

CuCl₂ – HCl system:



Let's denote Cu species with 1, proton with 2 and chloride with 3. The Nernst-Planck equations are:

$$\begin{cases} -\frac{j_1}{D_1} = -\frac{I}{2FD_1} = \frac{dc_1}{dx} + 2c_1f \frac{d\phi}{dx} \\ -\frac{j_2}{D_2} = 0 = \frac{dc_2}{dx} + c_2f \frac{d\phi}{dx} \\ -\frac{j_3}{D_3} = 0 = \frac{dc_3}{dx} - c_3f \frac{d\phi}{dx} \end{cases}$$

Case i)

$$\begin{cases} -\frac{j_1}{D_1} = -\frac{I}{2FD_1} = \frac{dc_1}{dx} + c_1f \frac{d\phi}{dx} \\ -\frac{j_2}{D_2} = 0 = \frac{dc_2}{dx} + c_2f \frac{d\phi}{dx} \\ -\frac{j_3}{D_3} = +\frac{I}{2FD_3} = \frac{dc_3}{dx} - c_3f \frac{d\phi}{dx} \end{cases}$$

Case ii)

$$\begin{cases} -\frac{j_1}{D_1} = -\frac{I}{2FD_1} = \frac{dc_1}{dx} \\ -\frac{j_2}{D_2} = 0 = \frac{dc_2}{dx} + c_2f \frac{d\phi}{dx} \\ -\frac{j_3}{D_3} = +\frac{I}{FD_3} = \frac{dc_3}{dx} - c_3f \frac{d\phi}{dx} \end{cases}$$

Case iii)

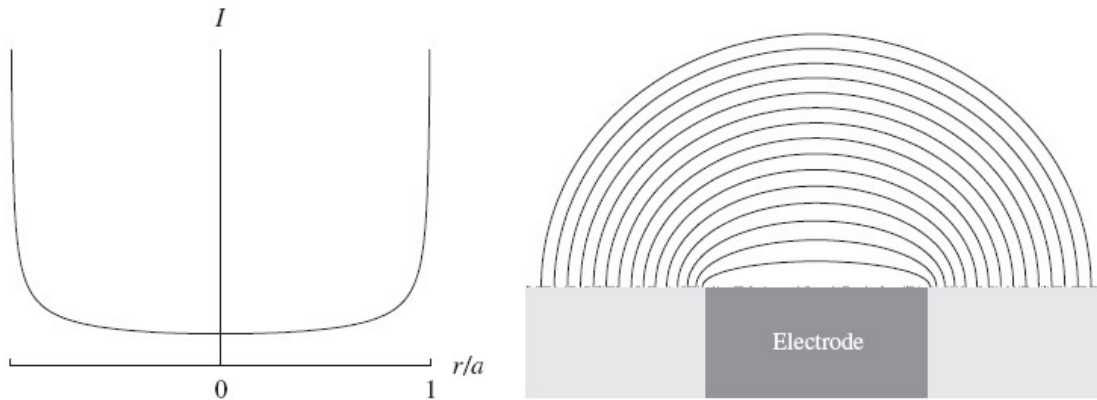
Textbook p. 91, error: Only one electroactive species in each case. Anion fluxes come from the mass balance.

$$j_i = \frac{v_i I}{nF} \quad \text{Textbook (3.4)}$$

Ultramicroelectrodes

If some dimension of an electrode (radius, width, length) is of the order $< 100 \mu\text{m}$, we talk about ultramicroelectrodes. Their current-voltage characteristics changes because mass transfer to the electrode surface is enhanced significantly. Therefore, transient experiments begin to resemble steady-state experiments. Because electric currents on ultramicroelectrodes are of the order of $< 1 \mu\text{A}$ ohmic losses in the solution become insignificant and experiments can be carried out in poorly conducting media, such as in organic solvents. Also power consumption is so low, of the order of $< \mu\text{W}$, that a signal generator and a sensitive ampere meter suffice as a measuring equipment. This makes it possible to utilize very fast perturbation functions (current/voltage) because a potentiostat is not limiting the response rate. Hence, with ultramicroelectrodes much faster kinetics can be studied than with normal sized (order of cm) electrodes. We consider here a disk ultramicroelectrode.

In the picture below, the concentration field around a microdisk is depicted. As can be seen, it has a spherical symmetry except very close to the electrode surface. Therefore, the analysis is done in spherical coordinates.



Left: Current distribution on a microdisk electrode.
Right: Equiconcentration lines around the electrode.

It can be proved that the current distribution on a microdisk electrode is (a is the disk radius)

$$I \propto \frac{1}{\sqrt{1-(r/a)^2}} \quad (5.1)$$

Although current approaches infinity at the disk edge ($r = a$), the integral over the disk is finite.

At steady-state the diffusion problem to be solved is

$$\nabla^2 c_k = \frac{\partial^2 c_k}{\partial r^2} + \frac{2}{r} \frac{\partial c_k}{\partial r} = 0 \quad ; \quad c_k(r \rightarrow \infty) = c_k^b \quad ; \quad c_k(a) = c_k^s \quad ; \quad \frac{I}{nF} = \pm D_k \left(\frac{\partial c_k}{\partial r} \right)_{r=a} \quad (5.2)$$

Under the limiting current condition, $c_k(a) = 0$ and the concentration profile is

$$c_k(r) = c_k^b (1 - a/r) \quad (5.3)$$

and the limiting current density:

$$I_L = \pm nFD_k \left(\frac{dc_k}{dr} \right)_{r=a} = \pm nFD_k (c_k^b / a) \quad (5.4)$$

