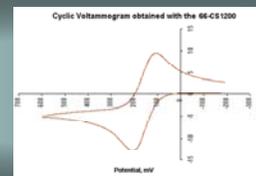


Experiments in Analytical Electrochemistry



1. Cyclic Voltammetry At Solid Electrodes

PURPOSE: To learn the basics of cyclic voltammetry with a well-behaved eChem system

BACKGROUND: Cyclic voltammetry (CV) is popular for its relative simplicity and its high information content. It is used most often as a diagnostic tool for elucidating electrode mechanisms. Although it was first practiced at a hanging mercury drop electrode [ref. 1], it gained widespread use when solid electrodes like Pt, Au and carbonaceous electrodes were used, particularly to study anodic oxidations [ref. 2]. A major advance was made when mechanistic diagnostics and accompanying quantitations became known through the computer simulations in publications of Nicholson and Shain [ref. 3] and Feldberg [ref. 4]. Several monographs [refs. 5, 6] and texts [refs. 7, 8] provide excellent descriptive materials on fundamentals of CV. Example websites with content that complements this CV experiment are <http://poohbah.cem.msu.edu/courses/cem419/>, www.bioanalytical.com/mcns/EC_epsilon/Techniques/cycvolt.cv.html and <http://poohbah.cem.msu.edu/courses/cem419/>. Figures 1-6 in this latter site show diffusional profiles and analyses of cyclic voltammograms.

In this experiment, the basics of CV will be illustrated by looking at the one electron reduction of ferricyanide to ferrocyanide. This redox couple exhibits nearly a reversible electrode reaction without any complications of proceeding or post chemical reactions. Thus, ferricyanide/ferrocyanide couple has been a popular choice through the years to use as a standard to demonstrate CV, as evidence by experiments described in several of the references listed herein.

There are not many such ideal electrode reactions. For example, the oxidation of ferrocene to ferricinium ion is a fast reversible electron transfer reaction at most electrodes. However, ferrocene is water insoluble necessitating the use of a non-aqueous solvent like acetonitrile. On the other hand, ferrocene carboxylic acid (FCA) and ferrocene acetic acid (FAA) are water soluble and undergo a facile one-electron oxidation to the ferricinium state. An optional experiment with FCA is proposed at the end of the main experiment.

The usual laboratory safety practices apply in the conduct of this experiment. Consult with the laboratory supervisor about proper use of chemicals and instrument.

THEORY: The waveform of the voltage applied to a working electrode in CV is triangular shaped (i.e., the forward and reverse scan). Since this voltage varies linearly with time, the scan rate is the slope (V/s). An example of a CV for the reduction of ferricyanide to ferrocyanide is shown in Figure 1. The experiment conditions are listed in the figure caption. The peak shape of the reductive and reverse oxidative current vs. electrode potential curve (I-E) in Figure 1 is typical of an electrode reaction in which the rate is governed by diffusion of the electroactive species to a planar electrode surface. That is,

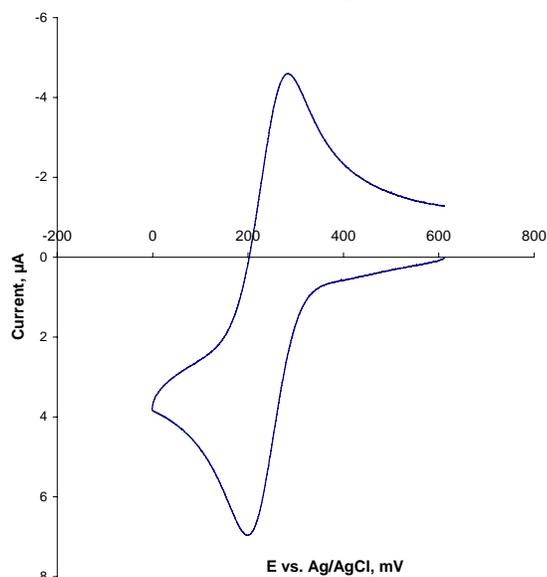


Figure 1. CV for the reduction of 4.8 mM ferricyanide in 0.1 M KCl at a 1.0 mm glassy carbon electrode. Scan rate is 100 mV/s.

the rate of the electron transfer step is fast compared to the rate at which ferricyanide is transported (diffuses) from the bulk solution to the electrode surface due to a concentration gradient, as ferricyanide is reduced to ferrocyanide. In such a case the peak current, I_p , is governed by the Randle-Sevcik relationship

$$I_p = k n^{3/2} A D^{1/2} C^b v^{1/2} \quad (1)$$

where the constant $k = 2.72 \times 10^5$; n is the number of moles of electrons transferred per mole of electroactive species (e.g., ferricyanide); A is the area of the electrode in cm^2 ; D is the diffusion coefficient in cm^2/s ; C^b is the solution concentration in mole/L; and v is the scan rate of the potential in volt/s.

