effects via $C_{\text{dl}}$ are involved in EC determination. Now, the effect of the Pt black electrode can be easily explained. The electrolyte resistance, $R_{\text{el}}$ of Figure 9.21b, is determined by the electrode area $A_{\text{geometric}}$, and is not affected by the rough surface and remains constant at constant electrolyte concentration. The double layer capacitance, $C_{\text{dl}}$, however, is determined by the rough electrode surface and thus by $A_{\text{effective}}$. As the impedance of $C_{\text{dl}}$ ($=1/j\omega C_{\text{dl}} + 1/A_{\text{effective}}$) dramatically decreases with a likewise dramatically increasing $A_{\text{effective}}$ with respect to $A_{\text{geometric}}$, due to the Pt-black formation, the impedance of $C_{\text{dl}}$ can virtually be neglected with respect to $R_{\text{el}}$ at a suitable measuring frequency. Thus, the goal as stated at the start of this section: an unambiguous determination of $R_{\text{el}}$, by decreasing the effect of the interface impedance, is obtained.

However, by fouling and/or degeneration of the initial rough Pt surface, the ratio $A_{\text{effective}} / A_{\text{geometric}}$ gradually decreases, thereby lowering the favourable effect of the treatment. Moreover, the Pt black electrode is mechanically rather weak, making (mechanical) cleaning not very well possible. Therefore, periodic regeneration of the Pt black electrode is necessary in order to keep its favourable behaviour.

The conventional 4-points EC measurement
A well-known alternative to the previously described approach is the 4-points measuring method, as schematically depicted in Figure 9.23 (see Section 7.1.4).

By separating the current injection electrodes from the voltage measurement electrodes, the voltage drop over the electrode impedance, $Z_{\text{electrode}}$ in Figure 9.22, is no longer present in the measured potential. Moreover, as there are no longer strict demands on the current electrodes, they can be designed very small.

Also this method, however, has some disadvantages. Firstly, the design of the probe is more complicated due to the increased number of electrodes and their interrelation. Secondly, the design and implementation of the electronics is also a bit more complicated. Thirdly, the signal-to-noise ratio of the whole sensor plus electronics is a critical and difficult to tackle parameter, due to the high impedance of the potential sensing electrodes.
Example 9.5 EC sensing with an interdigitated electrode pair

One of the common manifestations of an EC sensor is the so-called interdigitated conductivity electrode [4]. Especially in small (chemical micro-)systems, the planar structure is an advantage. Moreover, this device can be fabricated in a clean room with usual photolithographic techniques. A typical lay out of such a device is depicted in Figure 9.23a.

![Diagram of an interdigitated electrolyte conductivity electrode](image)

Figure 9.23 a) Impression of an interdigitated electrolyte conductivity electrode; b) admittance versus potassium-nitrate concentration, measured at 200 kHz. The range from 0.5 to 20 mM KNO3 is equivalent to 0.072 to 2.9 mS/cm.

The overall dimensions are 1 x 1 mm². In reality, the device consists of 9 fingers in total. In order to minimize the interfering effect of the double layer impedance, the operating frequency had to be chosen at 200 kHz. The result of a set of measurements in different potassium nitrate (KNO₃) concentrations is shown in Figure 9.23b. Here, the reciprocal value of $R_{el}$ is plotted as a function of the concentration, because then a linear dependence is expected (and obtained). The calculation of the cell constant of such an interdigitated structure is a mathematically complicated task, not repeated here [5]. The calculated cell constant of this device is 1.28 cm⁻¹ and the experimentally determined value is 1.24 cm⁻¹.

9.5 FURTHER READING


This excellent book is not a standard textbook concerning electrochemical sensors as such, but a very fundamental and at the same time well-readable book about all possible electrochemical aspects on electrode – solution interfaces and much more.

9.6 REFERENCES

9.7 EXERCISES

1. What is the dimension of $RT/F$? What is the quantity of $RT/F$ at room temperature ($T=298\text{K}$)?

2. Why is measuring the electrode potential using a voltmeter with relatively low input impedance not wise in potentiometry?

3. What is the potential difference between a silver electrode and an aluminium electrode, immersed in an aqueous solution at room temperature containing $50 \cdot 10^{-3}$ mol/dm$^3$ AgNO$_3$ and $20 \cdot 10^{-3}$ mol/dm$^3$ Al(NO$_3$)$_3$?

4. What is the flux of electrons at a distance of 1 meter from an electron emitter, spraying electrons homogeneously in all directions? A current of 1 $\mu$A is applied to the emitter.

5. An O$_2$-sensitive Clark electrode is used in an aqueous solution in which 5 millimol/dm$^3$ of O$_2$ is dissolved. The measured limiting current is 4 $\mu$A. The thickness of the O$_2$-permeable membrane is 20 $\mu$m and the surface area of the Pt-electrode is 1 mm$^2$. Calculate the diffusion coefficient $D_{O2}$ of oxygen in the membrane.

6. Referring to example 9.2, what is the electrochemical deposition rate of Ag on the electrode (expressed in thickness increase per time)? Additional data: 1 mol Ag weighs 0.108 kg and 1 m$^3$ Ag weighs $7.9 \cdot 10^3$ kg.

7. Conductivity is temperature dependent. What parameter causes this temperature dependence and will the conductivity increase or decrease when raising the temperature?

8. Express the capacitance $C$ and the resistance $R$ of the configuration of Figure 9.18, using its cell-constant, in case a block of material is placed between the electrodes with relative permittivity $\varepsilon_r$ and resistivity $\rho$. In addition, derive the expression for the $RC$-product. What is the dimension of $RC$?

9. Check the experimentally determined curve shown in Figure 9.23b for [KNO$_3$]=10 mM, knowing that $\mu_{K^+}=7.62 \cdot 10^{-8}$ m$^2$/sV, $\mu_{NO_3^-}=7.40 \cdot 10^{-8}$ m$^2$/sV at $T=298\text{ K}$ and the cell-constant is $k=1.24 \text{ cm}^{-1}$. 

