Department of Inorganic Technology, ICT Prague

Technical Electrochemistry Group I, lab A023

DETERMINATION OF DIFFUSION COEFFICIENT USING A ROTATING-DISC ELECTRODE

THE TASK

- Record polarization curves at different rotation speeds of the rotating-disc electrode (RDE) using 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.
- Estimate whether the diffusion coefficient depends on the concentration of the diffusing ion.

PRINCIPLES OF THE METHOD

The rotating-disc electrode is a type of electrode which comprises of a cylinder made of an insulating material encasing a disc made of a conductive material. The cylinder is usually made of PTFE or PEEK, whereas the disc, which is the electrode itself, is made of 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. But its rotation speed can be precisely controlled by the operator.

When the electrode is rotated, it pumps fresh solution from the core of the electrolyte onto the disc. Although the solution moves towards the disc, at the very surface, there is a thin layer with no convection. In this layer, only diffusion takes place so it is called the *diffusion layer* and its thickness is the same across the whole surface of the disc (Fig. 1). Thickness of the diffusion layer can be changed by varying the rotation speed of the RDE. The equation to compute the diffusion layer thickness is known and can be used together with Fick's law of diffusion to calculate the mass transfer rate.

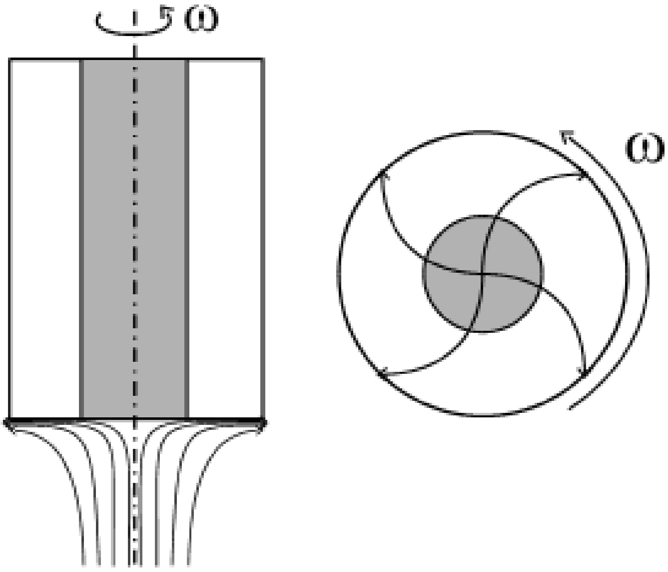

Fig. 1: Rotating-disc electrode and schematics of the solution flow towards its surface (left) and the flow of the solution near its surface (right). Grey areas show the conductive electrode material, the white areas are insulation.

MATHEMATICAL DESCRIPTION

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

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

J	mass transfer rate
D	diffusion coefficient of the transferred ion (in our case the $[Fe(CN)_6]^{3-}$)
c_0	concentration of the ion in the bulk of the solution
c_s	concentration of the ion on the surface of the disc
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], one revolution per second equals to 2π rad/s

Electrochemical reactions are heterogeneous reactions; 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 – the mass transport.
2) Charge transfer across the electrolyte-electrode interface – the kinetics.

The charge transferred at a given time is the current. The current must flow through the diffusion layer and across the electrolyte-electrode interface. A small fraction of the charge can accumulate in the double-layer, which acts as a capacitor, but in the steady-state conditions, the capacitor is not charging. The current passes through two successive resistances – the mass transfer resistance (R_d) and the charge transfer resistance (R_k). The measured current is then, according to Ohm's law, the voltage divided by the sum of the resistances (3).

$$I = \frac{V}{R} = \frac{V}{R_d + R_k}[A] \tag{3}$$

Consider two cases: First, when the kinetics is very fast compared to the mass transfer. Then the $R_k << R_d$ and the equation 3 becomes equation 4. The reaction is *mass transfer limited.*

$$I = I_d = \frac{V}{R_d}[A] \tag{4}$$

Second case is the opposite: When the mass transfer is fast, the $R_d << R_k$ and the equation 3 becomes equation 5. The reaction is *kinetically limited.*

$$I = I_k = \frac{V}{R_k}[A] \tag{5}$$

The reciprocal value of the total current can be then expressed using the I_k and I_d.

$$\frac{1}{I} = \frac{R_d + R_k}{V} = \frac{1}{I_d} + \frac{1}{I_k}\left[A^{-1}\right] \tag{6}$$

Now back to the mass transfer limited case: The total current is I_d and the diffusion mass transfer rate is J. Using the Faraday's law (7), combined equations (1), (4), (7), (8) and (9) give equation (10).

