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CHEM-E4185 Electrochemical kinetics

# **Electrochemical methods - Rotating disk electrode**

# 1 Introduction

Electrochemical reactions are studied by perturbing the equilibrium with a properly chosen signal and measuring the system's response to it. From the results, thermodynamic data of simple reactions or knowledge on the kinetics and mechanisms in more complicated cases is obtained. Here, we study a simple electron transfer reaction



which takes place on a glassy carbon electrode. From the laboratory works on cyclic voltammetry and potential step we have learned that the current can be connected to the rate of the redox reaction. However, the actual kinetics of the reaction is difficult to quantify as the reaction can, especially in the case of facile kinetics, quickly become limited by the rate of diffusion to the electrode. The rotating disk electrode (RDE) is designed to enhance the mass transport to the electrode through convection, thus decreasing the effect of diffusion.

# 2 Theory

The reaction (i) can be expressed more generally as



where  $n$  is number of transferred electrons in the reaction, and  $k_{red}$  and  $k_{ox}$  are the rate constants of the reduction and oxidation reactions, respectively. An electrochemical reaction is a combination of at least three steps which affect its observed rate. Firstly, the reactant (O) has to be transported from the bulk solution to the electrode surface. Secondly, at the electrode, the reaction occurs at some finite rate. Thirdly, the product (R) has to be transported away from the electrode. If one of these steps is slower than the others, it is said to be the limiting step of the reaction.

## 2.1 Convective electrodiffusion

The Nernst–Planck equation offers a practical starting point for the analysis of a transport process. The flux of species O (similarly for R) can be expressed as the sum of diffusive, migrational and convective fluxes, where the driving forces for these fluxes are the gradient of concentration  $\vec{\nabla}c$ , the gradient of electric potential  $\vec{\nabla}\phi$ , and the convective velocity  $\vec{v}$ :

$$\vec{j}_O = -D_O \vec{\nabla}c_O - \frac{D_O z_O F c_O}{RT} \vec{\nabla}\phi + c_O \vec{v} \quad (1)$$

$D_O$  is the diffusion coefficient of the oxidised species,  $z_O$  is the charge of O,  $F$  is the Faraday coefficient,  $R$  the gas constant and  $T$  temperature. In the case of a trace-ion, the migrational term can be omitted. The flux of O at the electrode surface is equal to the current density, which in the one-dimensional case can be expressed as:

$$j_O|_{x=0} = \frac{i}{nF} \quad (2)$$

where the number of transferred electrons is the difference of their charge numbers,  $n = z_O - z_R$ .

Let us first consider a case in the absence of convection. Then, current density can be expressed as

$$\frac{i}{nF} = -D_O \left( \frac{\partial c_O}{\partial x} \right)_{x=0} = D_R \left( \frac{\partial c_R}{\partial x} \right)_{x=0} \quad (3)$$

where  $D_O$  and  $D_R$  are the diffusion coefficients of the oxidised and reduced species, respectively. The concentration gradient can be estimated with the so-called Nernst diffusion model, which assumes that mass transport occurs only with diffusion and the gradient can be approximated as [1,2]:

$$\left( \frac{\partial c_O}{\partial x} \right)_{x=0} = \frac{(c_O^b - c_O^s)}{\delta} \quad (4)$$

where  $c_O^b$  and  $c_O^s$  are the bulk and surface concentration of the oxidised species and  $\delta$  is the thickness of the diffusion layer. From eq. (4) it is immediately seen that the gradient reaches its maximum value when  $c_O^s$  equals zero. Then the system is under diffusion control, and the resulting current is known as the limiting current density:

$$i_{\text{lim}} = -\frac{nFD_0c_0^b}{\delta} \quad (5)$$

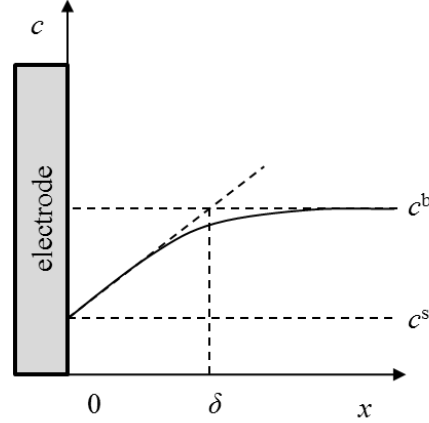


Figure 1. The Nernst diffusion model. The concentration gradient is approximated with a linear profile inside a diffusion layer of thickness  $\delta$ .

