Cyclic Voltammetry – Theoretical Experiments

PSAPP-005 Electrochemical Experiment

PalmSens
Compact Electrochemical Interfaces

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1   Instructions

The following instructions will guide you to perform the experiment. The theory on which these experiments are based, can easily be checked online at palmsens.com, then search for "Introduction to Cyclic Voltammetry". The material needed for the experiments can be ordered via https://www.palmsens.com/product/educational-kit/#contents

2   Devices and Equipment

- EmStat / EmStat Blue
- sensor cable
- sensor connector
- maybe a USB cable
- computing unit (PC, Laptop, notebook, tablet PC (Android), smartphone (Android))
- potentiostat software (PStrace, PStouch)
- calculation and plotting software (Excel, Origin, MatLab, Mathematica)
- counter electrode
- reference electrode
- working electrode
- retort stand
- retort clamp
- beaker (electrochemical cell)
- stirrer
- gas source (optional)

3   Chemicals

- 0.1 M KCl solution (prepared from solid KCl and demineralized water) for preparation of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ solutions
- Mixed $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ in 0.1 M KCl solutions with ratios of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ = 100/1, 10/1, 1/1, 1/10, 1/100 (hint 1: All these solutions should have the same sum of concentrations, that is $c(K_3[Fe(CN)_6]) + c(K_4[Fe(CN)_6])$ = constant; hint 2: A concentration for all solutions of (0.010 ± 0.001) M can be achieved by using 0.1 M solutions of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ in 0.1 M KCl with a pipette (20 ml) and variable microliter pipettes (10 - 100 µl and 100 – 1000 µl).)
- 0.1 M solutions of $K_3[Fe(CN)_6]$ in 0.1 M KCl
- 0.1 M solutions of $K_4[Fe(CN)_6]$ in 0.1 M KCl

Note: If you use the 50 mL beaker, you will need 40 mL of solution for your measurement. We recommend using a smaller vessel that allows the electrodes to be immersed in 5 mL solution for the enzyme catalysis experiment.

4 Instructions

4.1 Determination of the Formal Potential

1. Make $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ in 0.1 M KCl solutions with ratios of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ = 100/1, 10/1, 1/1, 1/10, 1/100
2. Choose from the techniques drop down menu the *Potentiometry / OCP.* Choose 300 s as *t run* (duration of the measurement) and 1 s as *t interval* (time between measurement points).
3. Immerse all three electrodes (reference, counter, and working electrode) into each one of the solutions. Press start and wait until the open circuit potential is stable. Note the solution ratio and the corresponding open circuit potential. Stop the measurement.
4. Repeat step 3 for each of the solutions. Rinse the electrodes carefully between changing the solutions.
5. Prepare a 5 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl solution, for example by adding 1 mL of 0.1 M $K_4[Fe(CN)_6]$ in 0.1 M KCl solution to 19 mL of 0.1 M KCl solution.
6. Fill the cell with the 5 mM solution. Immerse the three electrodes into the solution. If a method for performing a CV was already prepared for you load the method. If not choose *Cyclic Voltammetry* from the drop down menu. Choose the current ranges 1 µA, 10 µA, and 100 µA. The fields *Sample* and *Sensor* are for your own notes. Since we do not want a pre-treatment of the electrode set *t condition* and *t deposition* to 0. Set the other parameters to:
   a. *t equilibrium* = 8 s
   b. *E start* = 0 mV
   c. *E vertex1* = 0 mV
   d. *E vertex2* = 500 mV
   e. *E step* = 0.001 V
   f. *Scan rate* = 0.05 V/s
   g. Number of Cycles = 3
7. Start the measurement. Save the curve afterwards under the menu *Curve*.
8. Determine the formal potential from both measurements.
   a. Potentiometry: The formal potential from the open circuit potentials can be determined via the Nernst equation (equation 4.1).

$$E = E^{0\prime} + \frac{0.059\,V}{z} log \frac{c_{Ox}}{c_{Red}} \qquad\qquad 4.1$$

   When the ratio of c_{Ox} and c_{Red} is 1/1 the log will be 0 and the potential E is equal to the formal potential E^{0}'. A good way to determine the formal potential is to plot E versus log c_{Ox}/c_{Red}. A linear fit can be made and the E value at log c_{Ox}/c_{Red} = 0 is the formal potential.
   b. Voltammetry: Due to the fact that $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ have the same diffusion coefficient, determining the formal potential is simple. Read the peak potentials for the anodic and cathodic peaks $E_{p,a}$ and $E_{p,c}$ from the CV. Their average is the formal potential.