The I_p is linearly proportional to the bulk concentration, C^b , of the electroactive species, and the square root of the scan rate, $v^{1/2}$. Thus, an important diagnostic is a plot of the I_p vs. $v^{1/2}$. If the plot is linear, it is reasonably safe to say that the electrode reaction is controlled by diffusion, which is the mass transport rate of the electroactive species to the surface of the electrode across a concentration gradient. The thickness, δ , of the "diffusion" layer can be approximated by $\delta \sim [D t]^{1/2}$, where D is the diffusion coefficient and t is time in seconds. A quiet (i.e. unstirred solution) is required. The presence of supporting electrolyte, such as KNO_3 in this example, is required to prevent charged electroactive species from migrating in the electric field gradient.

Another important diagnostic for characterizing the electrode reaction is the value of the peak potential, E_p . When the rate of electron transfer is fast, the E_p value will be independent of the scan rate; indicating a reversible electrode reaction. Then the difference between the anodic peak potential, E_{pa} , and the cathodic, E_{pc} value will be equal to 57 mV/n. The thermodynamically reversible potential, E^0 , is found at $E_{0.85}$. That is, 85% of the way-up the I-E wave to E_p . This value should also be independent of the scan rate. There are a few issues to consider -

To compare your $E_{0.85}$ value with values listed in books, it must be corrected since you used an Ag/AgCl reference electrode rather than the Normal Hydrogen Electrode (NHE) that was used when the Standard Values of Electrode Potentials, E^0 , were defined from the Nernst expression.

Also the measured electrode potential must be corrected if there is a significant solution resistance (ohmic) between the working and reference electrode. The measured potential then contains an additional component, $E(\text{ohmic}) = iR$. It is best to minimize the possibility of such iR by use of a high background electrolyte concentration (ions that carry the current in the solution) and/or by placing the tip of the reference electrode close to (but not touching) the surface of the working electrode.

The electrode reaction during the scan from +600 mV to 0.0 mV is



The electrode potential, E , is thermodynamically determined by the Nernst relationship

$$E = E^0 + (0.0591/n) \log (a_{\text{ox}}/a_{\text{R}}) \quad (3)$$

where a_{ox} is the activity of the oxidized species, ferricyanide in the present case, and a_{R} is the activity of the reduced species, ferrocyanide. Experimentally, the activity is affected by the presence of other ions. For practicality, we therefore define a "formal potential" that uses concentration in mole/L rather than activity, which we do not know. The Nernst becomes

$$E = E^{\circ} + (0.0591/n) \log [C_{\text{ox}}/C_{\text{R}}] \quad (4)$$

The “formal” potential, E° , depends on the nature of electrolytes in the solution as seen in this list of Formal Potentials for ferri/ferrocyanide in aqueous solutions at 25°C vs. NHE:

$\text{Fe}(\text{CN})_6^{3-} + e^- = \text{Fe}(\text{CN})_6^{4-}$	<u>E° values</u>
	0.1 M HCl 0.56 V
	1.0 M HCl 0.71 V
	1.0 M HClO ₄ 0.72 V

The potential, E , at any point along the I-E wave should reflect the concentration of the ferricyanide and ferrocyanide at the electrode surface in the presence of whatever background electrolyte you are using.

Irreversibility is when the rate of electron transfer is sufficiently slow so that the potential no longer reflects the equilibrium activity of the redox couple at the electrode surface. In such a case, the E_p values will change as a function of the scan rate. The computer-controlled potentiostat has algorithms to evaluate the I_p and E_p values, calculate the area under the I-E curves (the integrated charge), and compute an estimated electron transfer rate constant. A unique feature of an electrochemical reaction is that a "reversible" electrode reaction at low scan rates can become "irreversible" at high scan rates. Why is this? [Click on “Concepts” on the home page for additional discussion of fundamentals.]