In the considered case (no convection) above,  $\delta$  is a function of time, which gives the current the well-known  $t^{-1/2}$  time dependency (cf. eq. (7) in instructions for Cyclic voltammetry and potential step). However, in the case of RDE, the electrode is rotated around its axis, which creates a well-determined velocity field for the solution. The rotation flings electrolyte to the sides of the electrode (parallel to the electrode), simultaneously drawing more solution from the bulk of the solution (perpendicular to the electrode). The outline of the fluid velocity field is shown in Figure 2. Due to frictional forces between the electrode surface and the solution, the velocity at the surface is zero, which is known as the non-slip condition. Near the surface, the perpendicular component of the velocity is close to zero, and the velocity is directed in parallel to the electrode surface. When distance to the electrode increases, the perpendicular component of the velocity field increases and goes through a maximum, and very far away the velocity naturally decreases to zero.

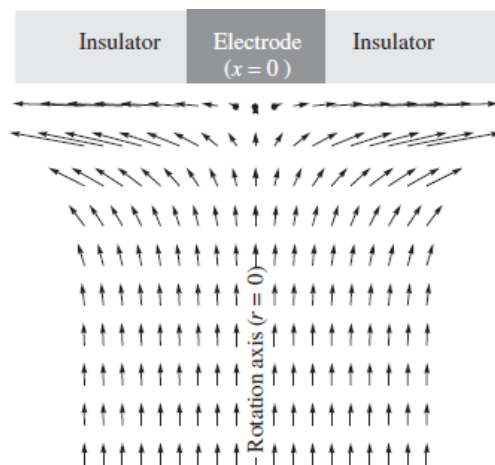


Figure 2. The rotation of the disk creates a velocity field towards the electrode [2]. The perpendicular component of the velocity is a function of the distance squared,  $x^2$ .

The velocity is calculated from the Navier-Stokes equation. Only the perpendicular component of the velocity field affects the current. The solution can be approximated with a series expansion as a function of the angular rotation speed (angular frequency)  $\omega$  of the electrode and the kinematic viscosity  $\nu$  of the solution [2]:

$$v_x = 0.510\omega^{3/2}\nu^{-1/2}x^2 \quad (6)$$

where  $x$  is the distance from the electrode surface.

Introducing eq. (6) into eq. (1) leads to

$$i_{\text{lim}} = \pm 0.620nFD^{2/3}c_i^b\nu^{-1/6}\omega^{1/2} \quad (7)$$

Eq. (7) is known as the Levich equation. Its key message is that with RDE, the limiting current is a function of the angular rotation speed. Increasing the rotational speed enhances the mass transport rate (decreases  $\delta$ ), which enables the study of faster reaction kinetics. Comparing Eq. (7) with Eq. (5), the thickness of the diffusion layer can be identified as

$$\delta_i = 1.61D_i^{1/3}\nu^{1/6}\omega^{-1/2} \quad (8)$$

For a more detailed derivation of the theory, see e.g. [2].

## 2.2 The Butler–Volmer equation

The kinetics of a reaction can be studied when the reaction is not limited by diffusion. The Butler–Volmer equation can be utilized to link the measured current to the reaction rate constants (which are functions of potential). The rate of the reaction (ii) is directly proportional to the measured current density,  $i$  [1]:

$$-\frac{i}{nF} = k_{red}c_O^S - k_{ox}c_R^S \quad (9)$$

When the reaction is at equilibrium, the net current density is zero, and the electrode potential  $E_{eq}$  can be calculated with the Nernst equation [1]:

$$E_{eq} = E^{0'} + \frac{RT}{nF} \ln \frac{c_O^S}{c_R^S} \quad (10)$$

where  $E^{0'}$  is the formal standard potential of the reaction. Since the reaction is at equilibrium, the surface concentrations are equal to the bulk concentrations. As the potential of a single electrode cannot be measured,  $E_{eq}$  is understood as the potential difference with respect to a reference electrode. When the electrode potential is changed, one of the reactions begins to take place faster than the other. Then the reaction is no longer at equilibrium, and a net current can be measured. The difference between the electrode potential and the equilibrium potential is known as overpotential  $\eta$ :

$$\eta = E - E_{eq} \quad (11)$$

The dependence of current density on overpotential is expressed by the Butler–Volmer equation [1]:

$$i_{BV} = i_0 \left[ \exp\left(\frac{(1-\alpha)nF}{RT}\eta\right) - \exp\left(-\frac{\alpha nF}{RT}\eta\right) \right] \quad (12)$$

where  $i_0$  is the exchange current density:

$$i_0 = nFk^0(c_O^b)^\alpha (c_R^b)^{1-\alpha} \quad (13)$$

and  $\alpha$  the transfer coefficient describing the symmetry of the energy landscape of the electron transfer reaction. If  $\alpha = 1/2$ , the energy landscape of the reaction is symmetric. For more information, see e.g. [1,3,4]. The exchange current density represents the rates of the cathodic and anodic reactions at equilibrium; the net current density is zero and both reactions occur at equal rate. Therefore, equation

(12) can be expressed as the sum of the cathodic and anodic current,  $i_{BV} = i_a + i_c$ . Figure 3 shows the cathodic, anodic and total current as a function of the overpotential.

