

PAUL SCHERRER INSTITUT

WS 2019/2020

Elektrochemie Prof. Petr Novák

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

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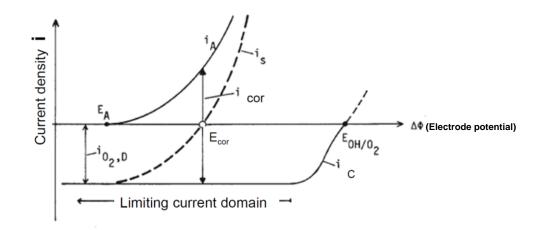
Exercise 1

- a) Provide the definition of the Nernst diffusion layer.
- b) 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 $3.9^{*10^{-4}}$ A cm⁻². The concentration of Fe²⁺ in the bulk solution is 10^{-2} M and the diffusion coefficient *D* of Fe²⁺ in the unstirred solution is 10^{-5} cm² s⁻¹.
- c) What happens to δ if the concentration of Fe²⁺ in the bulk is increase to 10⁻¹ M in the above example?
- d) 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 cm² s⁻¹ and 10⁻⁵ cm² s⁻¹ respectively.

Tip: To simplify the calculations consider N=1 rps (60rpm), N=4 rps (240), etc.

- e) Which conclusions can be drawn from your results with respect to δ ?
- f) Calculate the limiting current density for the deposition of Fe²⁺ in the rotating electrode with a surface area $a=1 \text{ cm}^2$ and rotating speed of 300 rpm. Assume again c = 10^{-2} M, $D = 10^{-5}$ cm² s⁻¹ and $v = 10^{-5}$ cm² s⁻¹ and draw your conclusion comparing the i_L for the quiescent and stirred solutions.
- g) 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 chargetransfer control and diffusion limited O_2 reduction. Consider the effect of the hydrodynamics on the cathodic curve to draw your conclusion.



Exercise 2

In lithium-ion battery technology, composite electrodes are often used. A negative electrode for lithium-ion batteries is made of the following materials:

- 1. Active mass graphite: 9.5 g
- 2. Polymer binder: 0.5 g
- 3. Conductive Carbon: 1.2 g

The electrode is coated on a Cu current collector ($m_{Cu}=24$ mg, diameter $d_{cu}=15$ mm, thickness 24 μ m).

- a) Calculate the **porosity** of the electrode, if the total thickness of the electrode is 140 μ m and the total mass is 33.7 mg (including Cu current collector). Assume that the average density of the solid material (not porous) is 2.2 g/cm³.
- b) Calculate the charge which can be stored in the electrode in relation to the mass of the active material, if the theoretical specific charge / capacity (=maximum stored charge) of graphite is 370 mAh/g. Do the same calculation per unit of volume of the electrode.
- c) If the electrode is pressed to half of the original thickness, how do the **porosity**, **gravimetric** and **volumetric capacities** change?
- d) Apply a current of +3.7 mA/mg of active material to the electrodes a) and
 c) cycled against Lithium as counter electrode as well as reference electrode (assuming no potential change of this electrode). Consider that:

I. The equilibrium electrode potential $E_0 = 90 \text{ mV}$ vs. Li⁺/Li

II. the working electrode potential is $E = 430 \text{ mV} \text{ vs. Li}^+/\text{Li}$ for electrode a) and $E = 471 \text{ mV} \text{ vs. Li}^+/\text{Li}$ for electrode c).

Calculate for both electrode a) and c).



(d.1) The **Ohmic overpotential** due to firstly the electrolyte (consider the electrolyte layer 0.1 mm, the conductivity of the electrolyte κ = 9.8 10⁻¹ mS/cm) and secondly the wire resistance of 0.08 Ω

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

$$Li_x C \rightarrow Li^+ + e^- + Li_y C$$

Consider α = 0.5, j= 7.0µA/cm² and a factor $R_f = \frac{A_{reaction}}{A_{geometry}} = 225$ 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 FeCl₃ solution of unknown concentration, Fe²⁺ ions are produced via reduction of Fe³⁺ ions. The solution also contains 1.5 M KCl as conducting salt. By applying an overpotential of -215mV and after reaching stationary conditions, the limiting, or maximum, current density of i_L of 14 µA/cm² was measured. The following limiting current densities were obtained from several experiments with known concentration FeCl₃:

| C (mM) | 1.0 | 1.5 | 2.0 | 2.5 |
|-------------|-----|-----|------|-----|
| j∟ (µA/cm²) | 6.4 | 9.6 | 12.9 | 16 |

- a) Calculate the unknown concentration c(FeCl₃).
- b) Calculate the diffusion coefficient D(Fe³⁺) when the Nernst diffusion layer thickness is 0.3mm.

Exercise 4

To a first approximation, significant evolution of H₂ and O₂ 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 α = 0.50.

a) What do you suggest to decrease the overpotential?