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

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Exercise 1

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 -215mV and after reaching stationary conditions, the limiting, or maximum, current density of i_L of 14 µA/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 (µA/cm^2)	6.4	9.6	12.9	16

a) Calculate the unknown concentration c($FeCl_3$).

b) Calculate the diffusion coefficient D(Fe^{3+}) when the Nernst diffusion layer thickness is 0.3mm.

Exercise 2

Calculate the limiting current density for the deposition of Cu^{2+} at a cathode in a quiescent (unstirred) solution assuming that the diffusion layer thickness δ is 0.5 mm. The concentration of Cu^{2+} in the bulk is 10^{-2} M and the diffusion coefficient D in the unstirred solution is 10^{-5} cm^2 s^{-1}.

a) Provide the definition of the Nernst diffusion layer based on a graph of Cu^{2+} concentration (y-axis) vs. distance from the electrode (x-axis). Calculate the limiting current density.

b) What happens to the current density if the concentration of Cu^{2+} in the bulk is increased to 10^{-1} M?

c) 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} cm^2 s^{-1} and 10^{-5} cm^2 s^{-1} respectively.

Tip: For a rotating electrode the diffusion layer thickness depends on the angular speed of rotation ω according to the following equation:

$$\delta = \frac{1.61\, D^{1/3} v^{1/6}}{\omega^{1/2}}$$

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

d) Which consideration can be drawn from your results?

e) Calculate the limiting current density for the deposition of Cu^{2+} in the rotating electrode with a rotating speed of 300 rpm.

Remember that the current density depends on ω according to the following equation:

$$i_L = \frac{0.62\, n\, F\, D^{2/3} c}{v^{1/6}} \sqrt{\omega}$$

Consider c = 10^{-2} M, D = 10^{-5} cm^2 s^{-1} and v = 10^{-5} cm^2 s^{-1} and draw your conclusion comparing the i_L for the quiescent and stirred solutions.

Exercise 3

In lithium batteries technology, composite electrodes are often used. A negative electrode for lithium 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 Φ_{cu}= 15 mm, thickness 24 μm).

a) Calculate the **porosity** of the electrode, if the total thickness of the electrode is 140 μm and the total mass is 33.7 mg. Assume that the average density of the solid material (not porous) is 2.2 g/cm^3.

b) Calculate the **charge** which can be stored in the electrode in relation to the mass of the active material, if the theoretical 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. Consider that:

I. The equilibrium electrode potential **E_0 = 90 mV** vs. Li^+/Li

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

Calculate for both electrode a) and c).

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

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

$$Li_xC \rightarrow Li^+ + e^- + Li_yC$$

Consider α= 0.5, j= 7.0μA/cm^2 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 4

Oxygen gas sensors (lambda sensors) based on ZrO_2 doped with CaO or Y_2O_3 are used in the exhaust systems of automobiles with combustion engines to monitor and control the air-fuel mixture. ZrO_2 is a solid electrolyte and oxygen ion conductor. By determining the potential difference between the inner (air atmosphere) and the outer electrode (exhaust gas) (see Figure 1), the air/fuel ratio can then be computed. The sensor is made of the following composition:

P_{O2} (I) [inner electrode: atmosphere] ¦Pt ¦Solid electrolyte (doped ZrO_2)¦Pt¦ P_{O2} (II) [outer electrode: exhaust gas]

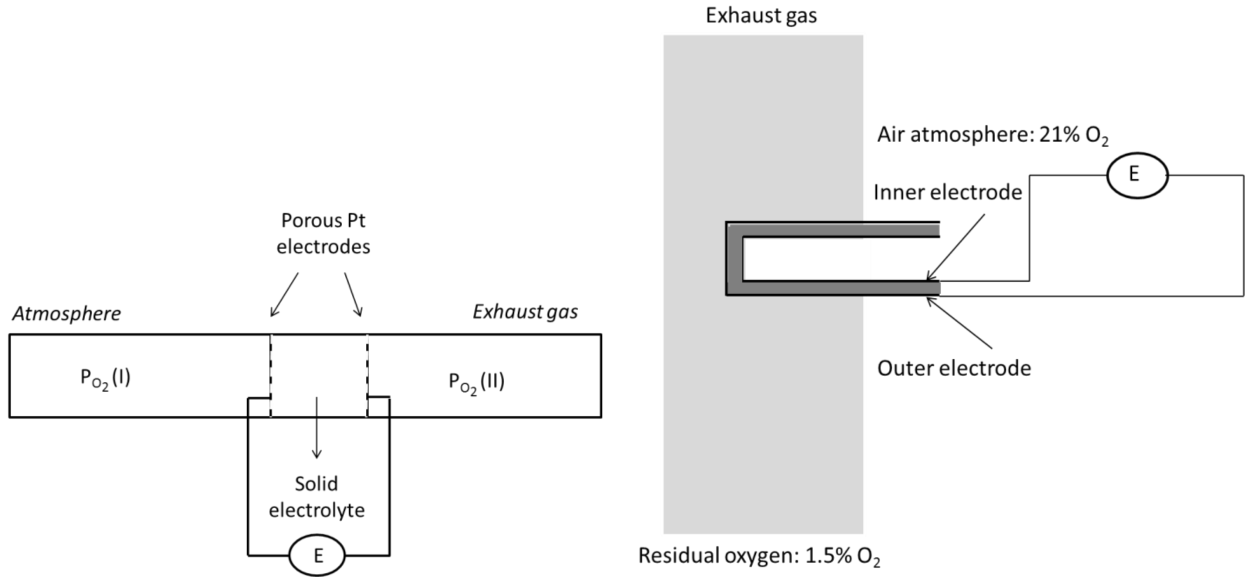

Figure 1. Schematics representing the O_2 sensor using zirconia oxide as solid electrolyte. Adapted from [1].

The electrochemical equilibrium can be achieved at temperatures higher than 650°C [1]:

$\frac{1}{2} O_2 + 2 e^- \leftrightarrow O^{2-}$

a) Compute the “measured” potential difference in case the oxygen content is 1.5% in volume ($P_{exhaust\ gas}$=101.3 kPa) and the temperature is 800°C. The concentration of O^{2-} can be considered as constant.

b) Is the potential difference decreasing or increasing if the oxygen amount in the exhaust gas is lower than 1.5% (vol.)?

Other useful data:

The composition of the air (atmosphere): 21% (vol.) O_2

P°= 101.325 kPa

R = 8.3145 J/Kmol

F = 96485 C/mol

[1] http://www.ak-hoffmann.chemie.uni-mainz.de/

Exercise 5

To a first approximation, significant evolution of H_2 and O_2 occurs in electrolysis only if the overpotential exceeds about 0.6 V. 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 $\alpha = 0.50$.

a) What do you suggest to decrease the overpotential?

Remark: If possible, please provide solutions in English. Thanks a lot in advance.