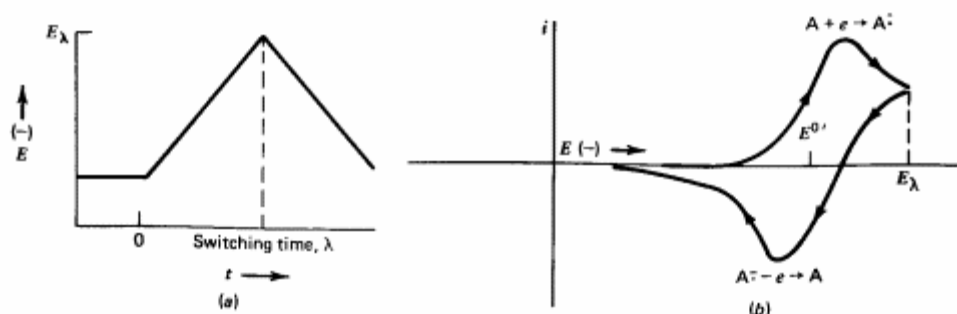# B II – 4 - Cyclic Voltammetry

1. Basic principles

In a typical cyclovoltammetric experiment a stationary working electrode is used which is dipped into an electrolyte solution. In order to minimize the ohmic resistance a three-electrode arrangement is preferable. In this arrangement the current passes between the working electrode (WE) and a counter electrode (CE). The potential of the working electrode is measured relative to a seperate reference electrode (RE) (f. e. SCE = standard calomel electrode). In this experiment the potential of the working electrode is varied linearly with time (Figure 1a)) with sweep rates between 10 mV/s and 200 mV/s. The referring current is recorded as a function of potential (Figure B II - 4.1).


(*a*) Cyclic potential sweep. (*b*) Resulting cyclic voltammogram.

Figure B II - 4.1

Provided the rate of electron transfer at the electrode surface is very fast (which corresponds to an absence of an inhibition), the concentration ratio of the oxidized and reduced species at the electrode surface is dictated by Nernstian equation:

$$E = E^0 + (RT/nF)\ln c_0(0,t)/c_R(0,t) \qquad (B\ II - 4 - 1)$$

Under these circumstances the electrode reaction is said to be reversible. The reaction investigated in this experiment is highly reversible:

$$[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{3-} + e^-$$
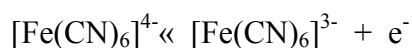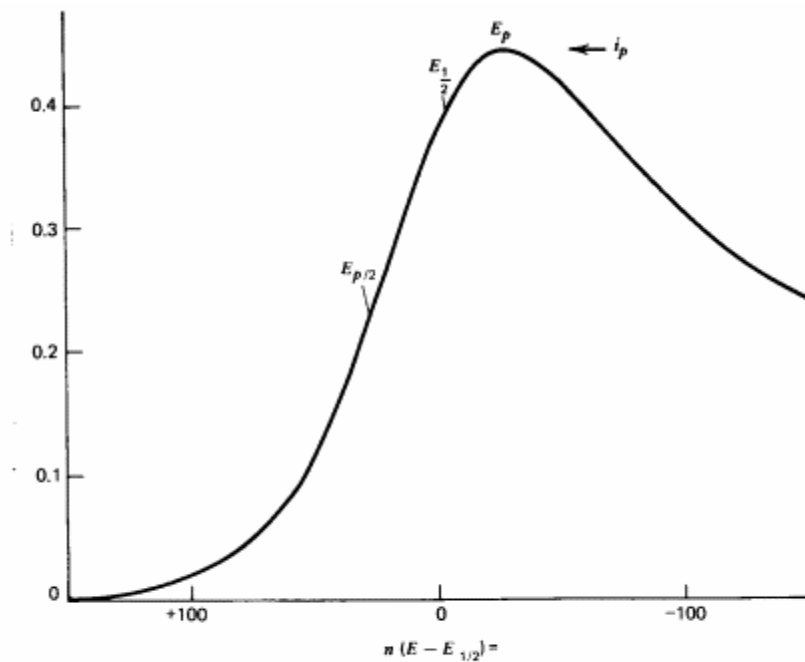
Linear potential sweep voltammogram in terms of dimensionless current function.

