Department of Inorganic Technology, ICT Prague

Technical Electrochemistry Group I, lab A023

DETERMINATION OF MASS TRANSFER COEFFICIENTS USING A ROTATING-DISC ELECTRODE

THE TASK

Determination of mass transfer coefficient of $[Fe(CN)_6]^{3-}$ using a rotating-disc electrode (RDE).

GOALS

- Record polarization curves at different rotation speeds of the RDE for two solutions with different concentration of the $[Fe(CN)_6]^{3-}$ ion.

- Find out whether the redox process under investigation is governed only by mass-transfer.

- Calculate the diffusion coefficient of the $[Fe(CN)_6]^{3-}$ ion.

PRINCIPLES OF THE METHOD

The rotating-disc electrode is a frequently used electrochemical setup, which comprises of a cylinder made of insulating material encasing a disc made of conductive material. The cylinder is usually made of PTFE or PEEK, whereas the disc, which is the electrode itself, is made from various conductive materials, such as platinum, gold, copper, glassy carbon etc.

The whole cylinder is screwed onto a metal shaft, which is fastened inside a rotator. The rotator is a device which operates much like a common drill. With the exception that its rotating speed is precisely controlled by the operator.

The electrode pumps fresh solution from the core of the electrolyte onto the disc. At the surface of the disc, there is a thin layer with no convection. This layer is therefore called the *diffusion layer* and its thickness is constant on the whole surface of the disc (Fig. 1). The mass transfer in this layer is determined by the rotation speed of the RDE and the equations are known and can be used to calculate the mass transfer rate.
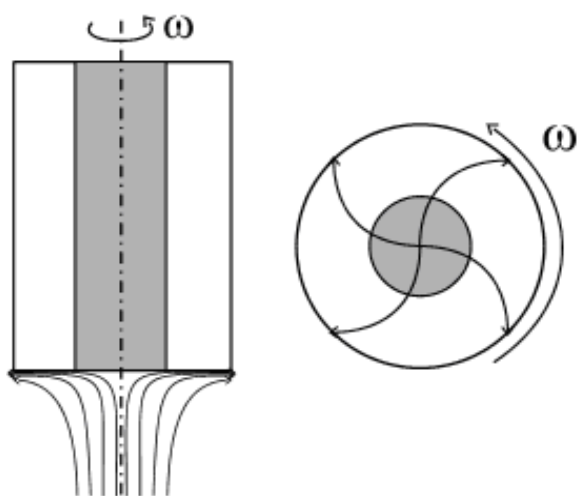

Fig. 1: The rotating disc electrode and schematics of the solution flow to its surface (left) and the flow of the solution on its surface (right). Gray areas show the conductive electrode material, the white areas is insulation.

MATHEMATICAL DESCRIPTION

Mass transfer rate in the diffusion layer is described by a special case of the Fick's first law (1):

$$J = \frac{D(c_s - c_0)}{\delta} \left[mol \cdot m^{-2} s^{-1} \right] \tag{1}$$

J   mass transfer rate

D   diffusion coefficient of the transferred ion (in our case the $[Fe(CN)_6]^{3-}$)

c_s concentration of the ion on the surface of the disc

c_0 concentration of the ion in the bulk of the solution

δ thickness of the diffusion layer

For the RDE, the diffusion layer thickness is described by equation (2):

$$\delta = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2} \left[m \right] \tag{2}$$

ν kinematic viscosity of the electrolyte

ω angular velocity of the RDE, [rad/s]

THE REACTION

Electrochemical reactions are heterogeneous in nature; the reaction takes place at the interface between the electrolyte and the electrode. In our case, two successive processes are happening:

1) Diffusion of the electroactive ion across the diffusion layer.

2) Charge transfer across the electrolyte-electrode interface, which is the kinetics of the reaction.

