

Transport at electrodes

The rate of an electrode reaction, r (mol cm⁻² s⁻¹), is expressed via the **Faraday law**:

$$r = \frac{I}{nF} \quad (4.1)$$

where I is the current density, n the number of electrons exchanged in the reaction and F the Faraday constant. Reaction rate is a **scalar** quantity but electric current is a **vector**. Coupling these two quantities of different tensorial degree takes place via the mass balance only at the electrode surface. Because r is always positive, I and n must have the same sign, i.e. for oxidation, according to the IUPAC convention, I and $n > 0$ and for reduction I and $n < 0$.

Current is carried by all ions in the solution according to their transport numbers but at the electrode only those ions which participate in the electrode reaction are charge carriers. Yet another issue worth noticing is that only the flux component **normal to the surface** is counted as an electric current. In the case of Cu²⁺ reduction to metallic copper,

$$I = 2Fj_{\text{Cu}^{2+}}^s \cdot \vec{n} < 0 \quad (4.2)$$

where \vec{n} is the unit vector normal to the surface. Keeping this in mind, the flux of an electroactive species at the electrode is

$$j_i = \frac{\nu_i I}{nF} \quad (4.3)$$

Let's consider the reaction $\text{Fe}(\text{CN})_6^{3-} + e^- \rightarrow \text{Fe}(\text{CN})_6^{4-}$, and denote ferricyanide (Fe³⁺) as species 1 and ferrocyanide (Fe²⁺) as species 2. The reaction is reduction, thus $I < 0$; $-\nu_1 = \nu_2 = 1$, and $n = -1$; $z_1 = -3$ and $z_2 = -4$. Therefore, $n = z_2 - z_1$. Current density can also be written as $I = F(z_1 j_1 + z_2 j_2)$. The only way this agrees with Eq. (4.3) is that $j_1 = -j_2 < 0$, minus sign indicating that the direction of j_1 is opposite to that of j_2 along the surface normal.

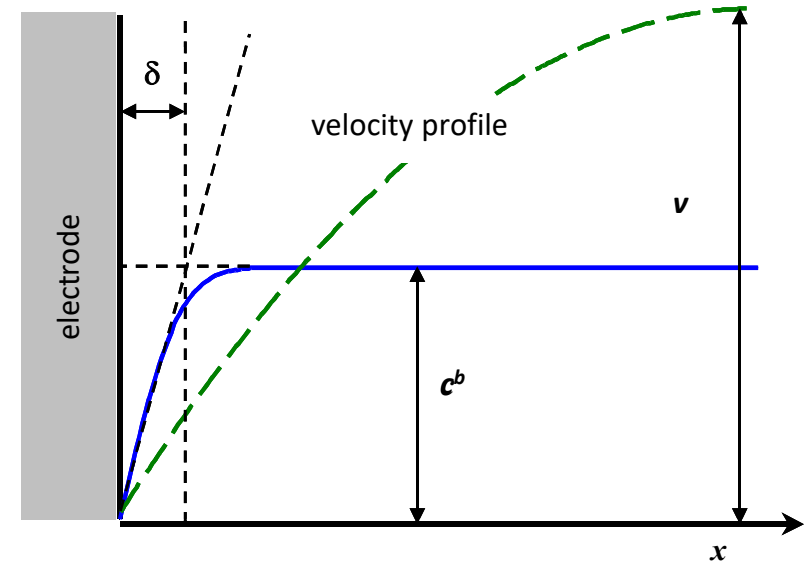
This example reveals a feature which may look self-evident: unless adsorption takes place at the electrode surface, the fluxes of the reactants and products must be the same but opposite in direction. But if we consider a reaction of a chloro complex $MCl_2 + 2e^- \rightarrow M^0 + 2Cl^-$ the situation is not that clear. Chloride anions released in the reaction must be transported away from the electrode surface, in order to maintain local electroneutrality. Therefore, $2j_{MCl_2} = -j_{Cl^-} = -I/F$, although Cl^- is not as such an electroactive species. Those species that do not participate electrode reactions have zero flux at the surface of an electrode which gives a useful boundary condition for their transport equations.

