

Experiment 4

Cyclic Voltammetry (CV) of Redox Reactions

Background

Voltammetry is a commonly employed electrochemical method to study the kinetics and mechanisms of reduction–oxidation (redox) reactions by monitoring the relationship between the current and voltage in an electrochemical cell. It has been proven very useful in both quantitative and qualitative analysis of dilute solutions for inorganic, organic, and biological components, measuring thermodynamic parameters for metal–ion complexes and oxidation reduction systems. Voltammetric techniques are based on controlling the electrode potential and measuring the resulting current. The fundamental equation that governs the relationship between the potential applied to an electrode and the concentration of the redox species at the electrode surface is the Nernst equation

$$E = E^{o'} + \frac{RT}{nF} \ln \frac{[ox]}{[red]} \quad (1)$$

Where

$E^{o'}$ = formal reduction potential of the couple vs. reference electrode

E = potential applied to electrode

R = constant (8.314 J/°C)

T = absolute temperature

n = number of electrons transferred during reaction

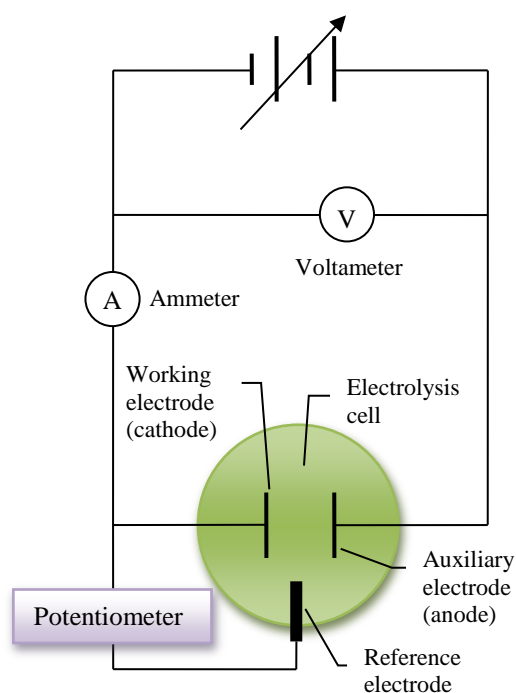
F = Faraday constant (96485 C/mol)

$[ox]$ = concentration of oxidized form of metal ions

$[red]$ = concentration of reduced form of metal ions

This equation applies to reversible systems, i.e. systems in which the ratio of concentrations of oxidized to reduced forms of the analyte at electrode surface instantly responds to any change in E . In other words the concentrations of oxidized and reduced forms are maintained at the level required by the Nernst equation.

During an electrochemical process a potentiostat is used to apply the desired potential between the working and reference electrodes. A potentiostat consists of an electric circuit which controls the potential across the cell by sensing changes in its resistance, varying accordingly the current supplied to the system: a higher resistance will result in a decreased current, while a lower resistance will result in an increased current, in order to keep the voltage constant. A potentiostat requires an electrochemical cell with three electrodes:



- The Working Electrode is the electrode where the potential is controlled and where the current is measured. For many physical electrochemistry experiments, the Working Electrode is an "inert" material such as gold, platinum, or glassy carbon. In these cases, the Working Electrode serves as a surface on which the electron transfer of the redox reaction occurs.
- The reference electrode is used in measuring the working electrode potential. A reference electrode should have a constant electrochemical potential as long as no current flows through it. The most common lab reference electrodes are the Saturated Calomel Electrode (SCE) and the Silver/Silver Chloride (Ag/AgCl) electrodes.
- Auxiliary electrode which serves to carry the current flowing through the cell necessary to sustain the electrolysis.

A potentiostat controls the voltage difference between a working electrode and a reference electrode by injecting current into the cell through an auxiliary electrode and measuring the current flow between the working and auxiliary electrodes. The controlled variable in a potentiostat is the cell potential and the measured variable is the cell current.

A voltammogram (Figure 1) (current–potential curve) is typically obtained by scanning the potential of an electrode in a linear fashion in positive or negative directions and recording the current. In cyclic voltammetry the electrode potential follows a linearly ramping potential vs. time as shown in Figure 2.