$$n = \frac{It}{zF}[mol] \tag{7}$$

n	amount of substance that is created on the electrode
I	average reaction current
t	time elapsed
z	number of electrons transferred per ion; negative for reduction
F	Faraday constant (96485 C/mol)

$$J = \frac{\Delta n_0}{At}\left[mol \cdot m^{-2}s^{-1}\right] \tag{8}$$

Δn_0	change of the amount of the ion that is transferred from the bulk of the solution
A	surface area of the electrode

The amount of substance that is created on an electrode is equal to the amount of substance that is taken from the solution. Because the solution *loses* substance, the change (Δn_0) is negative.

$$n = -\Delta n_0 [mol] \tag{9}$$

$$I_d = -zFAJ = zFAD\frac{c_0 - c_s}{\delta}[A] \tag{10}$$

When an electrode reaction is governed only by mass transfer, the concentration of the electroactive ion at the surface of the electrode is zero ($c_s = 0$). It is because the reaction is fast enough to instantly consume any reactant that arrives on the electrode. In the mass transfer limited case, the current flowing is called the *limiting current*, $I_{d,\,lim}$. Combining equations (2) and (10), limiting equation for the RDE is obtained (11). This equation is called the *Levich equation*. Note that the limiting current value depends on the square root of the RDE's rotation speed.

$$I_{d,\lim} = 0.62zFAD^{2/3}\omega^{1/2}\nu^{-1/6}c_0\left[A\right] \tag{11}$$

In practical work, current is often expressed per area of the electrode, forming *current density*, j (12).

$$j = \frac{I}{A}\left[A \cdot m^{-2}\right] \tag{12}$$

Equations (6) and (11) can then be expressed using current densities into equations (13) and (14) respectively.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d}\left[A^{-1} \cdot m^2\right] \tag{13}$$

$$j_{d,\lim} = 0.62zFD^{2/3}\omega^{1/2}\nu^{-1/6}c_0\left[A \cdot m^{-2}\right] \tag{14}$$

Because in real systems a reaction is not completely governed by mass transfer, the behaviour is better expressed by so-called *Koutecký-Levich equation* (15). This equation originated by substituting j_d from the equation (13) with $j_{d,\,lim}$ from the equation (14). Unlike the Levich equation, the Koutecký-Levich equation works also in cases where both mass transfer and kinetics contribute to the overall reaction rate.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{\nu^{1/6}}{0.62zFD^{2/3}\omega^{1/2}c_0}\left[A^{-1} \cdot m^2\right] \tag{15}$$

Equation (15) is a linear function $y = a.x + b$ (16) with constant coefficients a (17) and b (18).

$$j^{-1} = a + b\omega^{-1/2}\left[A^{-1}m^2\right] \tag{16}$$

$$a = \frac{1}{j_k}\left[A^{-1}m^2\right] \tag{17}$$

$$b = \frac{\nu^{1/6}}{0.62zFD^{2/3}c_0}\left[A^{-1}m^2s^{-1/2}\right] \tag{18}$$

The x-values are known from the rotation speed of the RDE, which is controlled. 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, kinetic 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 the potential between a *working* (WE) and a *reference electrode* (RE). At the same time, the potentiostat records the 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 frequently swept (changed) linearly 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. Using a sufficiently slow scan rate (the speed of change of the potential, also called *sweep rate*), pseudo steady-state conditions will be established on the electrode. In other words, the scan rate must be slow enough to allow 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 a thermostat, use 22 °C.
- 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 (16).
- Calculate the diffusion coefficient and kinetic current density 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	ν @ 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)

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

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

KOH, 85%

THE CELL SETUP SCHEMATICS

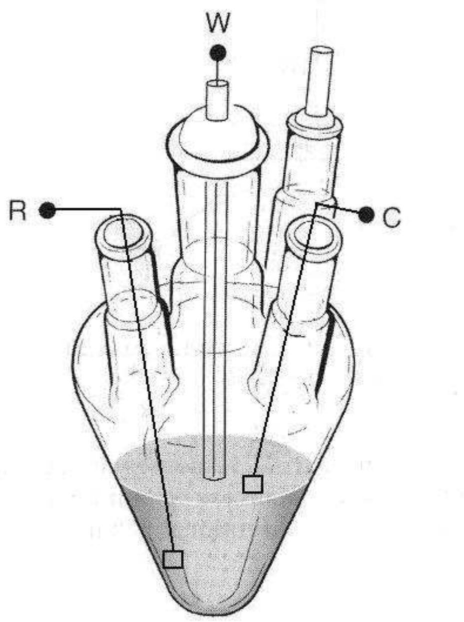

Fig. 2: Experimental electrochemical cell.

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

HOME PREPARATION – BEFORE YOU COME TO THE LAB

To save time, calculate how much of the substances you will need. You should come with a list with values calculated precisely to 1/10 mg, which is the resolution of our analytical balances.