EXPERIMENT

Equipment

- Obtain instructions on the use of a 3-electrode potentiostat from your laboratory instructor.
- Electrochemical cell and electrodes
 - A 3 - 4 mm diameter (planar) glassy carbon or Pt working electrode
 - Pt auxiliary electrode
 - Ag/AgCl reference electrode
 - Small volume electrochemical cell
 - Polishing kit
- Volumetric flasks with ground glass stoppers and pipettes

Chemical Solutions

- A. 100 ml of 1.0 M KNO₃
- B. 100 ml stock solution of 10 mM potassium ferricyanide [K₃Fe(CN)₆] in 0.1 M potassium nitrate [KNO₃]
- C. An unknown concentration of potassium ferricyanide solution provided by instructor (optional).

Procedure

1. Polishing: Prepare the working glassy carbon electrode by first lightly polishing the electrode surface with 1 μm or smaller particles of alumina (wet) on a flat polishing plate. Wash the electrode carefully with pure water to remove any alumina. If a sonicator is available, fill a small beaker with pure water, place the electrode (tip down) and sonicate for 1 minute. Remove, rinse with pure water and touch the edges of the tip with Kimwipe or clean tissue paper but do not touch the electrode surface.
2. Prepare 1, 2, 5 and 8 mM ferricyanide in 0.1 M KNO₃ in 50 ml volumetric flasks.
3. To run background scan, insert the electrodes (GC, reference Ag/AgCl and Pt auxiliary) and fill the cell with 0.1 M KNO₃ until the ends of the electrodes are immersed. Add stirring bar and turn ON the magnetic stirrer to stir the solution so that there is homogeneity of concentration from the surface of the electrode to the bulk solution. After the stirrer is turned OFF, if any tiny gas

bubbles should be adhering to the bottom of the electrodes, lightly tap the electrode to dislodge them. If a stirrer is not used, wait ~ 2 minutes before each scan to allow equilibration of the bulk concentration with that at the electrode surface.

4. Run a CV scan from an initial potential (E_i) of + 600 mV to 0.0 mV and then back to + 600 mV at a scan rate of 100 mV/s. Repeat the scan after stirring the solution for 10-15 seconds and allowing the solution to quiet. The two voltammograms should match each other within 2-3 %. If not, re-polish the GC electrode and rerun.
5. Run duplicate CVs on each ferricyanide solution (1, 2, 8 and 10 mM) at the scan rate of 100 mV/s.
6. Run duplicate CVs on the 2 mM ferricyanide solution at scan rates of 20, 50, 200 and 500 mV/s.
7. Label and save each CV with the “save function” if using a computerized potentiostat or print out a hardcopy of what you want to save.

REPORT (Data Analysis and Discussion):

Consult with your laboratory instructor about the content and format of your report for this experiment. The following are suggestions and considerations regarding the content.

Note: With computerized potentiostats you may be able to use Math function to determine E_p and I_p values. Similarly, the I_p values can often be corrected for the background charging current.

1. Write a short summary of what you did in this experiment, noting any deviations or substitutions in the procedure. Show example cyclic voltammograms.
2. Plot I_p vs. concentration of ferricyanide. It should be linear (background corrected?). Determine the concentration of the unknown sample of ferricyanide from this calibration plot.
3. Determine the $E^{o'}$ value from the voltammograms. If the values vary with the scan rate, plot them versus the scan rate and extrapolate to obtain the $E^{o'}$ at zero scan rate. Compare this value with the tabulated formal potential of ferri/ferrocyanide in 0.1 M HCl.
4. Tabulate the difference between E_{pc} and E_{pa} values – are they close to the theoretical value for a reversible electrode reaction? If not, can you account for the deviation?
5. Plot I_{pa} and I_{pc} vs. $v^{1/2}$, and from the slope, determine the value of the diffusion coefficient (must measure the electrode area). How does your value compare to the literature one of $0.62 \times 10^{-5} \text{ cm}^2/\text{s}$? Should there be a difference in the diffusion coefficient between ferricyanide and ferrocyanide? If so, why?
6. The $I_{pc}/I_{pa} = 1$ for a diffusion controlled reversible electrode reaction. [Note: the baseline needs to be extrapolated by drawing the best straight line so that the I_{pc} and I_{pa} can be corrected for the background solution] Do you get unity for this ratio from your CV experiments?
7. There is a current decrease at ~ 100 mV past I_{pc} or I_{pa} due to the concentration of the species being electrolyzed going to zero at the electrode surface. This condition is similar to that found in chronoamperometry where the rate is diffusion controlled. Under such a condition, the current decreases as a function of $1/[t]^{1/2}$. Do a plot of I vs. $t^{1/2}$, starting at ~ 60 mV past E_p and see if you get a linear plot. Does the same condition apply also to the anodic wave?