Let's call the charge transferred at a given time (i.e. the current) across the diffusion layer I_d and the charge transferred across the interface I_k. Both of those currents contribute to the total current, I_t, that is flowing through the electrode and is obtained experimentally (3).

$$\frac{1}{I_t} = \frac{1}{I_k} + \frac{1}{I_d} \left[A^{-1} \right] \tag{3}$$

Consider two cases, first, when the mass transfer is slow (or the kinetics is very fast) and so I_d is small. Then $1/I_d \gg 1/I_k$ and the process is governed by I_d. This case is called the *mass-transfer limited* reaction because the process is practically limited by the comparably slow mass transfer. Then, the equation (3) simplifies to equation (4).

$$I_t = I_d \left[A \right] \tag{4}$$

The second case follows naturally, when the mass transfer is much faster than the kinetics of the reaction and so $1/I_k \gg 1/I_d$. The process is then *kinetically limited*.

Now back to the mass-transfer limited case: The total current is I_d and the mass transfer rate is J. Using the Faraday's law (5), combined equations (1), (4), (5) and (6) give equation (7).

$$n = \frac{It}{zF} \, [mol] \tag{5}$$

n   amount of substance

I   current passed

t   time elapsed

z   number of electrons transferred per ion

F   Faraday constant (96485 C/mol)

$$J = \frac{n}{At} \, [mol \cdot m^{-2} s^{-1}] \tag{6}$$

A   surface area of the electrode

$$I_d = -zFAJ = -zFAD \frac{c_s - c_0}{\delta} \, [A] \tag{7}$$

If the reaction is governed only by the mass transfer, the concentration of the electroactive ion at the surface of the electrode can approach zero ($c_s = 0$). In this case, the current flowing is called the *limiting current*, $I_{d,\,lim}$. Combining equations (2) and (7), limiting equation for the RDE is obtained (8). This equation is called the *Levich equation*. Note that the limiting current value depends on the square root of the RDE's rotation speed.

$$I_{d,\mathrm{lim}} = 0.62zFAD^{2/3}\omega^{1/2}v^{-1/6}c_0 \, [A] \tag{8}$$

In practical work, current is often expressed per area of the electrode, forming *current density*, j (9).

$$j = \frac{I}{A} \, [A \cdot m^{-2}] \tag{9}$$

Equations (3) and (8) can then be expressed using current densities into equations (10) and (11) respectively.

$$\frac{1}{j_t} = \frac{1}{j_k} + \frac{1}{j_d} \left[A^{-1} \cdot m^2 \right] \qquad (10)$$

$$j_{d,\mathrm{lim}} = 0.62 z F D^{2/3} \omega^{1/2} \nu^{-1/6} c_0 \left[A \cdot m^{-2} \right] \qquad (11)$$

Because in real systems, a reaction is not completely governed by mass transfer, the behaviour is better expressed by so-called *Koutecký-Levich equation* (12). This equation originated by substituting J_d from the equation (10) with $J_{d,\ lim}$ from the equation (11). Now the equation is valid only for the limiting case when $c_s = 0$.

$$\frac{1}{j_{t,\mathrm{lim}}} = \frac{1}{j_k} + \frac{\nu^{1/6}}{0.62 z F D^{2/3} \omega^{1/2} c_0} \left[A^{-1} \cdot m^2 \right] \qquad (12)$$

Equation (12) is basically a linear function of the type $y = a.x + b$ (13) with constant coefficients a (14) and b (15).

$$j_{t,\mathrm{lim}}^{-1} = a + b \omega^{-1/2} \left[A^{-1} m^2 \right] \qquad (13)$$

$$a = \frac{1}{j_k} \left[A^{-1} m^2 \right] \qquad (14)$$

$$b = \frac{\nu^{1/6}}{0.62 z F D^{2/3} c_0} \left[A^{-1} m^2 s^{-1/2} \right] \qquad (15)$$

The x-values are known from the rotation speed of the RDE, which is set by the operator. The y-values are calculated from the current measured by the potentiostat and geometric surface area of the electrode. Using linear regression, values of the two coefficients can be obtained. Subsequently, kinetics current density, j_k, can be calculated from the coefficient a. From the coefficient b, the diffusion coefficient D can be calculated, which is your task.