The example waveform showed in Figure 2 implies the forward scan initiated at 0.8 V vs. Ag/AgCl in negative direction until the potential of -0.2 V is reached. This will produce a cathodic current peak for any analytes that can be reduced through the range of the potential scan. The current will increase as the potential reaches the reduction potential of the analyte, but then falls off as the concentration of the analyte is depleted close to the electrode surface. As the applied potential is reversed, it will eventually reach a potential that will reoxidize the product formed in the first reduction reaction, and produce an anodic current of reverse polarity from the forward scan. This oxidation peak will usually have a

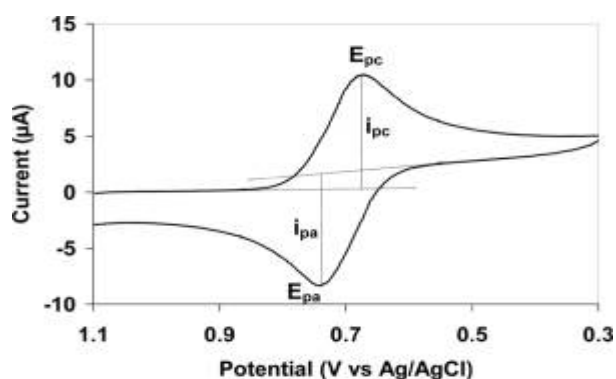


Figure 1. Typical Cyclic Voltammogram. (Wikipedia.org)

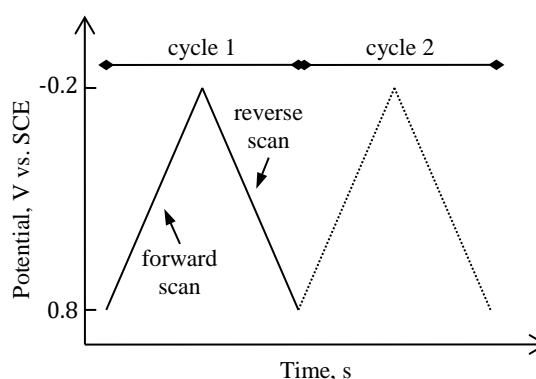


Figure 2. Cyclic voltammetry waveform.

similar shape to the reduction peak. As a result, information about the redox potential and electrochemical reaction rates of the compounds are obtained.

The key parameters for the reversible cyclic voltammogram (Figure 1) are the peak cathodic potential (E_{pc}), the peak anodic potential (E_{pa}), the peak cathodic current (i_{pc}), and the peak anodic current (i_{pa}).

For the electrochemically reversible couple the formal reduction potential (E^0) is centered between the E_{pa} and E_{pc} and can be used to obtain qualitative information about the redox couple inasmuch

$$E^{0'} = \frac{E_{pa} + E_{pc}}{2}$$

The peak separation in the cyclic voltammogram allows calculation of the number of electrons (n) transferred, according to equation:

$$\Delta E_p = (E_{pa} - E_{pc}) \approx \frac{0.0592}{n}$$

Quantitative information regarding analyte concentration can be obtained from the voltammogram using the Randles–Sevcik equation, which specifies the peak current, i_p (either anodic or cathodic), in terms of the analyte concentration, C .

$$i_p = 0.4463 n F A C \sqrt{\frac{n F \nu D}{RT}}$$

In this equation, n is the number of electrons appearing in half-reaction for the redox couple, ν is the rate at which the potential is swept (V/sec), C is the concentration (mol/cm³), F is Faraday's constant (96485 C/mol), A is the electrode area (cm²), R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (K), and D is the analyte's diffusion coefficient (cm²/sec).

Accordingly, i_p increases with $\sqrt{\nu}$ and is directly proportional to the concentration. The relationship to concentration is particularly important in analytical applications and in studies of electrode mechanisms. The values of i_{pa} and i_{pc} should be close for a simple reversible couple. That is, $\frac{i_{pa}}{i_{pc}} \approx 1$. However, the ratio of peak currents can be significantly influenced by chemical reactions coupled to the electrode process.

The chemical application of cyclic voltammetry include: quantitation of concentrations; diffusion effects; irreversibility; study of reaction intermediates; identification of electron transfer steps; and relationships to the Nernst equation. Voltammetric techniques have also a unique capability to distinguish between oxidation states that may affect a substance's reactivity.

Experiment

In this experiment you will use the cyclic voltammetry to study the reversible redox reaction. You will determine the E° and n values of the $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}/[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ couple. You will also evaluate the effects of sweep rate and concentrations of the electroactive species.

The reaction under study involves the oxidation of Fe(II) in potassium ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$ to $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ as the applied voltage makes the working electrode more and more positive, followed by the reduction of Fe(III) to Fe(II) in the cyanide complex as the voltage is returned to its starting value.

