

EXPERIMENT 5. CYCLIC VOLTAMMETRY

Objectives

1. To determine the capacitance of electrochemical interfaces.
2. To determine the formal potential and diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-}$.
3. To use cyclic voltammetry to understand the electrochemistry of $\text{Co}(\text{NH}_3)_6^{3+}$.
4. To investigate the effects of electrode contamination on cyclic voltammetry.

Introduction

Electrode Reactions and Electrode Capacitance

Figure 1 describes the process that occurs in simple electrode reactions. In the case of reduction, a species (O) capable of receiving an electron from the electrode diffuses to the surface, receives an electron and diffuses away from the surface. Current at the surface is generated by the transfer of electrons from the electrode to the redox species. In solution current is carried by migration of ions. You already studied this in your measurements of conductivity.

One can ask whether a current can occur if there is no species in the solution that can transfer electrons to the surface at the potential of interest. The answer is that a transient current can flow because the electrode-solution interface will behave as a capacitor. As the potential of the electrode is varied, ions move to the surface to form a double-layer as show in Figure 2.

Although strictly speaking an electrode-solution interface in the absence of a redox couple is not a pure parallel-plate capacitor, it behaves rather like one and a parallel-plate capacitor model is often adequate to describe electrochemical systems. Use of this model allows us to learn about the behavior of electrodes in the absence of a redox couple.

For a simple parallel plate capacitor, charge on the capacitor, Q , is proportional to the voltage drop across the capacitor, E :

$$Q = CE \quad (1)$$

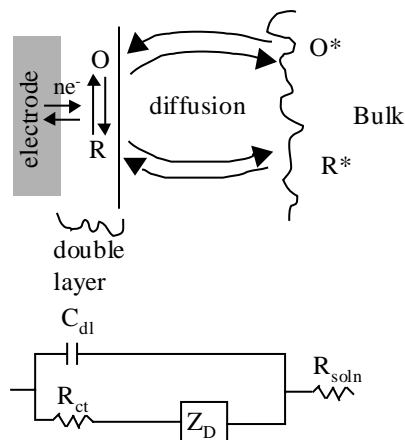


Figure 1. Electrochemical system that includes electron transfer along with its equivalent circuit.

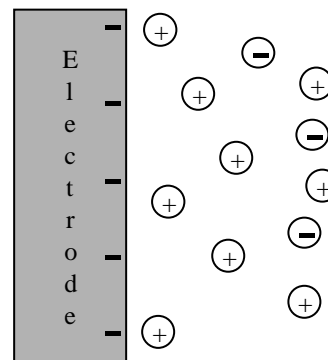


Figure 2. Schematic diagram of an electrical double layer.

The proportionality constant C is the capacitance of the medium. The simplest description of electrochemical capacitance is the Helmholtz model given by:

$$\frac{C}{A} = \frac{\epsilon\epsilon_0}{l} \quad (2)$$

where ϵ is the dielectric constant of the material separating the parallel plates, ϵ_0 is the permittivity of free space, l is the separation between the plates, and A is the area of the electrode. This model does not adequately describe all electrochemical interfaces as the capacitance can depend on both potential and the supporting electrolyte. Still it is a helpful construct.

Capacitance is a crucial factor in electrochemical experiments because it gives rise to current during the charging of the capacitor. Rather logically (and without imagination), we term this charging current. To calculate the magnitude of this current, we differentiate equation (1) with respect to t and assume that capacitance is constant:

$$\frac{dQ}{dt} = C \frac{dE}{dt} \quad (3)$$

Recognizing that dQ/dt is an expression for current and dE/dt is the potential scan rate v , we obtain:

$$i = Cv \quad (4)$$

From this very simple derivation, we have an expression for the charging current at steady state when applying a ramping voltage. Thus by measuring the charging current at a given scan rate, you can determine the capacitance of the system. If there is no possibility for electron transfer between the solution and the electrode (we don't add a redox couple) this is the only current that we will observe.