### EXPERIMENTAL SETUP—THE POTENTIOSTAT

A potentiostat is an electronic device that controls potential between a *working* (WE) and a *reference electrode* (RE). The device then records current that is flowing through the WE as a result of its polarization (different potential than the equilibrium potential). Because the RE cannot pass enough current (its potential would change, which must be avoided if it is a reference point), there is a third electrode, called *counter electrode* (CE), which is used only as a current source or sink for the WE.

A potentiostat is usually used for recording current flowing through the WE at different potentials. The potential is usually swept (changed) in a linear fashion from an initial potential to a final potential. The measured dependence of the current on the potential is called the *polarization curve* and the technique is called the *linear sweep voltammetry* (LSV).

In this work, it is important to perform measurements at steady-state conditions, i.e. when the current at a given potential does not change in time. This is in contradiction with the LSV technique

because the potential is swept. The solution to this problem lies in using a slow scan rate (speed of change of the potential, also called *sweep rate*). The scan rate must be slow enough to allow for the equilibrium to establish.

ELECTROCHEMICAL REACTION UNDER STUDY

$$[Fe(CN)_6]^{3-} + e^- \leftrightarrows [Fe(CN)_6]^{4-}$$
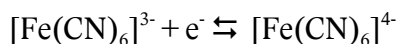
WHAT TO DO

- Prepare 100 mL of each of the two solutions (see below).

- Assemble the apparatus according to the schematics (Fig. 2).

- Connect the cell to the thermostat, use 22 °C setting.

- After validation of the apparatus, check the function of the potentiostat.

- Measure polarization curves using settings below:

Initial potential	0.25 V vs. RE
Final potential	-2 V vs. RE
Scan rate	20 mV/s
Equilibration time	5 s
Current range	10 mA
RDE rotation speeds	400, 900, 1600, 2500 rpm

- Read limiting current at -1.4V vs. RE and construct a graph according to the equation (13).

- Calculate the diffusion coefficient D for the studied reaction for both concentrations of $K_3[Fe(CN)_6]$.

SOLUTIONS

	$K_4[Fe(CN)_6]$	$K_3[Fe(CN)_6]$	KOH	v @ 22 °C
Solution 1	0.15 mol/dm^3	0.015 mol/dm^3	0.5 mol/dm^3	1.0074×10^{-6} m^{2}s^{-1}
Solution 2	0.15 mol/dm^3	0.0075 mol/dm^3	0.5 mol/dm^3	

STOCK CHEMICALS (SOLIDS)

$K_4[Fe(CN)_6] \cdot 3H_2O$, assume 100%

$K_3[Fe(CN)_6]$, assume 100%

KOH, 85%

THE CELL SETUP SCHEMATICS

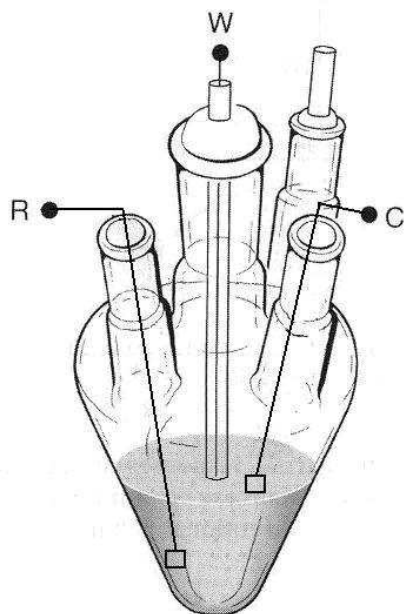**Fig. 2:** Experimental electrochemical cell.

R	reference electrode	saturated calomel electrode (SCE), E = +0.244 V vs. NHE
W	working electrode (RDE)	glassy carbon, 5mm diameter
C	counter electrode	nickel wire

QUESTIONS

1. What are the main advantages of the RDE?
2. What is the limiting current density?
3. What are the conditions and requirements for the RDE to be suitable for the diffusion coefficient determination?
4. What is the function of a potentiostat?