Elektrochemie, HS2018 08.10.2018

3^{rd} Exercise: Stofftransport im Elektrolyten

Assistant: Christoph Csoklich, ✉ christoph.csoklich@psi.ch

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1 General Considerations on Mass Transport in Electrolytes

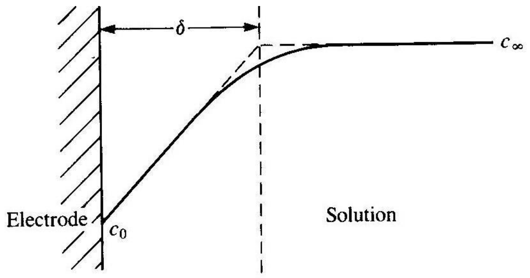
(a) Typically three types of mass transport exist in electrolyte. Describe their mechanisms:

Diffusion Movement of species under a concentration gradient ∇c.

Migration Movement of species under a potential gradient $\nabla \phi$, i.e. in an electric field.

Convection Movement of species due to external forces, such as stirring and heating.

(b) Draw a schematic view of the concentration (c) variation as a function of the distance (x) to the electrode during an electrochemical reaction when only the diffusion occurs as mass transport mechanism. Mark the thickness of the Nernst diffusion layer (δ).



(c) Explain why the Nernst diffusion layer is both time and diffusion coefficient dependent, i.e. $\delta = \delta(D, t)$.

$$\delta_N = \sqrt{\pi D t}$$

- Diffusion coefficient dependency: the diffusion coefficient D describes the mobility of a certain species in a surrounding medium. The higher it is, the faster a molecule will react to a concentration gradient. Therefore with a higher D, more reactants will diffuse towards the area with low concentrations and so extend the diffusion layer.
- Time dependency: With time, more and more reactants are consumed at the electrode and the concentration gradient decreases, i.e. the diffusion layer extends. Furthermore, the reactants from the bulk solution have more time to react to this gradient and will move towards the electrode, thus decreasing the original concentration at their position.

(d) The reaction $H^+ + e^- \longrightarrow \frac{1}{2} H_2$ may occur at a Pt catalyst. Consider a Pt electrode with a surface area of 1.1 cm x 1.1 cm in a 1 M[1] solution of HCl. A steady state current of 1.5 mA is

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[1] [M=mol/L]

observed. Calculate the current density (j, [A/cm^2]) and the flux (J, [mol/(cm^2 s)]).

$$\text{Current density:} \qquad j = \frac{I}{A} = \frac{1.5\,\mathrm{mA}}{1.21\,\mathrm{cm}^2} = 1.24 \times 10^{-3}\,\mathrm{A/cm}^2$$

$$\text{Flux:} \qquad J = \frac{j}{zF} = \frac{1.25 \times 10^{-3}\,\mathrm{A/cm}^2}{1 \cdot 96\,485.3\,\mathrm{C/mol}} = 1.285 \times 10^{-8}\,\mathrm{mol/(cm^2\,s)}$$

[2]

2 Diffusion and Migration

(a) Calculate the diffusion coefficient (D, [m^2/s]) for a Li$^+$ cation in H_2O at room temperature (ionic mobility $\mu_{\mathrm{Na}^+} = 5.2 \times 10^{-4}\,\mathrm{cm^2/(s\,V)}$, viscosity $\eta_{\mathrm{H_2O}} = 1 \times 10^{-3}\,\mathrm{kg/(m\,s)}$). Then use the Stokes-Einstein equation to calculate the effective hydrodynamic radius (r,[pm], [Å]).

$$D = \frac{RT}{6N_A\pi\eta r} \qquad \text{Stokes-Einstein equation}$$

Nernst-Einstein equation:

$$D_{\mathrm{Na}^+} = \frac{RT\mu}{zF} = \frac{8.31\,\mathrm{kg\,m^2/(s^2\,mol\,K)} \cdot 298\,\mathrm{K} \cdot 5.2 \times 10^{-4}\,\mathrm{cm^2/(s\,V)}}{1 \cdot 96\,485.3\,\mathrm{C/mol}} = 1.335 \times 10^{-9}\,\mathrm{m^2/s}$$

Stokes-Einstein equation:

$$D_{NE} = D_{SE} \;\Rightarrow\; \frac{RT\mu}{zF} = \frac{RT}{6N_A\pi\eta r}$$

$$\Rightarrow r = \frac{zF}{6N_A\pi\eta\mu} = \frac{1 \cdot 96\,485.3\,\mathrm{C/mol}}{6 \cdot 6.02 \times 10^{23}\pi 1 \times 10^{-3}\,\mathrm{kg/(m\,s)} 5.2 \times 10^{-4}\,\mathrm{cm^2/(s\,V)}} \Rightarrow$$

$$r = 1.635 \times 10^{-10}\,\mathrm{m} = 1.635\,\text{Å} = 163.5\,\mathrm{pm}$$

cf.: ionic radius of 116 pm

(b) In the table below the ionic mobilities for several ions are listed. Why is there a large difference between H$^+$, OH$^-$ and the other ions?

Table 1: Ionic mobilities at infinite dilution in aqueous solutions at 25°C. cf. Bard & Faulkner.

