Aalto University
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CHEM-E4185 Electrochemical kinetics

Electrochemical methods - Cyclic voltammetry and potential step

Aalto University

1 Introduction

An oxidation-reduction reaction or, more commonly, a redox reaction is an electron transfer reaction, where one chemical species donates and another accepts an electron. The species donating the electron is oxidized and the one accepting it is reduced. If the electron transfer is heterogeneous, *i.e.* occurs at an interface, such as a metal/liquid or a liquid/liquid interface, we define the reaction as electrochemical. The rate of an electrochemical reaction (r), is proportional to the electric current via the Faraday law, $r = \frac{\nu i}{nF}$, where ν is the stoichiometric coefficient of the reacting species, i the current density ($\mathrm{A\,cm^{-2}}$), n the number of electrons and F the Faraday constant.

A specific feature of an electrochemical reaction is that its rate depends on *potential*. Since electric current can exist only in a closed circuit and only potential differences can be measured, at least two electrodes are needed in a measurement, and the electrodes must be connected via an external resistance (load). The reaction of interest takes place at the *working electrode*, and some other reaction closing the circuit takes place at the *counter electrode*. In the modern experimental set-up, the potential of the working electrode is measured against a *reference electrode*, through which no current passes. The idea of the reference electrode is to separate current measurement from potential measurement, also eliminating ohmic losses. Figure 1 shows the schematic of an electrochemical system.

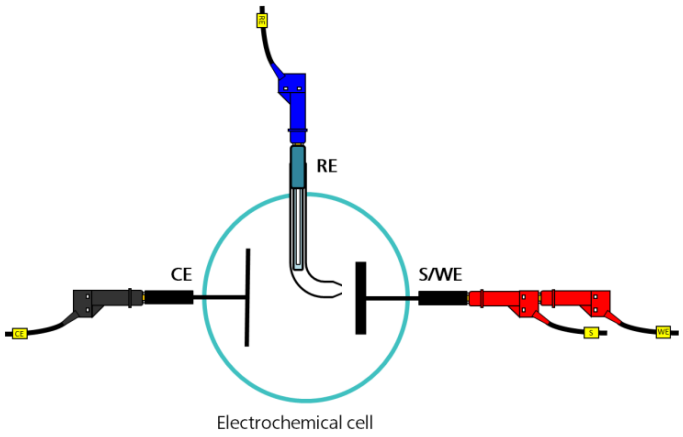

Figure 1. Schematic of an electrochemical cell. The studied reaction takes place at the working electrode (WE). Current flows between the WE and the counter electrode (CE).

Potential difference is measured between the working and the reference electrodes (RE) with a potentiostat.

2 Theory

This section provides the basic theory of the potential step and the cyclic voltammetry (CV) methods (chronoamperometry). In these methods, the potential of the working electrode is varied and the current is measured. However, in order to obtain any quantitative information from the measurement, the current has to be mathematically linked to the reaction rates. The starting point for most measurements is the electrochemical redox reaction:

$$\mathrm{R} \underset{k_{red}}{\overset{k_{ox}}{\rightleftharpoons}} \mathrm{O} + n\mathrm{e}^- \tag{i}$$

where R is the reduced and O the oxidized species, and k_{ox} and k_{red} are the reaction rate constants. Nernst-Planck equation describes the flux of species $k = \mathrm{O}, \mathrm{R}$ across a reference plane [1] (no convection):

$$\vec{j}_k = -D_k \vec{\nabla} c_k - \frac{z_k F}{RT} D_k c_k \vec{\nabla} \phi \tag{1}$$

D_k is the diffusion coefficient, c_k the concentration, z_k the charge of the ion k, F is the Faraday constant, R the gas constant, T temperature and ϕ potential. If k is present in the system only as a trace-ion (excess supporting electrolyte), the latter term in eq. (1) can be neglected, and the equation reduces to Fick's first law.

