

## Solutions to the tasks: Chapter 2 – Electrochemical theory

### Task 2.1 (Faraday's law)

While this task is a little superficial, you become familiar with Faraday's law and the influence of the number of electrons in a reaction. Expanding the charge  $Q$  in the classical formulation with the current density  $i$ , the electrode area  $A$ , and the deposition time  $t$ , the Faraday's law is:

$$m = \frac{M}{zF} \cdot Q = \frac{M}{zF} \cdot iAt$$

The two plating baths should result in the same mass, so we get with the current density  $i_{2e}$  for the two-electron and  $i_{1e}$  for the one-electron process:

$$\frac{M}{-2F} \cdot i_{2e}At = \frac{M}{-1F} \cdot i_{1e}At$$

Metal deposition typically occurs at the cathode, so we assume negative number for  $z$  (although, the sign would cancel out anyway). Rearranging and simplifying above equation leads to the answer:

$$i_{2e} = 2i_{1e}$$

The plating bath following the two-electron process needs double the current density than the one-electron process to yield in the same deposited mass.

### Task 2.2 (Nernst equation)

Often, the Nernst equation is more handsome when rewritten with the decadic instead of the natural logarithm.

A quick reminder of logarithm rules: a logarithm of  $a$  to the base  $b$  expands to another logarithm of  $a$  to a new base  $c$  divided by the logarithm of  $b$  to the new base  $c$ :

$$\log_b a = \frac{\log_c a}{\log_c b}$$

Applied to our problem, the decadic logarithm  $\lg x$  expands rewritten with the natural logarithm

$\ln x$  to

$$\lg x = \frac{\ln x}{\ln 10}$$

with the constant  $\ln 10 = 2.303$ . With this in mind we can rewrite the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_O}{a_R}$$

using the decadic logarithm:

$$E = E^0 + \frac{2.303 \cdot RT}{nF} \lg \frac{a_O}{a_R}$$

For a one-electron process ( $n = 1$ ) the factor before the logarithm is 59.1 mV at room temperature ( $T = 273 \text{ K} + 25 \text{ K}$ ). That means, the electrode potential changes by approximately 60 mV per decade of activity change.

### Task 2.3 (Charge transfer close to equilibrium)

While electrochemical systems are essentially nonlinear as expressed by the Butler–Volmer equation

$$i = i_0 \cdot \left( \exp \frac{(1 - \alpha)nF \cdot \eta}{RT} - \exp \frac{-\alpha nF \cdot \eta}{RT} \right)$$

close to equilibrium (small overpotential  $\eta$ ) linearization is possible.

The approximation of an exponential function

$$\exp x \approx 1 + x$$

for small values of  $x$  applied to the Butler–Volmer equation results in:

$$i \approx i_0 \cdot \left( 1 + \frac{(1 - \alpha)nF \cdot \eta}{RT} - 1 - \frac{-\alpha nF \cdot \eta}{RT} \right) = i_0 \cdot \frac{nF}{RT} \cdot \eta$$

### Task 2.4 (Cottrell equation)

Deriving the Cottrell equation is far from a routine task when applying electrochemical methods. However, I strongly recommend trying it yourself, and if you get stuck following the above route, to obtain a better feeling for this equation.

To keep it simple, we focus on an infinite planar electrode reducing the situation to a one-dimensional diffusion problem with a coordinate  $x$  measuring the distance from the electrode. The concentration of the considered species  $c(x, t)$  depends on the location  $x$  and the time  $t$ .

Initially, the bulk concentration  $c_\infty$  of the considered species is everywhere:

$$c(x, 0) = c_\infty \quad (1)$$

At time zero, the electrode is polarized to ensure all species are consumed resulting in the boundary condition at the electrode:

$$c(0, t) = 0 \quad (2)$$

Far from the electrode ( $x \rightarrow \infty$ ) there is an infinite source of the species:

$$x \rightarrow \infty : c(x, t) = c_\infty \quad (3)$$

The derivation requires solving Fick's second law, a second-order linear partial differential equation:

$$\frac{\partial c(x, t)}{\partial t} = D \cdot \frac{\partial^2 c(x, t)}{\partial x^2}$$

As we advance and try solving the differential equation, e.g., with the help of the Laplace transformation, we might get stuck and realize it would be much simpler when the initial condition (1) would be zero.

Seeking easy going we introduce a substitution to make the initial condition more handsome:

$$\bar{c}(x, t) = c(x, t) - c_\infty$$

The additional constant in the substitution vanishes in the derivative, so our differential equation looks the same:

$$\frac{\partial \bar{c}(x, t)}{\partial t} = D \cdot \frac{\partial^2 \bar{c}(x, t)}{\partial x^2}$$

The new initial condition is what we were looking for:

$$\bar{c}(x, 0) = 0 \quad (S1)$$

The boundary condition at the electrode became

$$\bar{c}(0, t) = -c_\infty \quad (S2)$$

and far away:

$$x \rightarrow \infty : \bar{c}(x, t) = 0 \quad (S3)$$

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Brief reminder: the *Laplace transformation* converts between a function  $f(x, t)$  in the time domain (variable  $t$ ) and a function  $F(x, s)$  in the frequency domain (variable  $s$ ):

$$\mathcal{L}\{f(x, t)\} = \int_0^{\infty} f(x, t) \cdot \exp(-st) dt = F(x, s)$$

While it would be possible to use the above definition of the Laplace transformation for our task, it is much easier to rely on correspondence tables or ask math software allowing symbolic calculations for help.