Equation (12) can be more easily analysed in the extreme values of  $\eta$ . For large anodic overpotentials ( $\eta \gg 0$ ) eq. (12) yields

$$\ln i_{BV} = \ln i_0 + \frac{(1 - \alpha)nF}{RT} \eta \quad (14)$$

and for large cathodic overpotentials ( $\eta \ll 0$ )

$$\ln i_{BV} = \ln i_0 - \frac{\alpha nF}{RT} \eta \quad (15)$$

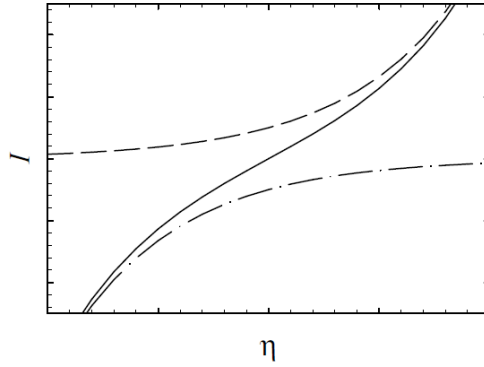


Figure 3. The dependence of the anodic (---), cathodic (-.-) and total current (—) on the overpotential according to the Butler-Volmer equation.

With eqs. (3) – (5), the original eq. (9) can be expressed as:

$$-\frac{i}{nF} = k_{red}c_0^b \left(1 + \frac{i}{i_{lim,O}}\right) - k_{ox}c_R^b \left(1 - \frac{i}{i_{lim,R}}\right) \quad (16)$$

From eq. (16), we can solve for the current density:

$$i = \frac{nF(k_{ox}c_R^b - k_{red}c_0^b)}{1 + \frac{k_{red}}{i_{lim,O}} + \frac{k_{ox}}{i_{lim,R}}} \quad (17)$$

The inverse of eq. (17) yields

$$\frac{1}{i} = \frac{1}{nF(k_{ox}c_R^b - k_{red}c_O^b)} + \frac{\frac{k_{red}}{i_{lim,O}} - \frac{k_{ox}}{i_{lim,R}}}{nF(k_{ox}c_R^b + k_{red}c_O^b)} = \frac{1}{i_{BV}} + \frac{1}{i_{diff}} \quad (18)$$

As  $i_{lim} \sim \omega^{1/2}$ , eq. (18) shows that at any given potential, the inverse of the current density is linearly dependent of  $\omega^{-1/2}$ . When  $\omega^{-1/2} \rightarrow 0$ ,  $\omega \rightarrow \infty$ . Therefore, the kinetic current ( $i_{BV}$ ) can be determined from the intercept.

### 3 Experimental

A solution of 3 mmol/L FeCl<sub>3</sub> and 2 mmol/L FeCl<sub>2</sub> in 0.5 mol/L HCl is prepared to a 100 mL volumetric flask. The cell is filled half-full with the solution, and a glassy carbon working electrode (GC,  $d = 0.5$  cm), a Pt counter electrode, and a saturated calomel reference electrode (SCE) are placed in the cell, and connected to a potentiostat according to the instructions of the assistant. The current-voltage curves are measured between 700 mV and 100 mV vs. SCE at the sweep rate of 5 mV/s at five different rotational frequencies (5, 15, 25, 35, 45 Hz).

### 4 Results

Show the measured voltammograms for all rotational frequencies.

1. Determine the limiting current for both reactions, and use eq. (8) to calculate the diffusion coefficient for both the reduced and oxidised species. Then, estimate the effective thickness of the diffusion layer at different rotational frequencies for both species with eq. (7).
2. Use eqs. (8) and (18) to determine the kinetic current  $i_{BV}$  as a function of  $\eta$ . Plot  $\ln i_{BV}$  as a function of  $\eta$ , and use eqs. (14) and (15) for determining the exchange current density  $i_0$  and  $\alpha$  for the anodic and cathodic reactions.



3. Use eq. (13) to calculate  $k^0$  for the reactions.
4. Use regression analysis for the limiting currents to obtain the error for the diffusion coefficients (95% confidence interval).
5. Use regression analysis for the kinetic currents to obtain the error for the exchange current density (intercept) and for  $\alpha$  (slope) (95% confidence interval). Finally, approximate the resulting error for  $k^0$  from eq. (13) using the total derivative method.
6. Compare your results with the literature values. Discuss the reasons for possible differences.

## References

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