From the balance equation of k, we can deduce that in the absence of homogeneous chemical reactions, Fick's second law is obtained:

$$\frac{\partial c_k}{\partial t} = -\vec{\nabla} \cdot \vec{j}_k = D_i \vec{\nabla}^2 c_k \tag{2}$$

where eq. (1) is used. In most cases, it is sufficient to consider the problem in only one dimension x perpendicular to the working electrode. The analysis of all methods aims at solving the partial differential equation above, and the selected method determines the mathematical boundary conditions which are applied in the solution. If it is assumed that initially only one species is present in the system and the concentration is uniform, the initial condition is

$$c_k(0, x) = c_k^b \tag{3}$$

where c_k^b is the bulk concentration of k. As electrochemical reactions take place at the working electrode, concentration changes are developed in its proximity, but "far away" from the electrode concentrations are equal to the bulk concentration:

$$\lim_{x \to \infty} c_k(x) = c_k^b \tag{4}$$

This is known as the semi-infinite diffusion boundary condition. The other boundary condition is obtained considering the charge and mass balance at the working electrode. In a reaction O is transformed to R (or vice versa), and if neither of them is adsorbed at the electrode their fluxes at the electrode must be equal but opposite in direction. The number of electrons exchanged, n, is the difference of their charge numbers, $n = z_O - z_R$. Therefore,

$$\vec{J}_O|_{x=0} = -\vec{J}_R|_{x=0} = \frac{i}{nF} \tag{5}$$

The problem can be solved e.g. by taking the Laplace transform of eq. (2), solving the resulting ordinary differential equation with the selected initial and boundary conditions, and finally taking the inverse transform of the solution.

2.1 Potential step

In the potential step method the potential of the working electrode is changed in a step-like fashion shown in Figure 2. When the potential is changed sufficiently far from the equilibrium potential (Figure 2a), the surface concentration of O drops to zero (Figure 2b). The reaction takes place as fast as O diffuses to the electrode surface; the system is said to be under diffusion control, and the current density decreases as a function of $t^{-1/2}$ (Figure 2c).

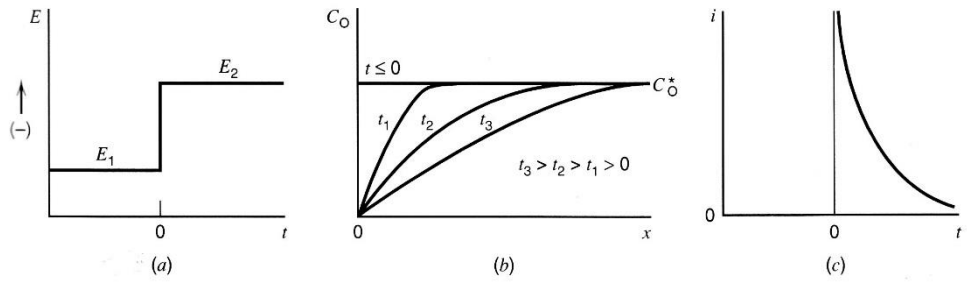

Figure 2. a) Potential step takes place from E_1 to E_2 at $t = 0$. b) If the potential step is large enough, the surface concentration of O decreases to zero. c) The current density decreases as a function of $t^{-1/2}$. [1]

For a reversible reaction, the electrode potential follows the Nernst equation:

$$E = E^0 + \frac{RT}{nF}\ln\left(\frac{\gamma_{\mathrm{O}} c_{\mathrm{O}}^s}{\gamma_{\mathrm{R}} c_{\mathrm{R}}^s}\right) = E^{0\prime} + \frac{RT}{nF}\ln\left(\frac{c_{\mathrm{O}}^s}{c_{\mathrm{R}}^s}\right) \tag{6}$$

where E^0 and $E^{0\prime}$ are the standard reduction and the formal potentials, respectively, γ is the activity coefficient, and the superscript s indicates concentrations at the electrode surface. By solving eq. (2) with the initial and boundary conditions, eqs. (3) - (5), for an arbitrary potential step and a system with only O initially present, the current density can be expressed as [2]