4.2 Identification of a Reversible, Quasi-reversible, or Irreversible System

1. Prepare a 5 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl solution, for example by adding 2 mL of 0.1 M $K_4[Fe(CN)_6]$ in 0.1 M KCl solution to 38 mL of 0.1 M KCl solution.
2. Fill the cell with the 5 mM solution. Immerse the three electrodes into the solution. If a method for performing a CV was already prepared for you load the method. If not choose *Cyclic Voltammetry* from the drop down menu. Choose the current ranges 1 µA, 10 µA and 100 µA. The fields *Sample* and *Sensor* are for your own notes. Since we do not want a pre-treatment of the electrode set *t condition* and *t deposition* to 0. Set the other parameters to:
   a. *t equilibrium* = 8 s
   b. *E start* = 0 mV
   c. *E vertex1* = 0 mV

      d.   *E vertex2* = 500 mV
      e.   *E step* = 0.001 V
      f.   *Scan rate* = 0.005 V/s
      g.   Number of Cycles = 3

3. Start the measurement. Save the curve under the menu *Curve*.
4. Repeat the measurement with a *Scan rate* of 0.01 V/s, 0.025 V/s, 0.05 V/s, 0.1 V/s, 0.25 V/s, and 0.5 V/s. Save each curve.
5. The goal is to use Table 4.1 to identify if $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ is a reversible, quasi-reversible, or irreversible system. Using the list of criteria different parameters need to be extracted from the CV and compared.

Table 4.1: diagnostic criteria for reversible, quasi-reversible and electrochemical irreversible systems

Reversible	Quasi-reversible	Electrochemical irreversible
$\Delta E_p = (E_{p,a}-E_{p,c}) = 59$ mV/z (298K)	$\Delta E_p = (E_{p,a}-E_{p,c}) = f(v)$	E_p shift about 30 mV/αz (298 K) with tenfold higher v (α = unknown factor)
$E^{0\prime} = 0{,}5\,(E_{pa}+E_{pc})\,(D_{Ox}=D_{Red})$	$E^{0\prime} = 0{,}5\,(E_{pa}+E_{pc})\,(D_{Ox}=D_{Red})$	-
$I_{p,a} \propto v^{1/2}$ $I_{p,a} = \mathrm{const_1}\, v^{1/2}$	-	$I_{p,a} \propto v^{1/2}$ $I_{p,a} = \mathrm{const_2}\, v^{1/2}$
$I_{p,a}/I_{p,c} = 1$ for all v	$I_{p,a}/I_{p,c} = 1$ for all v	One peak current ($I_{p,c}$) missing

Extracting the $I_{p,c}$ is not directly possible due to the fact that there is no direct baseline available. When the scan rate is inversed there is still current flowing due to conversion of the $[Fe(CN)6]^{4-}$. The current overlaps with the baseline of the cathodic sweep, so either a graphical or mathematical extrapolation has to be done. The graphical method is rather difficult, since parts of the curve has to be guessed. The mathematical way just needs a single equation and some parameters from the curve. Determine $I_{p,c,0}$ and I_{vertex} according to Figure 4.1 and use equation 4.2 to determine $I_{p,c}$.

$$\left|I_{p,c}\right| = \left|I_{p,c,0}\right| + 0.485\,I_{vertex} + 0.086\left|I_{p,a}\right| \qquad\qquad 4.2$$

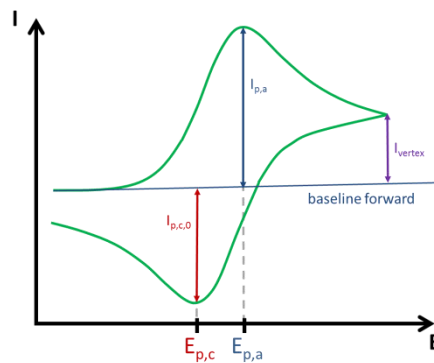Discuss which system $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ is.

Figure 4.1: scheme of a CV indicating how to determine $I_{p,c,0}$ and I_{vertex}

In these experiments you determined the formal potential and identified reversible, quasi-reversible and irreversible systems using cyclic voltammetry.

Please note that teachers can request the answers to the question in the instructions, using
https://www.palmsens.com/contact/