Figure B II – 4 .2[1]: General features of a voltammogram

The peak potential E_P in the case of a reversible linear potential sweep is given by:

$$E_P = E_{1/2} +/- 1.109(RT/nF) \quad [2] \quad (B\ II – 4 - 2)$$

$E_{1/2}$ is the polarographic half-wave potential, which is very close to the standard potential E^0 (compare: Gileadi, p.382). The positive sign in eq. (B II – 4 - 2) corresponds to an anodic (E_{P+}) and the negative sign to a cathodic peak (E_{P-}). For the reversible case the peak potential is independent of sweep rate and concentration. These characteristics can be used as a criterion of reversibility. Also the differnce between E_{P+} and E_{P-} can be applied as diagnostic test of a reversible (Nernstian) reaction. Although ΔEP is slightly a function of the switching potential E_λ (figure 1) in general it can be assumed that:

$$\Delta EP = | E_{P+} - E_{P-} |= 2.3(RT/nF) = 59/n \text{ mV (at 25 °C)} \qquad (B\ II – 4 - 3)$$

For repeated cycling the cathodic peak current decreases and the anodic one increases until a steady-state pattern is attained where $\Delta EP = 58/n$ mV (at 25 °C). Also the current during the first cycle is quite different from that in the second cycle. After 5-10 cycles the system has settled down and the voltammogram is independent of time.

Usually the peak in the voltammogram is rather broad, so that the peak potential may be difficult to determine. That is why it is sometimes more convenient to report the potential at 0.5 i_P, called the half-peak potential $E_{P/2}$, which is:

$$E_{P/2}= E_{1/2}+1.09RT/nF \qquad (B\ II – 4 - 4)$$

The difference between E_P and $E_{P/2}$ is:

$| E_P - E_{P/2} | = 2.2\ RT/nF = 56.5/n$ mV (at 25°C)   (B II – 4 - 5)

The peak current i_P for a reversible linear potential sweep is given by the Randles-Ševčik equation:

$$i_P = k\ n^{3/2}\ A\ D^{1/2}\ c\ v^{1/2} \qquad\qquad\qquad\qquad \text{(B II – 4 - 6)}$$

A – area
D – diffusion constant
c- concentration
n – number of exchanged electrons
v – sweep rate
k - Randles-Ševčik-constant ($2.69*10^5$ As/V$^{1/2}$ mol)

2. Additional questions

1.) Explain the concepts of thermodynamic reversibility, chemical reversibility and electro-chemical reversibility.
2.) Where does the peak shape in the voltammogram result from?
3.) What is an electrode of first and second kind?
4.) Why is a supporting electrolyte added?
5.) Which properties does the supporting electrolyte have to have?
6.) Under which circumstances is $E_{1/2} = E^0$

3. Experimental part

1.) Fill 20 ml of 1molar KCl-solution into the cell. After that add 1ml of a 0.1molar $K_4[Fe(CN)_6]$ solution. Afterwards the electrodes are connected (Rinse the SCE before and after use with destilled water!) Now the solution is degased for 15 min with nitrogen. The scan range is set between –200mV and +800mV. An appropriate current range has to be determined (usually 1mA). Thereafter the cell is connected (cell off/on button). **Don't forget to disconnect the cell whenever manipulations are made at the cell or the potentiostat !** The plotter is switched on and the starting point is marked on the paper. The plotter settings for the X-axis and the Y-axis at the plotter are given in V/cm. To transform the Y values into a current note the chosen current range at the potentiostat (the maximum value there corresponds to 1V). For starting the measurement press the start button at the potentiostat. Check if the current range is reasonable. You are asked to record the voltage-current curves at following sweep rates: 5 mV/s, 10 mV/s, 20 mV/s, 50 mV/s and 100 mV/s starting with the highest sweep rate.

a) In order to verify the electrochemical reversibility of the system plot ΔE_P against v, extrapolate to v = 0 and compare to the theoretical value of eq. (B II – 4 - 3).

b) Determine the diffusion coefficient D for $K_4[Fe(CN)_6]$- from the slope of $i_P = f(v^{1/2})$ (equation (B II – 4 - 5)). The diameter of the electrode is 2mm.

