

Übung 7: Elektrochemische Kinetik (2. Teil) – Konzentrationsüberspannung

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Exercise 1

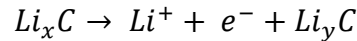
- Provide the definition of the Nernst diffusion layer.
- Calculate the Nernst diffusion layer δ during steady-state deposition of Fe at a cathode in a stirred solution assuming that the limiting current density is $3.9 \cdot 10^{-4} \text{ A cm}^{-2}$. The concentration of Fe^{2+} in the bulk solution is 10^{-2} M and the diffusion coefficient D of Fe^{2+} in the unstirred solution is $10^{-5} \text{ cm}^2 \text{ s}^{-1}$.
- What happens to δ if the concentration of Fe^{2+} in the bulk is increase to 10^{-1} M in the above example?
- Determine the diffusion layer thickness for a rotating electrode at 60, 240 and 360 rpm. The kinematic viscosity and the diffusion coefficient are $10^{-2} \text{ cm}^2 \text{ s}^{-1}$ and $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ respectively.

Tip: To simplify the calculations consider $N=1$ rps (60rpm), $N=4$ rps (240), etc.
- Which conclusions can be drawn from your results with respect to δ ?
- Calculate the limiting current density for the deposition of Fe^{2+} in the rotating electrode with a surface area $a=1 \text{ cm}^2$ and rotating speed of 300 rpm. Assume again $c = 10^{-2} \text{ M}$, $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $\nu = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ and draw your conclusion comparing the i_L for the quiescent and stirred solutions.
- Can you explain why the corrosion potential of a pipeline consisting of unalloyed steel increases with the increasing speed of the fluid? Explain this finding using a schematic potential-current diagram. What is the effect on the corrosion potential?

Tip: the graph below shows the current density for a corroding system under charge-transfer control and diffusion limited O_2 reduction. Consider the effect of the hydrodynamics on the cathodic curve to draw your conclusion.

(d.1) The **Ohmic overpotential** due to firstly the electrolyte (consider the electrolyte layer 0.1 mm, the conductivity of the electrolyte $\kappa = 9.8 \cdot 10^{-1} \text{ mS/cm}$) and secondly the wire resistance of 0.08Ω

(d.2) the **charge transfer overpotential** for the following electrode process:



Consider $\alpha = 0.5$, $j = 7.0 \mu\text{A/cm}^2$ and a factor $R_f = \frac{A_{\text{reaction}}}{A_{\text{geometry}}} = 225$ for electrode a) and $R_f = 121$ for electrode c).

Tip: use Tafel equation

(d.3) the concentration overpotential for electrode a) and c)

Exercise 3

In a very diluted aqueous FeCl_3 solution of unknown concentration, Fe^{2+} ions are produced via reduction of Fe^{3+} ions. The solution also contains 1.5 M KCl as conducting salt. By applying an overpotential of -215 mV and after reaching stationary conditions, the limiting, or maximum, current density of i_L of $14 \mu\text{A/cm}^2$ was measured. The following limiting current densities were obtained from several experiments with known concentration FeCl_3 :

C (mM)	1.0	1.5	2.0	2.5
i_L ($\mu\text{A/cm}^2$)	6.4	9.6	12.9	16

- Calculate the unknown concentration $c(\text{FeCl}_3)$.
- Calculate the diffusion coefficient $D(\text{Fe}^{3+})$ when the Nernst diffusion layer thickness is 0.3 mm .

Exercise 4

To a first approximation, significant evolution of H_2 and O_2 occurs in electrolysis only if the overpotential exceeds about 0.6 V (assuming alkaline conditions). To illustrate this criterion determine the effect that increasing the overpotential from 0.5 V to 0.6 V has on the current density in the electrolysis of 1.0 M NaOH (aq) , which is 1.22 mA cm^{-2} at 0.5 V and 25° C . Take $\alpha = 0.50$.

- What do you suggest to decrease the overpotential?