Oxidation: $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-} \rightarrow [\text{Fe}^{\text{III}}(\text{CN})_6]^{3-} + e^-$

Reduction: $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-} + e^- \rightarrow [\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$

The initial potential E_i of -0.200 eV is chosen to avoid any electrolysis of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ when the electrode is switched on. During the forward scan when the potential becomes sufficiently positive the oxidation of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ to $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ generates the anodic current. The scan direction is then reversed at 0.600 eV for the reverse scan in negative direction. When the electrode becomes a sufficiently strong reductant, $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ is reduced by the electrode process and the cathodic current is measured.

This experiment uses three electrodes. The working electrode, 1 mm in diameter, is made from an inert material (platinum in this case), the Ag/AgCl reference electrode and the auxiliary (counter) electrode is simply a platinum-coated wire that completes the cell circuit.

In choosing a solvent we are concerned with the total dissolution of the analyte, but must be careful to not choose too polar of a solvent. The less polar the solvent the lower amount of current required for the redox reaction to proceed. This is especially important when analyzing scant quantities of a sample, allowing the user to use micro-amp currents from the potentiostat.

Materials and Chemicals

Potentiostat	Reference electrode (AgCl electrode)
Electrolytic cell	25 mL vol. flasks (x2)
Working electrode – 1 mm diameter (platinum)	10 mM Potassium ferrocyanide solution, $\text{K}_4\text{Fe}(\text{CN})_6$
Auxiliary electrode (platinum wire)	0.05 M Potassium chloride solution, KCl

Procedure

The procedure for this lab has many steps and requires patience, but everything is outlined in five major sections with specific instructions.

1. Sample preparation – Potassium ferrocyanide and potassium chloride
2. Assembly of electrolytic cell
3. Settings for the potentiostat and running the sample
- 4 and 5. Software calculations

1. *Sample preparation*

Before preparing the samples, make sure that all glassware is as clean as possible as impurities will show on the voltammogram. Two 50 mL volumetric flasks are provided solely for the use of this experiment and a small Pyrex cell is specifically designed for the equipment in use.

- Prepare 50 mL of 10 mM solution of potassium ferrocyanide, $K_4Fe(CN)_6$, in 0.05 M potassium chloride, KCl, solution.
- Prepare 50 mL of 5 mM solution of potassium ferrocyanide, $K_4Fe(CN)_6$, in 0.05 M potassium chloride, KCl, stock solution.

2. *Electrolytic cell assembly*

The Pyrex cell is small but very effective in creating a functioning cell from small sample sizes. The cap has several holes at the top into which the various electrodes will be inserted. A nitrogen gas purge tube will also be used to rid the system of excess oxygen that may oxidize the sample solution. Make sure to keep the electrodes from coming into contact with one another.

Fill the Pyrex cell with the 10 mM solution of potassium ferrocyanide leaving a small space of air at the top. There will be three electrodes within the cell: the working electrode (platinum), the reference electrode (Ag/AgCl) and the auxiliary electrode (coiled Pt wire). Each electrode will be connected to its respective cable.

Working electrode – clip the orange and red cables together

Reference electrode – white cable

Auxiliary electrode – green cable

The working electrode is dark gray with a small Pt disk at the bottom. Use the rubber O-ring to keep it suspended within the cell and prevent it from falling to the bottom and possibly touching other electrodes.

The reference electrode (Ag/AgCl) is the thinnest electrode and is stored in KCl solution in a small vial. Insert this into one of the smaller holes and use the o-ring to keep it suspended as well.

The auxiliary electrode is a platinum coated coiled wire. Do not attempt to abrade or polish this wire. A rinse under DI water will suffice.

The following step should not be started until everything is set up and ready to be tested. Open the brown knob on the workbench to allow nitrogen to flow to the tabletop regulator. Barely crack open the tabletop regulator until the small spheres are halfway up the meter. Place the plastic tube into one of two remaining holes in the cap of the Pyrex cell and adjust the flow of gas with the tabletop regulator until steady bubbling is achieved. About 5 bubbles per second is sufficient. Allow the cell to purge for about 5 minutes. If it is bubbling too fast the solution will spill out of the cell. After several minutes have passed move the purge tube up to the top of the cell to minimize disturbance on the liquid/electrode interface. If the bubbles are too close to the working electrode, the voltammogram will appear distorted.