Let's now consider the very simple cyclic voltammetry (no active redox couple present) experiment shown in Figure 3. We apply the potential form shown in the figure. Initially, we have a sharp rise in current because of a sharp change in the scan rate v . The current then reaches steady state as we are constantly varying the voltage. At reversal of the scan rate, the current

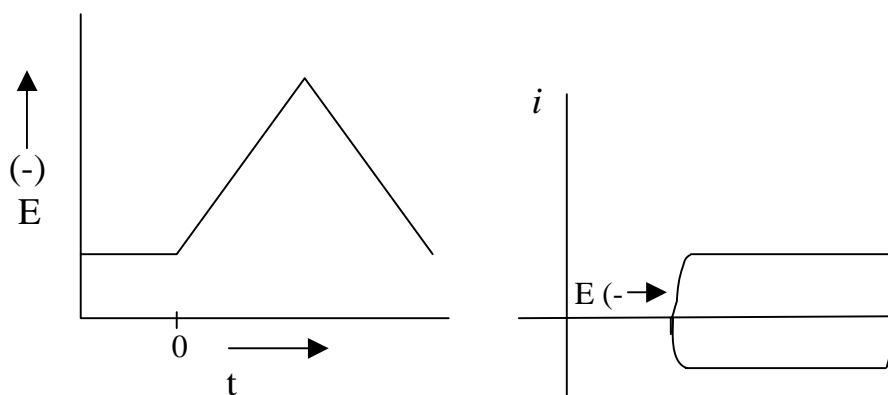


Figure 3. Schematic explanation of a cyclic voltammetry experiment in the absence of a redox couple.

changes sign, and when we stop scanning, current goes to zero.

In the first part of this laboratory, you will run a CV without a redox couple and determine the capacitance of the electrode. Typically values of C/A are about $20 \mu\text{F}/\text{cm}^2$. From the value of the capacitance, you can estimate the value of the dielectric constant. You can assume a separation of about 3 \AA between the electrode and electrostatically bound ions. A reasonable value for dielectric constants of organic compounds is 2-3. The dielectric constant of water is about 80. Double layer dielectric constants are generally not the same as that of water because the first few layers of water on a surface do not behave as bulk water.

We will also try to vary the distance between the ions and the surface by depositing an ultrathin organic layer between the electrode and the solution. This should increase the separation between ions and the surface and hence decrease the capacitance. To do this, we will simply coat our electrode with a monolayer of octadecane thiol as shown in Figure 4. Normally such layers are about 25 \AA thick and have dielectric constants of around 3. Using this information and equation 3, you can compare theory with your experimentally determined capacitance values. (Your values of dielectric constant for these monolayers will likely be higher than 3 because the monolayers are defective.)

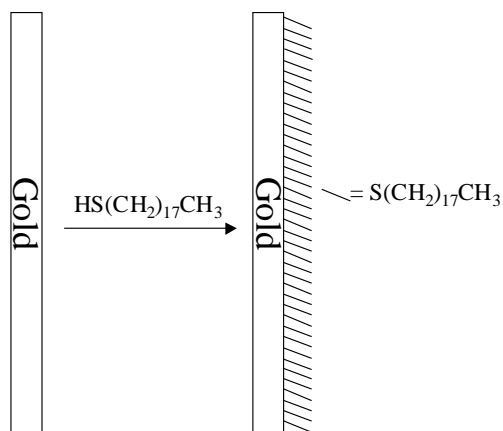


Figure 4. Synthesis of a self-assembled monolayer on gold.

Cyclic Voltammetry with an Active Redox Couple

Although you need to be aware of capacitive currents in cyclic voltammetry, the real power of this technique lies in its ability to investigate mechanisms and potentials of electrode reactions. Usually we use conditions where capacitive current is small compared to current from electron transfer (Faradaic current).

Faradaic current depends on two things: the kinetics of electron transfer and the rate at which the redox species diffuses to the surface. For the redox couple $\text{Fe}(\text{CN})_6^{3-/4-}$, the kinetics of electron transfer are reasonably fast, so we will assume at least for the moment that at the surface, the concentrations of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ can be described by the Nernst equation:

$$E = E^{0'} - 0.0592 \log \left(\frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{CN})_6^{4-}]} \right) \quad (5)$$

Where E is the applied potential and $E^{0'}$ is the formal electrode potential. You can see that as the applied potential becomes more negative the concentration of $\text{Fe}(\text{CN})_6^{3-}$ must decrease at the electrode surface. It is being reduced to $\text{Fe}(\text{CN})_6^{4-}$.