If the electrode were a true hemisphere the limiting current would be $i_{lim} = \pm 2\pi nFc_k^b a$ but it has been proved that for a disk electrode it is

$$i_L = \pm 4nFD_k c_k^b a \quad (5.5)$$

In practice, calculations are carried out in spherical coordinates and results are corrected by multiplying current with $2/\pi$. In a general case the concentration profile is

$$c_k(r) = c_k^b \mp \frac{Ia}{nFD_k} \left(\frac{a}{r} \right) \Rightarrow c_k^s = c_k^b \mp \frac{Ia}{nFD_k} \quad (5.6)$$

In a transient experiment the problem is analogously:

$$\frac{\partial c_k}{\partial t} = D_k \left[\frac{\partial^2 c_k}{\partial r^2} + \frac{2}{r} \frac{\partial c_k}{\partial r} \right] = 0 \quad ; \quad c_k(r \rightarrow \infty, t) = c_k^b \quad ; \quad c_k(t = 0, r) = c_k^b \quad ; \quad \frac{I}{nF} = \pm D_k \left(\frac{\partial c_k}{\partial r} \right)_{r=a} \quad (5.7)$$

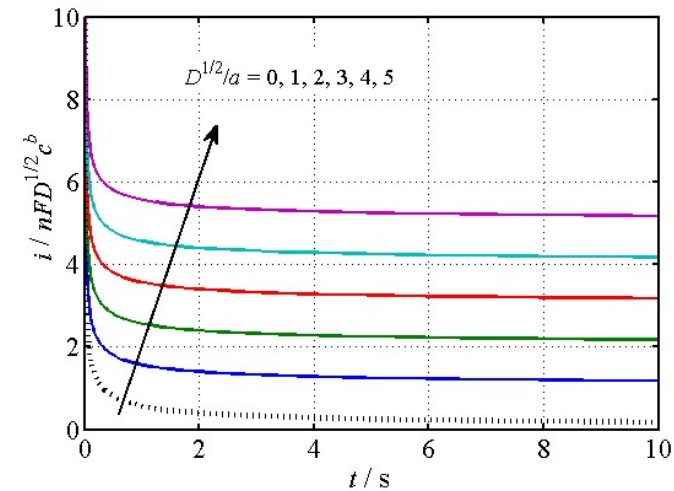
The surface concentration in Laplace domain is

$$\bar{c}_k^s = \frac{c_k^b}{s} \mp \frac{\bar{I}(s)}{nF\sqrt{D_k}(\sqrt{s} + \sqrt{D_k}/a)} \quad (5.8)$$

If the surface concentration is set to zero, like in the Cottrell experiment,

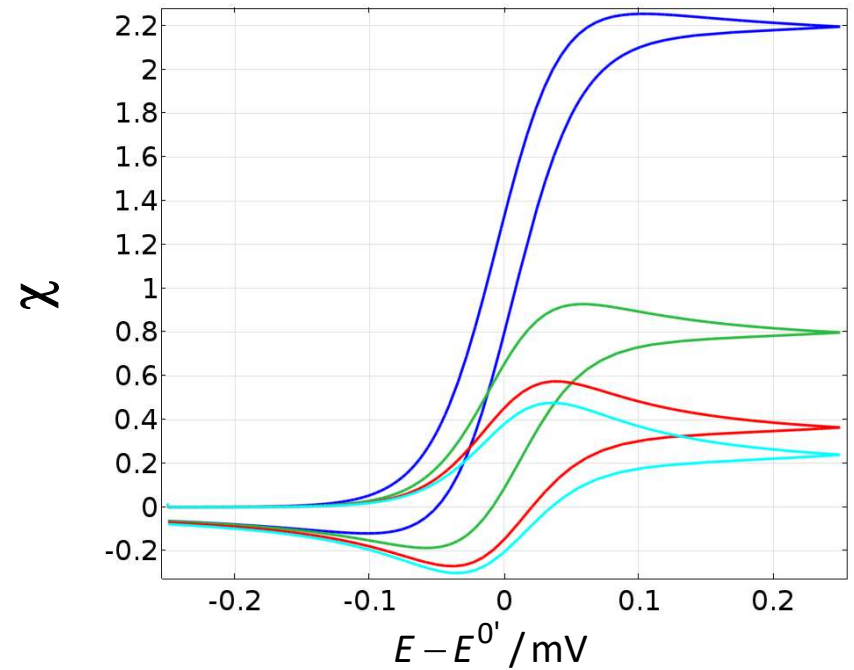
$$\bar{I}(s) = \pm nF\sqrt{D_k} c_k^b \left(\frac{1}{\sqrt{s}} + \frac{1}{s} \frac{\sqrt{D_k}}{a} \right) \Rightarrow I(t) = nF\sqrt{D_k} c_k^b \left(\frac{1}{\sqrt{\pi t}} + \frac{\sqrt{D_k}}{a} \right) \quad (5.12)$$

Current at an ultramicroelectrode thus remains to the steady-state (eq. (5.8)) after a transient phase. Aside a simulation varying the parameter $\sqrt{D_k}/a$. The black dotted line corresponds to the Cottrell experiment where $a \rightarrow \infty$.



The behavior of an ultramicroelectrode is best demonstrated with cyclic voltammetry. Aside a simulation varying the parameter $\sigma a^2/D$. At high enough parameter values the behavior approaches to a “normal” electrode, *i.e.* χ approaches to 0.4463 while the at low parameter values the CV approaches a steady-state current-voltage curve.

$$\sigma = \frac{Fv}{RT}$$



Simulation of CVs at an ultramicroelectrode with $\sigma a^2/D = 0.01$ (blue), 0.1 (green), 1 (red), and 10 (turquoise).