$$i(t) = -\frac{nF\sqrt{D_{\mathrm{R}}}\theta c_{\mathrm{O}}^b}{1+\xi\theta}\frac{1}{\sqrt{\pi}}\frac{1}{\sqrt{t}} \tag{7}$$

where $\theta = \exp\left[\frac{nF}{RT}(E - E^{0\prime})\right]$ and $\xi = \sqrt{D_{\mathrm{O}}/D_{\mathrm{R}}}$. If the potential step is done to a potential where the surface concentration of O drops to zero, i.e. $\xi\theta \gg 1$, the current density declines according to the Cottrell equation [1]:

$$i_d(t) = -nF\sqrt{\frac{D_{\mathrm{O}}}{\pi}} c_{\mathrm{O}}^b \frac{1}{\sqrt{t}} \tag{8}$$

The formulation of this equation is left as a homework.

If the electrochemical reaction has more sluggish kinetics, the reaction is called *quasi-reversible,* and the reaction rate has to be taken into account [1]:

$$\frac{i}{nF} = k_{ox} c_R^s - k_{red} c_O^s \tag{9}$$

The surface concentrations are solved as described earlier. The exact solution is

$$i(t) = -nF k_{red} c_O^b \exp(\lambda^2 t)\,\mathrm{erfc}\left(\lambda\sqrt{t}\right) \tag{10}$$

where $\lambda = (k_{ox}/\sqrt{D_R} + k_{red}/\sqrt{D_O})$ and where the inverse Laplace transform

$$\mathcal{L}^{-1}\left\{\frac{1}{\sqrt{s}\left(\sqrt{s}+a\right)}\right\} = \exp(a^2 t)\,\mathrm{erfc}\left(a\sqrt{t}\right) \tag{11}$$

has been used. From eq. (10), it is useful to examine the extremum with respect to t. Firstly, for $t \ll 1$ a Taylor expansion at $t = 0$ shows that

$$i(t) = -nFk_{red}c_O^b\left(1 - \frac{2\lambda}{\sqrt{\pi}}\sqrt{t}\right) \tag{12}$$

Equation (11) shows that the rate constant can be obtained by extrapolating the current density as a function of $\sqrt{t}$ to $t = 0$. On the other hand, when $t \to \infty$, the current approaches $1/\sqrt{t}$ dependency.

2.2 Cyclic voltammetry

In cyclic voltammetry the electrode potential is changed in cycles and the current is measured. The method can be used to evaluate the reversibility of an electrochemical system or to obtain quantitative information of the kinetics of the reaction. Usually, a CV is initiated at a potential where no reaction takes place. From there, the potential is scanned linearly to one direction until the first switch (or vertex) potential is reached and the potential is scanned back to the initial potential. A scheme of this procedure is shown in Figure 3. With digital instruments, the potential is changed in small steps, and the current is sampled either continuously (linear scan), or at the end of the steps (staircase scan). Keeping the step size at 1-2 mV, the results are identical.

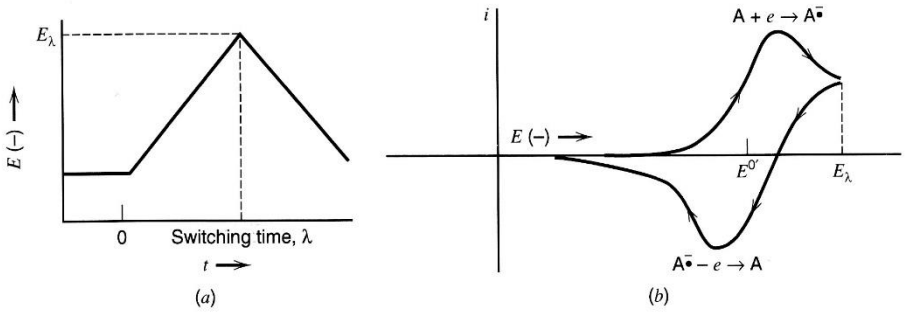

Figure 3. a) In CV, potential is scanned at a constant scan rate until the vertex potential E_λ is reached. b) A reduces to a radical, and at the reverse scan oxidizes back to A. The resulting current density i is shown as a function of the applied potential E. [1]*

* This presentation follows the old polarographic convention where reduction current is shown as positive. The IUPAC convention defines oxidation current positive.

