

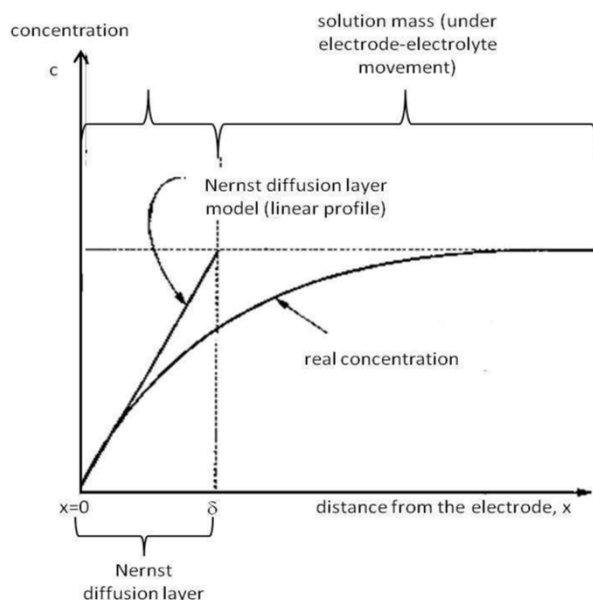
Übung 7: Elektrochemische Kinetik (2. Teil) – Konzentrationsüberspannung

Lösung

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Exercise 1

(a) Once an electrochemical process is initiated, the concentration of those species taking part in the reaction will normally differ at the electrode/electrolyte interface compared to the bulk solution (see figure below). In particular when a current is flowing in the system, the surface concentration of the electroactive species decrease to a certain value. It can be seen that the concentration profile thus formed extends into the solution near the electrode surface by a length δ , termed the *Nernst diffusion layer*. The thickness of δ strongly depends on the hydrodynamic flow due to any stirring or convective effects, as shown in the following exercise.



(b) The diffusion layer thickness δ is given by the following equation:

$$\delta = \frac{nFD}{i_L} c_b = \frac{2 * 96485 \text{ As/mol} * 10^{-5} \text{ cm}^2/\text{s} * 10^{-5} \text{ mol/cm}^3}{3.9 * 10^{-4} \text{ A cm}^{-2}} = 0.05 \text{ cm}$$

(c) In the same way we can find that for $c_b = 10^{-4} \text{ mol/cm}^3$, $\delta = 0.5 \text{ cm}$

(d) The rotation speed ω in radians per second (= angular velocity) is replaced by $\omega = 2\pi N$, where N is the number of rotation per second (rps).

The relation between ω , ν and D is described by the following expression:

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

Assuming $N=1$ rps (60 rpm), one can get $\delta = \frac{1.61 \cdot (10^{-5} \text{ cm}^2/\text{s})^{1/3} \cdot (10^{-2} \text{ cm}^2/\text{s})^{1/6}}{\sqrt{2\pi}} = 64 \text{ }\mu\text{m}$

if $N=4$ rps (240 rpm), $\delta = 32 \text{ }\mu\text{m}$

$N=6$ rps (360 rpm), $\delta = 26 \text{ }\mu\text{m}$

(e) As the rotation speed increases, the thickness of the diffusion layer decreases (the stronger the convection, the smaller the value of δ).

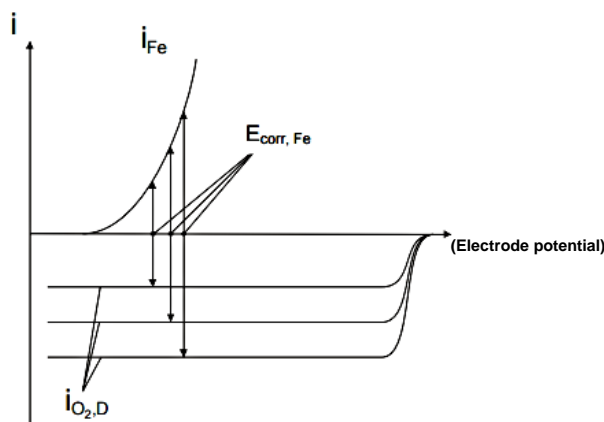
(f) The current density depends on ω according to the following equation (Levich equation):

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

$$i_L = \frac{0.62 \cdot 2 \cdot 96485 \cdot (10^{-5})^{2/3} \cdot 10^{-5}}{(10^{-5})^{1/6}} \sqrt{2\pi \cdot 5} = 21.2 \text{ mA cm}^{-2}$$

In the stirred solution, as the diffusion layer decreases, the current density increases.

g) The diffusion layer depends on the hydrodynamics of the flow. A faster flow rate increases the oxygen limiting current density, with a consequent increasing of the corrosion potential and corrosion rate.