Ion	μ[cm^2/(s V)]	Ion	μ[cm^2/(s V)]
H^+	3.625×10^{-3}	OH^-	2.05×10^{-3}
Li^+	4.010×10^{-4}	Cl^-	7.912×10^{-4}
Na^+	5.193×10^{-4}	$3/2SO_4^{2-}$	8.27×10^{-4}
K^+	7.619×10^{-4}	HCO_3^-	4.61×10^{-4}

For protons in aqueous solutions there exists a faster transport mechanism than diffusion: through fast reorientation of the hydrogen bonds around H_3O^+-molecules the charge can be transferred much faster than the ion (c.f. Grotthus mechanism). A similar effect can be observed for the OH$^-$ anions. This structural diffusion mechanism differs significantly from the diffusion of other ions.

(c) Assume an ideal diluted aqueous electrolyte solution in a very long electrochemical cell. Will a charged particle experience a constant acceleration in the electrolyte due to the electric potential gradient induced by the charged electrodes? And why? No, the particle is only accelerated up to the velocity v_{max} at which the force of the electric field on the particle is equal to the Stokes friction force. The maximal velocity v_{max} is given by the formulae:

$$\vec{F}_{el} = ze_0\vec{E}$$

$$F_{fr} = 6\pi\eta r v$$

$$\Rightarrow v_{max} = \frac{ze_0|E|}{6\pi\eta r}$$

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[2] [C]=[A s]

3 Convection

(a) A rotating disk electrode (RDE) rotates with the angular frequency $\omega = 2\pi \cdot f$[3] in 1 M HCl. With this setup, the Nernst diffusion layer thickness can be expressed as:

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

The diffusion limited current density is defined as:

$$j = 0.62 \cdot nFD^{2/3} \nu^{-1/6} \omega^{1/2} c_0$$

where n is the number of electrons involved in the electrode reaction. Consider the reduction of Fe^{3+} to Fe^{2+}:

$$\mathrm{Fe^{3+}} + \mathrm{e^-} \longrightarrow \mathrm{Fe^{2+}}$$

and calculate the Nernst diffusion layer (δ, [µm]) and the diffusion limited current density (j, [A/cm^2]) for the disk electrode rotating at 100 Hz.

(Use the following electrolyte properties for HCl: $D_{\mathrm{Fe^{3+}}} = 4.96 \times 10^{-6}\,\mathrm{cm^2/s}$, $c_{\mathrm{Fe^{3+}}} = 1.5\,\mathrm{mmol/L}$, kinematic viscosity $\nu_{\mathrm{H_2O}} = 1 \times 10^{-6}\,\mathrm{m^2/s}$.[4])

$\omega = 2\pi f = 2\pi \cdot 250\,\mathrm{Hz} = 1571\,\mathrm{Hz}$

$\delta = 1.61 \cdot (4.96 \times 10^{-6}\,\mathrm{cm^2/s})^{1/3} (1 \times 10^{-6}\,\mathrm{m^2/s})^{1/6} (1571\,\mathrm{Hz})^{-1/2} = 5.084 \times 10^{-6}\,\mathrm{m}$

$\delta = 3.126\,\mu\mathrm{m}$

$j = 0.62 \cdot 1 \cdot 96\,485.3\,\mathrm{C/mol} (4.96 \times 10^{-6}\,\mathrm{cm^2/s})^{2/3} (1 \times 10^{-6}\,\mathrm{m^2/s})^{-1/6} (1571/\mathrm{s})^{1/2} \cdot 1.5\,\mathrm{mmol/L}$

$j = 2.228 \times 10^{-3}\,\mathrm{A/cm^2}$

[5]

(b) Explain the interest of the rotating disks for electro-analytical application.

The RDE creates a steady-state situation and constant diffusion-limited current (no time dependence). The mass transport is driven by convection and diffusion. The RDE system could therefore be more sensitive and enable the detection of lower currents induced by lower concentrations of reactants in the electrolyte.

4 Multiple Choice Summary

1. Which condition(s) has/have to be fulfilled for diffusion limited current?[6]

   (a) $c_{bulk} = 0$

   (b) $c_{bulk} = c_{x=0}$

   (c) $c_{x=0} = 0$

2. Consider a 0.1 M aqueous solution of HCl. Which transport mode in the electrolyte (migration (M), diffusion (D) or convection (C)) is affected by the following changes:
   (Multiple answers as well as none of the above are possible.)

   (a) Increasing the potential gradient Migration ☐ M ☐ D ☐ C

   (b) Increasing the concentration gradient of the reactant Diffusion ☐ M ☐ D ☐ C

   (c) Increasing the concentration of the electrolyte from 0.1 M to 1 M HCl ☐ M ☐ D ☐ C
   Migration, (Convection)

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[3] [rad/s=2πHz]

[4] S. Tanimoto, A. Ichimura, J. Chem. Educ., 2013, 90 (6), pp 778–781, DOI: 10.1021/ed200604m

[5] $[\frac{cm^{2/3} \cdot m^{1/3} s^{1/2}}{s^{1/3} s^{1/6}}]$=[m]

[6] $c_{x=0}$: concentration at the electrode surface

(d) Increasing the temperature Migration, Diffusion, Convection ☐ M ☐ D ☐ C

(e) Changing the transference number[7] of the ion Migration ☐ M ☐ D ☐ C

(f) Increasing the radius of the solvated ion Migration, Diffusion ☐ M ☐ D ☐ C

(g) Changing the density gradient of the solvent Convection ☐ M ☐ D ☐ C

(h) Changing the solvent of the electrolyte ☐ M ☐ D ☐ C
Migration (μ), Diffusion (D), Convection (η)

(i) Changing the external wires from copper to gold no effect ☐ M ☐ D ☐ C

$$j = -F \sum_n z_n D_n \nabla c_n - F \sum_n z_n c_n u_n \nabla \phi + F \sum_n z_n c_n |\vec{v}|$$

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[7] Überführungszahl