The notation in the textbook is such that the electrode surface resides at $x = 0$ ($r = a$ at spherical electrodes*) and a solution extends to $x > 0$ ($r > a$). The Galvani potential at the electrode surface is $\phi(0) = \phi^s$ and in the bulk solution ϕ^b ; $\Delta\phi = \phi^b - \phi^s$. For oxidation $\Delta\phi < 0$ and for reduction $\Delta\phi > 0$. Note that ϕ^s is not the electrode potential. Electrode potential is $E = \phi^M - \phi^s$ where ϕ^M is the potential of an electron in the Fermi level of an electrode (metal) and is expressed via the Nernst equation (at equilibrium).

*Here r is not the reaction rate but the spatial coordinate in spherical geometry.

Transport at electrodes at steady-state

When electric current flows concentrations at the electrode surface change due to the electrode reactions; reaction rate is coupled to mass transfer as discussed above. At steady-state, in the absence of chemical reactions, $-(\partial c_i / \partial t) = \nabla \cdot j_i = 0$. A true steady-state can be achieved only by stirring the solution (an exception is found in spherical geometry that is discussed later on). Yet, there always remains an unstirred layer close to the surface. Its thickness δ depends on the viscosity of the solution and the type of stirring. In aqueous solutions the thickness of the unstirred layer typically is 1 - 10 μm , depending on the geometry and stirring rate. In the absence of stirring, natural convection may take place at the electrode due to the changes in the solution density (i.e. partial molar volumes). Also in this case an unstirred layer is formed; its thickness is of the order of 50 - 100 μm .



When the solution is stirred the situation is something like what is depicted in the picture above. At the electrode the solution velocity is zero but increases towards the bulk of the solution (green line) with a manner that depends on the stirring method. The concentration profile (blue line) may develop much faster to its bulk value, c^b . The thickness of the boundary layer is defined as depicted but it is only a thought, virtual definition, because we cannot measure it. Therefore, it is eliminated from the solution of the transport problem with the measurable limiting current, as explained shortly, and assuming that in the region $0 < x < \delta$ there is no convection. In order to fully utilize stirring we have to resort to methods where the velocity profile can be explicitly known; a stirrer bar or a paddle does not create a well-defined velocity profile.

According to the Nernst-Planck equation, the flux of a species consists of diffusion, migration and convection contributions. It was assumed that within $0 < x < \delta$ there is no convection but even if δ were zero, $v = 0$ at $x = 0$, which is known as the **non-slip condition**. We also saw (Eqs. (3.7) – (3.9)) that adding a sufficient amount of an inert, non-electroactive electrolyte in the solution, the Galvani potential gradient can be made insignificantly small. In that case, the transport of an electroactive species has only the diffusion contribution: $j_i = -D_i \nabla c_i$. In linear geometry the flux density j_i does not depend on the location, $j_i \neq j_i(x)$, which means that $dc_i/dx = \text{constant}$. In a more quantitative manner, assuming a constant diffusion coefficient,

$$\nabla \cdot j_i = \frac{\partial}{\partial x} \left(-D_i \frac{\partial c_i}{\partial x} \right) = -D_i \frac{\partial^2 c_i}{\partial x^2} = 0 \Rightarrow c_i(x) = Ax + B = c_i^s + \frac{c_i^b - c_i^s}{\delta} x \quad (4.4)$$

where the boundary conditions $c_i(0) = c^s$ and $c_i(\delta) = c^b$ are used. Electric current density thus becomes

$$\frac{v_i I}{nF} = -D_i \left(\frac{\partial c_i}{\partial x} \right)_s = -D_i \frac{c_i^b - c_i^s}{\delta} \Leftrightarrow c_i^s = c_i^b + \frac{v_i I \delta}{nFD_i} \quad (4.5)$$

The lowest value that the surface concentration can take is naturally zero, which gives the highest possible current density, the **limiting current density**,

$$I_{L,i} = -\frac{nFD_i c_i^b}{v_i \delta} \quad (4.6)$$

The above equation applies to a **trace-ion** the concentration, which is ca. 1-2% of the concentration of the **supporting electrolyte**, making its migration contribution insignificantly small. The motivation of using trace-ions is obvious: calculus remains relatively simple. Therefore, most of electrochemical experiments are carried out adding a supporting electrolyte. In industrial electrolysis that is, however, not the case and we have to consider it later on.