3. The Potentiostat

Turn on the Wavenow potentiostat with a button located on the side of the instrument. The status should be a green blinking light. Open the Aftermath program and press “ok” to log in (there is no password). “Pinewavenow” should show up under “Instruments” at the bottom left-hand corner of the program homepage. Click “Home” and under the “Perform an Experiment” box, click “Cyclic Voltammetry”.

In the “Basic” tab set the following values:

- Number of segments = 6
- Initial potential (Ei) = -0.2 V
- Initial direction = rising
- Upper potential (E1) = 0.6 V
- Lower potential (E2) = -0.2 V
- Final potential (E2) = -0.2 V
- Sweep rate = 0.1 V/s

After all wires have been connected and the cell has been purging for a few minutes you are ready to run the sample. Click “Perform” to start the CV experiment.

The effect of the scan rate (v) on the voltammogram is observed by using the same solution, the 10 mM $K_4Fe(CN)_6$ in 50 mM KCl, and recording CVs at the following rates: 0.02, 0.05, 0.075, 0.1, 0.125, 0.15, 0.175, and 0.2 V/s. Between each scan the initial conditions at the working electrode are restored by moving the working electrode up and down without actually removing it from the solution.

Finally, the effect of the concentration of the electroactive species is investigated by using the 5 mM $K_4Fe(CN)_6$ in 50 mM KCl. Clean the cell and refill with the new solution. Follow the same procedure as above to obtain the CV of the $Fe^{III}(CN)_6^{3-}/Fe^{II}(CN)_6^{4-}$ couple using the same parameters as before. For this solution, you will need to obtain only one voltammogram using a scan rate of 0.1 V/s.

When the scans are finished (each segment is half of a full scan and corresponds to either the anodic or cathodic process), calculate the peak height of the anodic and cathodic processes, and label the potential at the maximum point for each (see sections 4 and 5 for procedures on how to do this). Using the printer icon, print the image of each voltammogram including the peak height and potential data, and be sure to label each voltammogram accordingly.

4. Calculating Peak Height

On the Archives panel (left), pick the experiment you want to analyze. Click “voltammogram” to see the data. Follow the steps below to label the peak height for both the anodic and cathodic curves of the voltammograms:

- a) Right click the curve to select all the points.
- b) Click “Select Points” to bring up the “Trace point selection” dialogue box.
- c) Check off the last segment on the list (should be segment 6) and press “okay”.
- d) Right click on the selected points, select “Add Tool”, then click “Peak Height”.
- e) Move the pink dots (gathered at the pointed edge of the voltammogram) to create a straight baseline, following the example of the baselines in Figure 1 on page 2 of this handout. The green dot indicates the point of maximum current for that process.
- f) Repeat steps a-e for the second-to-last segment of the voltammogram.

5. Labeling the Potential of the Anodic and Cathodic Processes

Repeat steps a-c in section 4. Right click on the selected points, select “Add Tool”, and then click “Crosshair”. Drag the green dot to the same position as the green dot from the Peak Height calculation. Move the text box to a location where it is easy to see the points.

Analysis/Discussion

1. Determine the formal reduction potential, $E^{\circ'}$ and n for the $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}/\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ couple in 50 mM KCl from one of the cyclic voltammograms on Pt electrode. Identify the cathodic (reduction) and anodic (oxidation) processes in the curves. Compare your value with one reported in the literature.
2. Determine the effect of the scan rate on peak height by calculating i_{pc} and i_{pa} for the various scan rates and discuss the results. Plot i_{pc} and i_{pa} vs. $v^{1/2}$.
3. Determine the effect of the scan rate on ΔE_{p} by plotting ΔE_{p} vs. v . Explain what causes ΔE_{p} to increase.
4. Determine the effect of concentration by plotting i_{pa} and i_{pc} vs. concentration of $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$.
5. Using Randles–Sevcik equation calculate the diffusion coefficient for the Fe(III).

References:

1. Kolthoff, I. M.; Tomsicek, Wm. J., *Journal of Physical Chemistry* (1935), *39*, 945–54.
2. D. H. Evans, *Acct. Chem. Res.*, (1977), *10*, 313.
3. **Principles of Instrumental Analysis** by Douglas Skoog, 5th ed. Saunders, Philadelphia (1998), Chapter 25, and **Electrochemical Methods: Fundamentals and Applications**, by Allen J. Bard, 2nd ed. John Wiley & Sons, New York (2001), Chapter 6, for further details on Voltammetry.