The current density is shown in Figure 3b, where A is first reduced to a negatively charged radical. First, the current increases exponentially with the potential (see eq. (13) below) until the surface concentration of the reactant and diffusion begins to limit the rate. When the scan direction is reversed, the rate of the oxidation reaction increases, until the surface concentration of the reduced species begins to limit the current. The process yields the characteristic peaks for a CV which at first glance may all look very similar, but for an experienced eye it immediately offers both quantitative and qualitative information about the electrochemical nature of the system. For example, qualitative information is readily obtained about the kinetics and the amount of electrons transferred. Moreover, different mechanisms such as adsorption, homogenous reaction, and disproportionation all give their characteristic response in a CV. Due to its generality and ability to offer an overview of the characteristics of the system, cyclic voltammetry is the most popular basic methods in electrochemistry. For example, for a CV measurement of a reversible reaction, three general features apply [1]:

1. The ratio of the peak currents equals one
2. Peak potential separation at 25 °C equals 59 mV/n, where n is the number of electrons transferred in the reaction, regardless of the scan rate.
3. Peak current density i_p depends linearly on the square root of the scan rate, $\sqrt{v}$, and follows the Randles-Ševčík equation:

$$\pm i_{\mathrm{p},k} = 0.4463\, nFc_k^b \sqrt{\frac{D_k nF}{RT}}\sqrt{v} \tag{13}$$

where k is either O or R, which also determines the sign of the peak current.

For a quasi-reversible system, the theoretical consideration begins again from eq. (8). The rate constants depend on the potential according to the Butler-Volmer equation [1]:

$$\begin{aligned} k_{red} &= k^0 \exp\left[\frac{\alpha nF}{RT}\left(E - E^{0'}\right)\right] \\ k_{ox} &= k^0 \exp\left[(\alpha - 1)\frac{nF}{RT}\left(E - E^{0'}\right)\right] \end{aligned} \tag{14}$$

where k^0 is the standard rate coefficient (cm/s).

In cyclic voltammetry, the potential is varied linearly with time:

$$E = E_i + vt - 2H(t - t_s)v(t - t_s) \tag{15}$$

where E_i is the initial potential, v is the scan rate, t_s is the switch time and

$$H(x) = \begin{cases} 0, & x < 0 \\ 1, & x \geq 0 \end{cases} \tag{16}$$

is the Heaviside step function. If only species R is initially present, the initial and boundary conditions are

$$\begin{gathered} c_{\mathrm{O}}(x,0) = 0 = \lim_{x\to\infty} c_{\mathrm{O}}(x,t) \\ c_{\mathrm{R}}(x,0) = c_{\mathrm{R}}^{b} = \lim_{x\to\infty} c_{\mathrm{R}}(x,t) \\ \frac{i}{nF} = -D_{\mathrm{O}}\left(\frac{\partial c_{\mathrm{O}}(x,t)}{\partial x}\right)_{x=0} = D_{\mathrm{R}}\left(\frac{\partial c_{\mathrm{R}}(x,t)}{\partial x}\right)_{x=0} \end{gathered} \tag{17}$$

which leads to the surface concentrations

$$\begin{gathered} c_{\mathrm{O}}^{s} = \frac{1}{nF\sqrt{D_{\mathrm{O}}\pi}}\int_0^t \frac{i(u)}{\sqrt{t-u}}du \\ c_{\mathrm{R}}^{s} = c_{\mathrm{R}}^{b} - \frac{1}{nF\sqrt{D_{\mathrm{R}}\pi}}\int_0^t \frac{i(u)}{\sqrt{t-u}}du \end{gathered} \tag{18}$$

where u is a dummy variable. Inserting eqs. (14)-(16) and (18) into eq. (9), a tedious looking integral is obtained:

$$\frac{i(t)}{nFk^0} = e^{\frac{\alpha nF}{RT}E(t)}\left[e^{-\frac{nF}{RT}E(t)} - \left(\frac{e^{-\frac{nF}{RT}E(t)}}{nF\sqrt{D_R\pi}} + \frac{1}{nF\sqrt{D_O\pi}}\right)\int_0^t \frac{i(u)}{\sqrt{t-u}}\mathrm{d}u\right] \tag{19}$$