Using Eq. (4.6) the bulk concentration can be written as $c_i^b = -\frac{v_i I_{L,i} \delta}{nFD_i}$ and inserting this into (4.5) leads to a very useful form,

$$c_i^s = c_i^b \left(1 - \frac{l}{l_{L,i}} \right) \quad (4.7)$$

Eq. (4.7) has only measurable quantities without need to know, e.g. the thickness of the diffusion boundary layer, δ . There are naturally electrochemical means of determining D_i , hence δ can be calculated (if needed) from the above expression of the bulk concentration.

If there is only one electroactive species that is denoted as species 1, it carries all the current at steady-state, i.e. $I = z_1 F j_1$. In this case the limiting current density can be written as

$$I_{L,1} = -\frac{z_1 F D_1 c_1^b}{\delta} \quad (4.8)$$

Binary solution

Let's consider a binary solution of CuCl_2 where Cu^{2+} is reduced to metallic copper; $[\text{Cu}^{2+}] = c_1 = c_{12}$ and $[\text{Cl}^-] = c_2 = 2c_{12}$. We learnt earlier that the Nernst-Planck equation can be written in the following form:

$$j_1 = -D_{12} \frac{dc_{12}}{dx} + \frac{t_1 I}{2F} = \frac{I}{2F}$$

$$j_2 = -2D_{12} \frac{dc_{12}}{dx} - \frac{(1-t_1)I}{F} = 0 \quad \Rightarrow \quad \frac{dc_{12}}{dx} = -\frac{(1-t_1)I}{2FD_{12}} \quad (4.9)$$

Eq. (4.9) is easy to integrate using the boundary condition $c_{12}(\delta) = c_{12}^b$. The result is

$$c_{12}(x) = c_{12}^b + \frac{(1-t_1)I}{2FD_{12}}(\delta-x) \quad \text{and} \quad c_{12}^s = c_{12}^b + \frac{t_2I\delta}{2FD_{12}} = c_{12}^b + \frac{I\delta}{6FD_1} \quad (4.10)$$

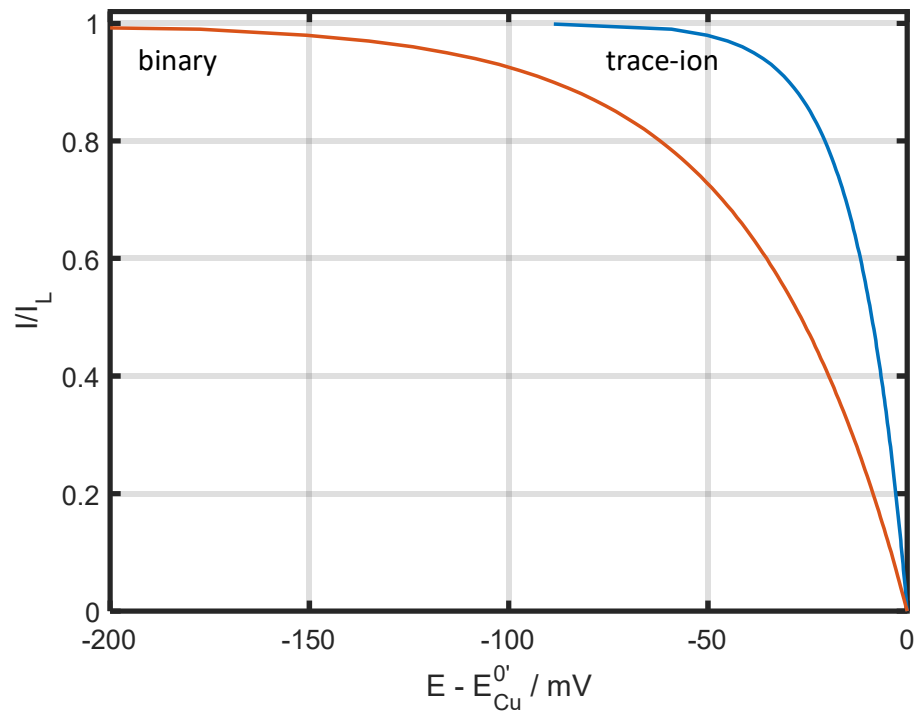
where the Nernst-Hartley equation (3.13) and the transport number, Eq. (3.14) have been used. The limiting current density now becomes