2.) Verify the criterion of reversibility for the hexacyano ferrate system by recording the cyclic voltammogram five times at a sweep rate of 10 mV/s.

3.) Record voltammograms at 50 mV/s for different Fe^{2+}-concentrations. Degase for 10 min between measurements. The cell should be filled with

      a) 20 ml KCl and 1ml of a 0.1molar $K_4[Fe(CN)_6]$-solution
      b) 20 ml KCl and 1.5 ml of a 0.1molar $K_4[Fe(CN)_6]$-solution
      c) 20 ml KCl and 2 ml of a 0.1molar $K_4[Fe(CN)_6]$-solution
      d) 20 ml KCl and 2.5 ml of a 0.1molar $K_4[Fe(CN)_6]$-solution

Verify the reversibility of the system at the different concentrations (ΔE_P, i_{P-}/i_{P+}).

Determine the diffusion coefficient D for $K_4Fe(CN)_6$ from the slope of $i_P = f(c)$ (equation (B II – 4 - 6)) and compare with the result obtained in 1b).

The experimental set-up
- measuring cell
- platinum-capillary electrode (working electrode)
- standard calomel electrode SCE (reference electrode), saturated, $E_B = +0.24$ V against normal hydrogen electrode (Don't overturn! Before and after use rinse with destilled water. After usage store the SCE in the prepared KCl solution)
- Pt-electrode (counter electrode)
- potentiostat
- x, y – plotter

The voltage-current curves are measured in a potentiostatic circuit. In a three-electrode arrangement the potentiostat controls the potential difference between the working electrode WE and the reference electrode RE, which serves as the potential basis for the working electrode, to a predetermined value. In this experiment the difference potential U $_{WE-RE}$ is varied continuously from –500mV to +300mV. A current flows from the working electrode to the counter electrode when the redox species are converted in each other. This current (Y entry of the plotter) is plotted against U $_{WE-RE}$ (X entry of the plotter).
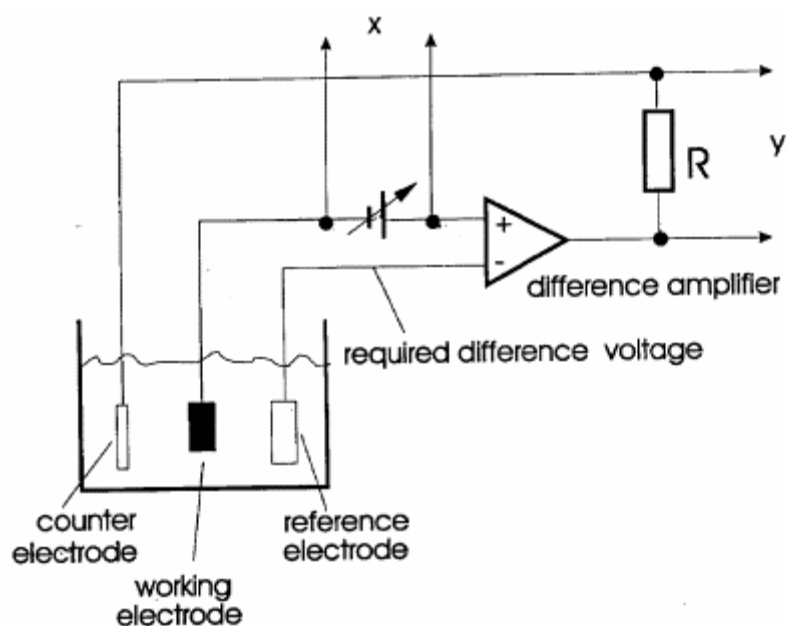

Fig. B II – 4 .3

4. Literature

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2.) Gileadi, E., Electrode kinetics for chemists, engineers and material scientists, Weinheim 1993
3.) Heinze, J., Cyclovoltammetrie – die Spektroskopie des Elektrochemikers, Angew. Chem. 96 (1984), 823
4.) Speiser, B., Cyclische Voltammetrie, Chemie in unserer Zeit, Nr. 2 (1981), 62