8. Calculate δ at I_p of a CV at a scan rate of 100 mV/s, assuming $t = 0$ occurs at the start of the rising portion of the CV wave. This value of δ is only a rough approximation but will give you a "feel" for dimensions of the diffusion layer thickness.

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OPTIONAL EXPERIMENTS:

1. Run CV of ferricyanide with a Pt working electrode in place of glassy carbon. Oxygen is reduced more readily at Pt than GC so the scan should not go below 0.0 V. Which electrode gave results closest to what is expected for a reversible electrode reaction? How close to the theoretical value of I_p did you get for the reduction of ferricyanide?
2. Run CVs of ferrocene carboxylic acid (FCA, concentration at 3–5 mM) in pH 7 buffer containing 0.1M KNO_3 . FCA is water soluble as the carboxylate ion. It undergoes a nearly ideal one-electron transfer reaction without any complications. The E_p separation between the E_{pa} and E_{pc} should be close to the theoretical value. Do scan rate studies and tabulate E_{pa} , E_{pc} , $(E_{pa} + E_{pc})/2$, and the I_{pa} and I_{pc} (corrected for baseline) in your report. Comment on FCA's electron transfer reversibility compared to ferri/ferrocyanide.

The F.W. of FCA is 230.04. It can be purchased in small quantities from Sigma Aldrich chemicals. Please read the manufacturers label about care in handling.

An example CV for the oxidation of FCA at a GC electrode is shown in Figure 2.

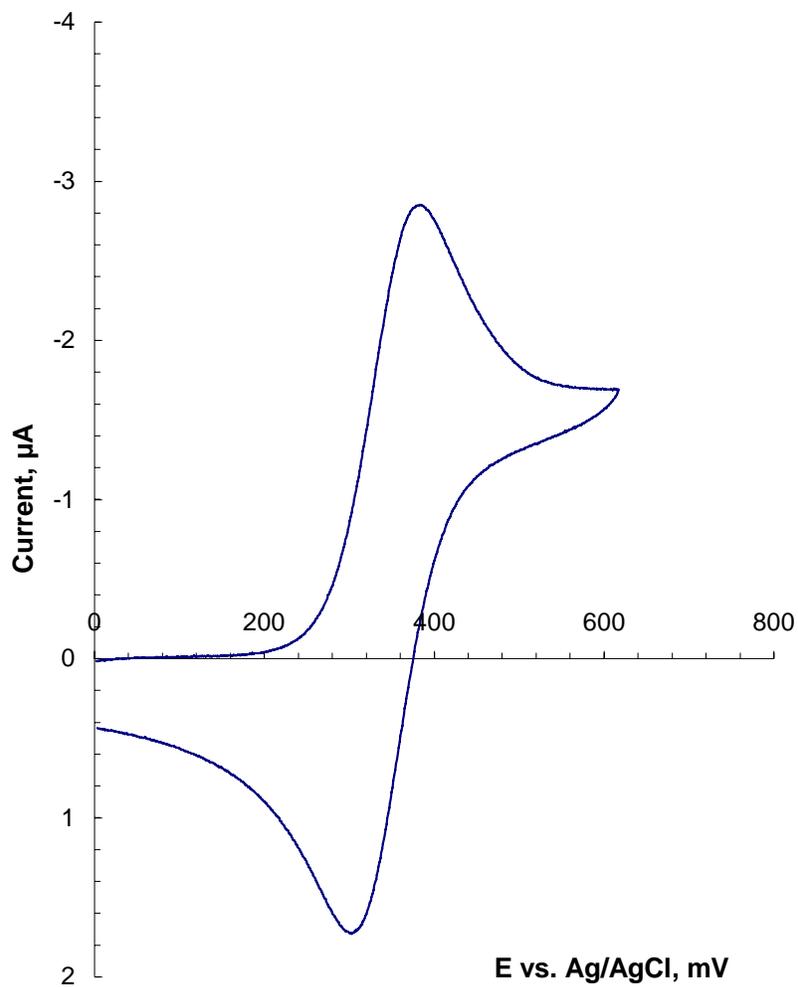


Figure 2. CV for the oxidation of 2 mM ferrocene carboxylic acid at pH 7. Scan rate is 100 mV/s