$$I_L = -\frac{6FD_1c_{12}^b}{\delta} \quad (4.11)$$

which is thrice that of a trace-ion. This phenomenon is known as the **supporting electrolyte paradox**: although adding a supporting electrolyte increases the conductivity of the solution, the limiting current decreases. The reason is that in a binary case the transport of Cu^{2+} still has the migration contribution that enhances its flux, consequently increasing the limiting current.

It is also worth noticing that, because of electroneutrality, the concentration profile of Cl^- follows the profile of Cu^{2+} . This means that close to the limiting current, conductivity of the solution at the electrode is very low because the concentration of CuCl_2 is close to zero, causing an extra potential drop in the solution. If we write down the Nernst-Planck equation of Cl^- :

$$\begin{aligned} j_2 = 0 &= -D_2 \left(\frac{dc_2}{dx} - c_2 f \frac{d\phi}{dx} \right) \Rightarrow d\phi = \frac{1}{f} d \ln c_{12} \\ \Rightarrow \Delta\phi = \phi^b - \phi^s &= -\frac{RT}{F} \ln \frac{c_{12}^s}{c_{12}^b} = -\frac{RT}{F} \ln \left(1 - \frac{I}{I_L} \right) \Leftrightarrow I = I_L \left(1 - e^{-f\Delta\phi} \right) \end{aligned} \quad (4.12)$$



In the figure aside the current-voltage curve is simulated for the Cu^{2+} deposition. In the case of the binary solution the potential values include also $\Delta\phi$ while in the trace case only Nernst equation is used:

$$E - E_{\text{Cu}}^{0'} = \frac{RT}{2F} \ln\left(\frac{c_1^s}{c^*}\right) = \frac{RT}{2F} \ln\left(\frac{c_1^b}{c^*}\right) + \frac{RT}{2F} \ln\left(1 - \frac{I}{I_L}\right) \quad (4.13)$$

where c^* is the standard concentration, 1 mol/L and $c_1^b = c^*$.

Based on the figure above, it is obvious that an industrial process cannot be run too close to the limiting current because potential losses increase substantially.

Multicomponent system, one electroactive species

The electroactive species is denoted by subscript 1, hence $I = z_1 F j_1$. The fluxes of all the other species is zero at steady-state. From their Nernst-Planck equation, integration from x to δ gives

$$j_i = 0 = -D_i \left(\frac{dc_i}{dx} + z_i c_i f \frac{d\phi}{dx} \right) \Rightarrow c_i(x) = c_i^b e^{-z_i \phi}, \quad i \neq 1, \quad \phi = f[\phi(x) - \phi^b] \quad (4.14)$$

The surface concentration of the non-electroactive species thus is $c_i^s = c_i^b e^{z_i f \Delta \phi}$. From electroneutrality,

$$c_1(x) = -\frac{1}{z_1} \sum_{i \neq 1} z_i c_i(x) = -\frac{1}{z_1} \sum_{i \neq 1} z_i c_i^b e^{-z_i \phi} \quad (4.15)$$

Summing (j_i/D_i) gives

$$\sum_i \frac{j_i}{D_i} = \frac{j_1}{D_1} = \frac{I}{z_1 F D_1} = -\sum_i \frac{dc_i}{dx} - f \frac{d\phi}{dx} \sum_i z_i c_i = -\frac{dc_T}{dx} \quad (4.16)$$

where c_T is the total ionic concentration and electroneutrality is used. Eq. (4.16) can be integrated from $x = 0$ to $x = \delta$ with the help of Eqs. (4.14) and (4.15):

$$j_1 = \frac{D_1}{\delta} [c_T(0) - c_T^b] = \frac{D_1}{\delta} \sum_{i \neq 1} \left(1 - \frac{z_i}{z_1} \right) c_i^b (e^{z_i f \Delta \phi} - 1) \quad (4.17)$$