The equation is solved numerically, see e.g. [3]. The main result of the analysis is that the peak potential difference increases with an increasing scan rate. For a one-step, one-electron process with $0.3 < \alpha < 0.7$, the relationship between the dimensionless parameter [1]

$$\Psi = \frac{\xi^{\frac{\alpha}{2}}k^0}{\sqrt{\frac{F}{RT}D_O\pi v}} \tag{20}$$

and the peak potential separation follows the values of Ψ given in Table 1. Thus, by measuring the peak potential separation at different scan rates, the standard rate constant of a quasi-reversible reaction can be estimated. This approach is known as the method of Nicholson.

Table 1. The dependency of the dimensionless parameter $\boldsymbol{\Psi}$ on the peak potential difference for a one-step electron transfer reaction.

Ψ	20	7	6	5	4	3	2	1	0.75	0.50	0.35	0.25	0.10
$n\Delta E_\mathrm{p}$ [mV]	61	63	64	65	66	68	72	84	92	105	121	141	212

3 Experimental

The redox-reaction of iron(III) is an example of a one-step, one electron transfer reaction:

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

for which $E^0 = 0.771$ V vs. NHE. A solution of 5 mmol/L $FeCl_3$ in 0.5 mol/L HCl is prepared to a 100 mL volumetric flask. The cell is filled 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 (Metrohm Autolab PGSTAT100).

The measurements are run with Metrohm Autolab Nova software. The three measurement procedures are built with the software according to the assistant's instructions: general CV for characterizing the electrochemical system, potential step, and CV with different scan rates.

First, the electrochemical system is characterized by performing a CV measurement inside the electrochemical window of the electrolyte. From this general measurement, correct options for the potential step and CV measurements are obtained. Then, the potential step measurement is executed from a potential where only the Fe^{3+} species is present and no current is detected,

to a potential where the reduction to Fe^{2+} takes place. Finally, the CV measurement is run at different scan rates (e.g. v = 10, 22.5, 40, 62.5, 90, 122.5, and 160 mV/s).

4 Results

The first CV measurement is used to characterise the system: use this data to justify the selected potential range in the measurements which follow.

Show the CV measurements with different scan rates. Use these measurements to explain and justify whether the reaction is reversible, quasi-reversible or irreversible. Apply the method of Nicholson to determine the standard rate constant of the reaction. Hints: You can assume that $\alpha = 1/2$. Fit an equation to the data in Table 1[**], and apply this fit to your measured ΔE_P to obtain the Ψ corresponding to your experimental values. Calculate k^0 from the obtained Ψ values. Use the diffusion coefficients for Fe^{2+} and Fe^{3+} from the literature.

Show the potential step data. Plot $i(\sqrt{t})$ and calculate the standard rate constant. Plot $i(t^{-1/2})$ and calculate the diffusion coefficient. Compare these values with the value obtained from CV measurements.

Finally, compare the literature values of the diffusion coefficients and standard rate constants to the values determined in this work. Discuss the possible discrepancies and sources of error. What effect conductivity has on the measurements, and can it be decreased?

Derive the Cottrell equation for an arbitrary reversible redox reaction.

[**] Select the ΔE_P interval which corresponds to your measurements. You can use Excel trendline, e.g. power function, to make the fit.

References

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2. Sundholm G., *Sähkökemia 502,* Otakustantamo, Hämeenlinna 1987.
3. Nicholson R. S. and Shain I., *Anal. Chem.* **36** (1964) 706.