Exercise 2

$$(a) P = \frac{V_{pore}}{V_{tot}} = \frac{V_{tot} - V_{electrode\ material}}{V_{tot}}$$

$$V_{tot} = A_{electrode} * h = \frac{\pi d^2}{4} * h = \frac{\pi (1.5 \text{ cm})^2}{4} * (140 \mu\text{m} - 24 \mu\text{m}) \\ = 1.77 \text{ cm}^2 * 0.0116 \text{ cm} = 0.0205 \text{ cm}^3$$

$$V_{electrode\ material} = \frac{m_{el}}{\rho_{el}} = \frac{33.7 \text{ mg} - 24 \text{ mg}}{2.2 \text{ g/cm}^3} = 4.41 * 10^{-3} \text{ cm}^3$$

$$P = \frac{V_{tot} - V_{electrode\ material}}{V_{tot}} = \frac{(0.0205 - 4.41 * 10^{-3}) \text{ cm}^3}{0.0205 \text{ cm}^3} = 78.5 \%$$

$$(b) q = m_{active\ material} * q_{spec} = (33.7 - 24) \text{ mg} * \frac{9.5 \text{ g}}{11.2 \text{ g}} * 370 \frac{\text{mAh}}{\text{g}} = 3.044 \text{ mAh}$$

$$(m_{activemat} = 8.23 \text{ mg})$$

The specific charge / capacity is the amount of charge that can be stored in a material either per unit of mass or per unit of volume

$$q_{m,Electrode} = \frac{q}{m_{Electrode}} = \frac{3.05 \text{ mAh}}{33.7 \text{ mg}} = 90.33 \text{ mAh/g}$$

$$q_{v,Electrode} = \frac{q}{V_{Electrode}} = \frac{3.044 \text{ mAh}}{\frac{\pi (1.5 \text{ cm})^2}{4} * (140 \mu\text{m})} = 123.04 \text{ mAh/cm}^3$$

$$(c) V_{tot} = A_{electrode} * h = \frac{\pi d^2}{4} * h = 0.0103 \text{ cm}^3$$

$$P = \frac{V_{tot} - V_{electrode\ material}}{V_{tot}} = \frac{(0.0103 - 4.41 * 10^{-3}) \text{ cm}^3}{0.0103} = 57.2\%$$

Since the mass of the electrode is kept the same, the gravimetric capacity will not change. However the volume has been reduced to the half of the original value, thus the volumetric capacity will double.

$$q_{v,Electrode} = 2 * 122.9 \text{ mAh/cm}^3 = 245.8 \text{ mAh/cm}^3$$

(d.1)

$$i = 3.7 \frac{\text{mA}}{\text{mg}} * 8.23 \text{ mg} = 30.45 \text{ mA}$$

Ohmic drop, IR-drop – U= iR

$$R_{el} = \frac{1}{\kappa} * \frac{l}{A} = \frac{0.01 \text{ cm} * \text{cm} * \Omega}{9.8 * 10^{-4} * 1.77 \text{ cm}^2} = 5.77 \Omega$$

$$\Delta U_{ohm} = 30.45 \text{ mA} * (5.77 + 0.08) \Omega = 178 \text{ mV}$$

(d.2)

For electrode a), the exchange current is: $i_0 = 7.0 \frac{\mu A}{cm^2} * 225 * 1.77 cm^2 = 2.79 mA$

For electrode c), the exchange current is: $i_0 = 7.0 \frac{\mu A}{cm^2} * 121 * 1.77 cm^2 = 1.5 mA$

To calculate the charge transfer overpotential we can use the Tafel equation:

$$\eta_{CT} = \frac{RT}{\alpha z F} * \ln \left(\frac{j}{j_0} \right) = \mathbf{123 mV} \text{ for electrode a) and } \eta_{CT} = \mathbf{155 mV} \text{ for electrode c)}$$

(d.3)

The total overpotential takes the charge transfer overpotential, the Ohmic overpotential and the concentration overpotential into account.

The total overpotential is thus:

$$\eta_{tot(a)} = (430 - 90)mV = 340 mV$$

$$\eta_{tot(c)} = (471 - 90)mV = 381 mV$$

$$\eta_c = \eta_{tot} - IR - \eta_{CT}$$

$$\text{Electrode (a) } \eta_c = 340mV - 178 mV - 123 mV = 39 mV$$

$$\text{Electrode (c) } \eta_c = 381mV - 178 mV - 155 mV = 48 mV$$

Exercise 3**(a)**

$$i_L = zFD \frac{C_{\text{solution}}}{\delta}$$

Assumption: z , D , δ are constant.

C_{solution} can be thus determined and is equal to 2.19mM.

(b)

$$D = \frac{i_L \delta}{C_{\text{solution}} z F} = \frac{14 \mu\text{A}/\text{cm}^2 * 0.03 \text{cm} * 1000 \text{cm}^3}{2.19 * 10^{-3} \text{mol} * 1 * 96485 \text{As}} = 1.98 * 10^{-6} \frac{\text{cm}^2}{\text{s}}$$

Exercise 4

We can use the Tafel approximation:

$$j = j_0 e^{\alpha f \eta} \quad f = \frac{F}{RT} = 38.96 \text{ mV}$$

$$(1) 1.22 \text{mA}/\text{cm}^2 = j_0 e^{0.5 * f * 0.5V}$$

$$(2) j_{0.6} = j_0 e^{0.5 * f * 0.6V}$$

$$\frac{j_{0.5}}{j_{0.6}} = e^{-0.05 * f} \rightarrow j_{0.6} = \mathbf{8.56 \text{ mA}/\text{cm}^2}$$

Current density increases by 7 times. The applied voltage is a very efficient parameter to control the rate of the reaction.

(a) How to decrease overpotential?

- Decrease the distance between electrodes
- Improve electrolyte conductivity
- Optimize the size of the active material and the **composition of the electrode**.