Current can also be expressed in the form of Ohm's law $I = -\kappa_{\text{eff}} \nabla \phi$ where the effective conductivity κ_{eff} can be calculated as follows:

$$\begin{aligned}
I = z_1 F j_1 &= -F D_1 \left[\frac{d(z_1 c_1)}{dx} + z_1^2 c_1 f \frac{d\phi}{dx} \right] = F D_1 \left[\sum_{i \neq 1} \frac{d(z_i c_i)}{dx} - z_1^2 c_1 f \frac{d\phi}{dx} \right] \\
&= -F D_1 \left[\sum_{i \neq 1} z_i^2 c_i f \frac{d\phi}{dx} + z_1^2 c_1 f \frac{d\phi}{dx} \right] = -\frac{F^2 D_1}{RT} \sum_i z_i^2 c_i \left(\frac{d\phi}{dx} \right) = -\kappa_{\text{eff}} \left(\frac{d\phi}{dx} \right)
\end{aligned} \tag{4.18}$$

Note that κ_{eff} includes D_1 only because the other species do not move at steady-state. Let's continue with the CuCl_2 example adding NaCl as the supporting electrolyte. Cu^{2+} is species 1, Na^+ species 2 and Cl^- species 3. Therefore, $[\text{CuCl}_2] = c_{13}$ and $[\text{NaCl}] = c_{23}$. Furthermore, $c_1^b = c_{13}^b$, $c_2^b = c_{23}^b$, $c_3^b = 2c_{13}^b + c_{23}^b$, and $2c_1 + c_2 = c_3$. From Eq. (4.17):

$$j_1 = \frac{D_1}{\delta} \left[\frac{1}{2} c_{23}^b (e^{f\Delta\phi} - 1) + \frac{3}{2} (2c_{13}^b + c_{23}^b) (e^{-f\Delta\phi} - 1) \right] \tag{4.19}$$

At limiting current $c_1(0) = 0$ and electroneutrality states that $c_2(0) = c_3(0)$. Applying Eq. (4.14),

$$c_{23}^b e^{f\Delta\phi_L} = (2c_{13}^b + c_{23}^b) e^{-f\Delta\phi_L} \Leftrightarrow e^{f\Delta\phi_L} = \sqrt{\frac{2c_{13}^b + c_{23}^b}{c_{23}^b}} \tag{4.20}$$

Inserting (4.20) into (4.19), the limiting current density is obtained after some algebra as

$$\frac{I_L}{2F} = \frac{D_1}{\delta} \left[2\sqrt{c_{23}^b (2c_{13}^b + c_{23}^b)} - 3c_{13}^b - 2c_{23}^b \right] \tag{4.21}$$

Trace-ion case is obtained when $c_{13}^b \ll c_{23}^b$. In that case $\sqrt{c_{23}^b(2c_{13}^b + c_{23}^b)} \approx c_{23}^b + c_{13}^b$ and the limiting current density becomes

$$I_{L,1} = -\frac{2FD_1c_{13}^b}{\delta} \quad (4.22)$$

Binary case is reached by setting $c_{23}^b = 0$:

$$I_{L,0} = -\frac{6FD_1c_{13}^b}{\delta} \quad (4.23)$$

$$\frac{I_L}{I_{L,1}} = -2C_r^{-1}[\sqrt{1+2C_r} - 2] + 3 \approx 3 - 2C_r \quad ; \quad C_r = \frac{c_{13}^b}{c_{23}^b} \quad (4.24)$$

From Eqs. (4.19) and (4.21),

$$\frac{I}{I_L} = \frac{1}{2} \frac{(e^{f\Delta\phi} - 1) + 3(1 + C_r)(e^{-f\Delta\phi} - 1)}{2\sqrt{1+2C_r} - (3C_r + 2)} \quad (4.25)$$

Eq. (4.25) is perhaps the simplest way to study the potential drop in the diffusion boundary layer.

Comsol simulation of Zn^{2+} electrodeposition: $E^\circ = -0.7626 \text{ V}$, $[\text{ZnSO}_4] = 1.0 \text{ M}$, $[\text{H}_2\text{SO}_4]$ is varied. $k^\circ = 7.5 \cdot 10^{-7} \text{ cm/s}$.