Even with the assumption of Nernstian behavior, faithful reproduction of the $\text{Fe}(\text{CN})_6^{3-/4-}$ voltammogram (Figure 6) requires an analytical solution to two differential equations. We don't have time in this course to discuss the numerical solutions for cyclic voltammetry, but we will attempt to give you a qualitative feel for cyclic voltammetry and introduce quantitative aspects

without proof. (The details of CV simulations can be found in *Anal. Chem.*, **1964**, 36, 706 and *Anal. Chem.* **1965**, 37, 1351.)

First we give the qualitative, pictorial explanation. If we assume that concentrations at the surface are governed by the Nernst equation, the concentration of the oxidized species at the surface will decrease as the potential becomes more negative. Assuming that the electron transfer rate is very rapid, the current i that is measured as the potential is decreased will be directly related to diffusion rate of oxidized species to the electrode surface:

$$i = nFAJ \quad (6)$$

where n is the number of electrons, F is Faraday's constant, A is the area of the electrode surface and J is the flux of the oxidized species to that surface. The flux is governed by Fick's law:

$$J = -D \left(\frac{dC}{dx} \right)_{x=0} \cong D \frac{(C^* - C_{x=0})}{\Delta x} \quad (7)$$

where, D is the diffusion coefficient of the species, x is the distance from the electrode surface, $(dC/dx)_{x=0}$ is the concentration gradient at the surface, C^* is the concentration of the oxidized species in the bulk solution, and $C_{x=0}$ is its concentration at the surface. As you can see, the greater the concentration gradient, the greater the flux J and therefore by equation (6), the greater the cathodic current.

The change in the concentration gradient for the cathodic portion of the cyclic

voltammogram is shown in Figure 5. Before a potential is applied to the electrode ($t=0$), there is no concentration gradient, and the solution has the uniform bulk concentration C^* . As the potential is applied, the concentration of the oxidized species is depleted at the surface. This lower concentration at the surface gives a higher concentration gradient (at least initially) so according to Fick's law of diffusion equation (7), we will have more flux to the surface and hence a higher cathodic current. As we continue to make the potential more negative, the concentration of the oxidized species at the surface will eventually go to zero.

Simultaneously, the volume in the solution that is depleted of the oxidized species will increase and the concentration gradient will begin to decrease. As the concentration gradient decreases, we will have less flux to the surface and current will begin to decrease. All of this will result in a current-voltage curve that looks like the forward scan in Figure 6.

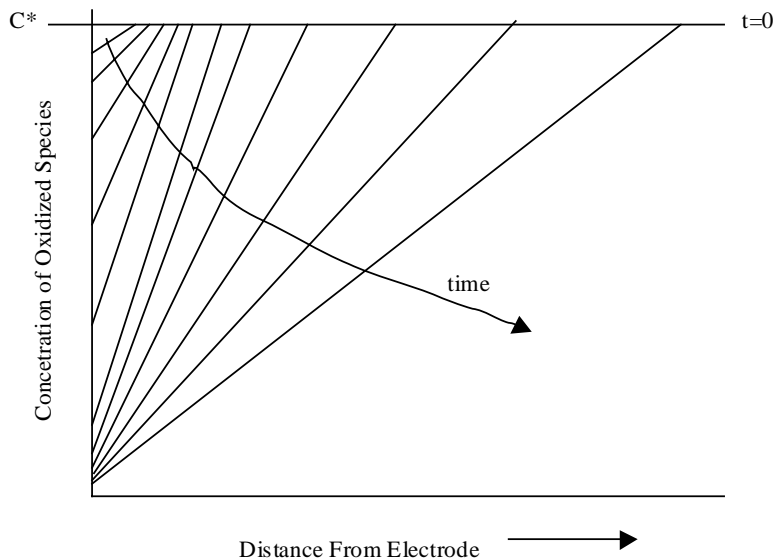


Figure 5. Crude concentration profiles at different time in a CV experiment (only the negative scan is shown). The equations are

As we reverse the voltage scan (not shown in Figure 5), we still have a layer depleted of the oxidized species, but the surface concentration begins to rise so current decreases further. Finally, we reach a region where anodic current begins to dominate (Figure 6). Then we begin to go through similar concentration profiles for the reduced species. We will achieve a peak negative current and then the current will decrease in magnitude as the depletion layer for the reduced species increases.

