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3^{rd} Exercise: Stofftransport im Elektrolyten

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Cave: a) present the result in the desired units, b) sign and staple all written pages.

1 General Considerations on Mass Transport in Electrolytes

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

Diffusion

Migration

Convection

(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. $\delta = \delta(D, t)$.

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

2 Diffusion and Migration

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

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

(b) In Table 1 below the ionic mobilities for several ions are listed[2]. Why is there a large difference between H^+, OH^- and the 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?

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[1] [M=mol/L]

[2] Bard, Allen J.; Faulkner, Larry R. (2000): Electrochemical methods and applications. 2nd ed. New York, London: Wiley-Interscience.

Table 1: Ionic mobilities at infinite dilution in aqueous solutions at 25°C.

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

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+}:

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

and calculate the Nernst diffusion layer (δ, [µm]) and the diffusion limited current density (j, [A/cm^2]) for the disk electrode rotating at 250 Hz.

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

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

4 Multiple Choice Summary

1. Which condition(s) has/have to be fulfilled for diffusion limited current?[4]

   (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 ☐ M ☐ D ☐ C

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

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

   (d) Increasing the temperature ☐ M ☐ D ☐ C

   (e) Changing the transference number[5] of the ion ☐ M ☐ D ☐ C

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

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

   (h) Changing the solvent of the electrolyte ☐ M ☐ D ☐ C

   (i) Changing the external wires from copper to gold ☐ M ☐ D ☐ C

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[3] [rad/s=2πHz]

[4] $c_{x=0}$: concentration at the electrode surface; c_{bulk}: bulk concentration

[5] Überführungszahl