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Transforming left side of the partial differential equation in the time domain and applying the initial condition (S1) leads to

$$\mathcal{L}\left\{\frac{\partial \bar{c}(x, t)}{\partial t}\right\} = s\bar{C}(x, s) - \underbrace{\bar{c}(x, 0)}_{=0} = s\bar{C}(x, s)$$

and the right side to

$$\mathcal{L}\left\{D \cdot \frac{\partial^2 \bar{c}(x, t)}{\partial x^2}\right\} = D \frac{d^2 \bar{C}(x, s)}{dx^2}$$

yielding an ordinary differential equation in the frequency domain:

$$s\bar{C}(x, s) = D \frac{d^2 \bar{C}(x, s)}{dx^2}$$

A good guess for the solution is an exponential function as Ansatz function with a constant  $a$ :

$$\bar{C}(x, s) = \exp(ax)$$

Its derivatives have similar shapes:

$$\frac{d\bar{C}(x, s)}{dx} = a \cdot \exp(ax)$$

$$\frac{d^2 \bar{C}(x, s)}{dx^2} = a^2 \cdot \exp(ax)$$

Introducing the Ansatz function into the ordinary differential equation leads to a quadratic equation and accordingly two solutions for  $a$ :

$$s \cdot \exp(ax) = D \cdot a^2 \cdot \exp(ax)$$

$$\Rightarrow a^2 = \frac{s}{D} \Rightarrow a = \pm \sqrt{\frac{s}{D}}$$

The overall solution is a linear combination of the individual solutions, here with the constants  $A$  and  $B$ :

$$\bar{C}(x, s) = A \cdot \exp\left(x\sqrt{\frac{s}{D}}\right) + B \cdot \exp\left(-x\sqrt{\frac{s}{D}}\right)$$

Condition (S3) requires that the first term in the overall solution disappears, that means  $A = 0$  and the solution reduces to:

$$\bar{C}(x, s) = B \cdot \exp\left(-x\sqrt{\frac{s}{D}}\right)$$

Evaluating the solution at the electrode ( $x = 0$ ) and comparing to the Laplace transformed boundary condition at the electrode (S2) determines the constant  $B$ :

$$\bar{C}(0, s) = B \quad \text{and} \quad \mathcal{L}\{\bar{c}(0, t)\} = \mathcal{L}\{-c_\infty\} = -\frac{c_\infty}{s} \quad \Rightarrow \quad B = -\frac{c_\infty}{s}$$

Therewith the solution in the frequency domain is determined and converts using the invers Laplace transformation to the solution in the time domain:

$$\bar{C}(x, s) = -c_\infty \frac{\exp\left(-x\sqrt{\frac{s}{D}}\right)}{s} \quad \Rightarrow \quad \bar{c}(x, t) = -c_\infty \cdot \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right)$$

Brief reminder: the *error function*, related to a cumulative distribution function in probability theory, is defined by an integral:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-y^2) dy$$

Its derivative is an exponential function according to the above definition:

$$\frac{d \operatorname{erf}(x)}{dx} = \frac{2}{\sqrt{\pi}} \exp(-x^2)$$

The complementary error function is a simple shortcut:

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$$

Inversion of the substitution provides the solution for  $c(x, t)$ :

$$c(x, t) = \bar{c}(x, t) + c_\infty = c_\infty \left( 1 - \operatorname{erfc} \left( \frac{x}{\sqrt{4Dt}} \right) \right) = c_\infty \cdot \operatorname{erf} \left( \frac{x}{\sqrt{4Dt}} \right)$$

This equation allows describing the time-dependency of the diffusion profile at any position. Its gradient at the electrode ( $x = 0$ ) represents the species flux density into the electrode:

$$j(t) = D \cdot \frac{\partial c(x, t)}{\partial x} \Big|_{x=0} = D c_\infty \exp \left( \frac{-x^2}{4Dt} \right) \cdot \frac{2}{\sqrt{\pi}} \cdot \frac{1}{\sqrt{4Dt}} \Big|_{x=0} = c_\infty \cdot \sqrt{\frac{D}{\pi t}}$$

Using a variant of Faraday's law linking the current density to the species flux density finally leads to the Cottrell equation:

$$i(t) = zF \cdot j(t) = zFc_\infty \sqrt{\frac{D}{\pi t}}$$

### Task 2.5 (Diffusion constant measurement)

Diffusion constant measurements are a typical application of the Cottrell equation. We compare the current response at a given time point for two substances, A and B:

$$i_A(t) = zFc_\infty \sqrt{\frac{D_A}{\pi t}} \quad \text{and} \quad i_B(t) = zFc_\infty \sqrt{\frac{D_B}{\pi t}}$$

As the task does not declare it explicitly, we assume the same valency  $z$  and same initial/bulk concentration  $c_\infty$  for A and B. At the same time after switching on (e.g., 2 s), for substance B, the current is twice the current for substance A:

$$i_B(t) = 2i_A(t)$$

Expanding and simplification provide the diffusion constant of B:

$$D_B = 4 \cdot D_A = 4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

This task hints at the quadratic dependency of the diffusion constant when derived from a measured current. However, practical measurements prefer evaluating the slope in an  $i$  over  $1/\sqrt{t}$  plot leading to more precise results. Additionally, such a plot would reveal parasitic effects (charging of the double layer capacity, disturbance of the diffusion profile by convection) as deviation from linearity.