

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

Assistant: Bernhard Pribyl (bernhard.pribyl@psi.ch)

Exercise 1

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

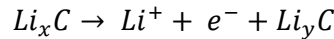
The electrode is coated on a Cu current collector ($m_{\text{Cu}}=24$ mg, diameter $d_{\text{Cu}}=15$ mm, thickness $24 \mu\text{m}$).

- a) Calculate the **porosity** of the electrode, if the total thickness of the electrode is $140 \mu\text{m}$ 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/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 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 $+3.7 \text{ mA/mg}$ 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 $E = 430 \text{ mV}$ vs. Li^+/Li for electrode a) and $E = 471 \text{ mV}$ vs. Li^+/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 $\kappa = 9.8 \cdot 10^{-1} \text{ mS/cm}$) 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 2

Calculate the exchange current density and the transfer coefficient for an anodic process involving a platinum electrode of area 2.0 cm^2 in contact with a Fe^{2+} containing solution at 25° C . Use the following anodic current values:

$\eta \text{ (mV)}$	50	100	150	200	250
$i \text{ (mA)}$	8.8	25.0	58.0	131	298

Exercise 3

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 $10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

- 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.
- What happens to the current density if the concentration of Cu^{2+} in the bulk is increased to 10^{-1} M ?
- 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: For a rotating electrode the diffusion layer thickness depends on the angular velocity ω according to the following equation:

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

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

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:

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

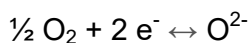
Consider $c = 10^{-2}$ M, $D = 10^{-5}$ $\text{cm}^2 \text{s}^{-1}$ and $\nu = 10^{-5}$ $\text{cm}^2 \text{s}^{-1}$ and draw your conclusion comparing the i_L for the quiescent and stirred solutions.

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_{O_2} (I) [inner electrode: atmosphere] | Pt | Solid electrolyte (doped ZrO_2) | Pt | P_{O_2} (II) [outer electrode: exhaust gas]

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



- Compute the “measured” potential difference in case the oxygen content is 1.5% in volume ($\text{P}_{\text{exhaust gas}}=101.3$ kPa) and the temperature is 800°C . The concentration of O^{2-} can be considered as constant.
- Is the potential difference decreasing or increasing if the oxygen amount in the exhaust gas is lower than 1.5% (vol.)?

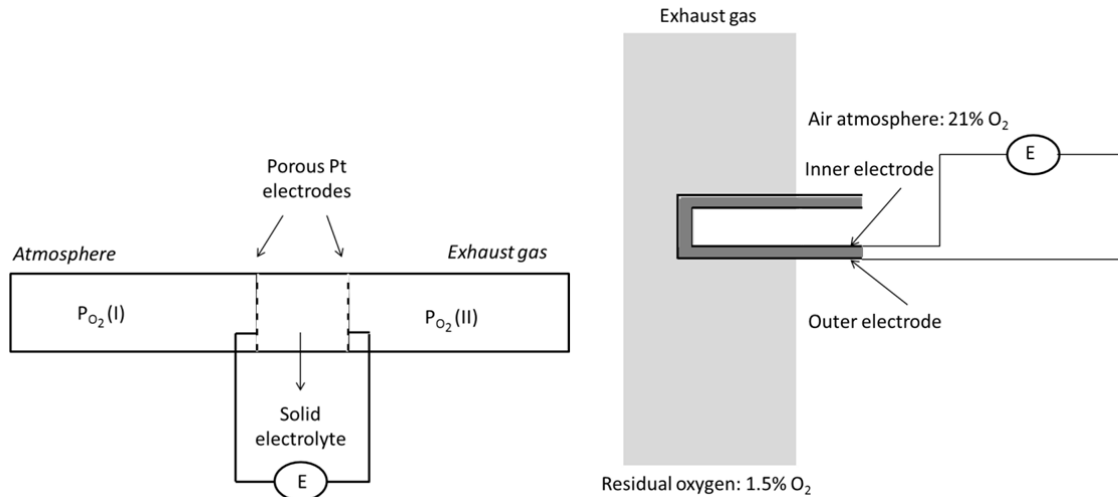


Figure 1. Schematics representing the O_2 sensor using calcia or yttria doped zirconia as solid electrolyte. Adapted from [1].

Other useful data:

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

$P^\circ = 101.325 \text{ kPa}$

$R = 8.3145 \text{ J/Kmol}$

$F = 96485 \text{ C/mol}$

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

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