That was a very qualitative description of CV. Nicholson and Shain performed quantitative simulations of CV in 1964 and the field of electrochemistry changed in a major way. All reversible voltammograms look the same and the typical shape is that shown in Figure 6. The quantitative simulations show several things for a Nernstian system. The peak current in a cyclic voltammogram containing only one species is described by:

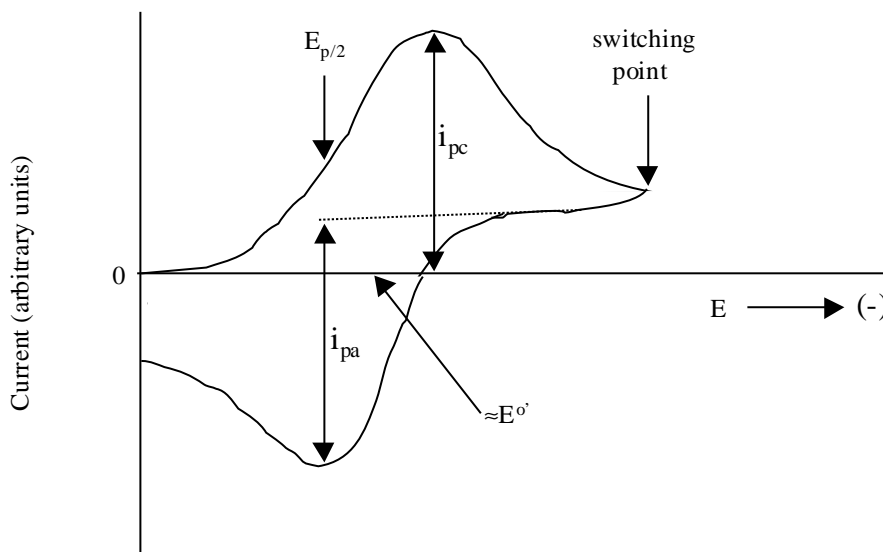


Figure 6. Shape of a cyclic voltammogram for a Nernstian electrochemical reaction.

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C^* \quad (8)$$

at 25 °C where i_p is the peak current, n is the number of electrons transferred, A is the electrode area, D is the diffusion coefficient of the species, ν is the scan rate and C^* is the bulk concentration of the species. The difference between E_p and the point where current is half that at E_p , $E_{p/2}$, is $56.5/n$ mV at 25 °C, where n is the number of electrons transferred. Note that for a Nernstian system, E_p should be independent of scan rate, but i_p will depend on the square root of scan rate. Another useful piece of information is that the separation of anodic and cathodic peaks is about $(59/n)$ mV at 25 °C. It is very difficult to achieve a $59/n$ mV splitting at most solid electrodes. (If you can achieve 70 mV, you will be doing well. This is a function of electrode preparation as well as scan rate.) If the diffusion constants for the oxidized and reduced species are similar, the value of E^o' can be estimated from the average of E_{pa} and E_{pc} , where E_{pa} is the potential of the anodic peak current and E_{pc} is the potential of the cathodic current. Thus, in your experiments you will use CV to estimate the value of E^o' for the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple. You will also use the peak current to estimate the diffusion coefficient for $\text{Fe}(\text{CN})_6^{3-}$. One other characteristic of a reversible system is that i_{pa} and i_{pc} are the same, but i_{pc} has to be determined as shown in Figure 6.

Completely Nernstian systems are difficult to find as electron transfer between an electrode and a redox-active molecule is often quite slow. You can make an electrode behave more like a Nernstian system by slowing down the scan rate. With less current flowing, the electron transfer rate has a better chance of being fast compared with diffusion.

However, as electrodes foul (or are coated with monolayers), systems become more sluggish and are apt to show some kinetic control. Nicholson and Shain have treated such cases as well as Nernstian cases, but this is beyond the scope of this class. We simply note that peak separation is a function of the rate constant for electron transfer, which decreases as redox couples are unable to reach the electrode surface. When you run a CV with your self-assembled monolayer, you should see a very different voltammogram. Using a self-assembled monolayer, we will attempt to show the critical role that electrode cleanliness plays in these reactions. You will compare the peak splitting with and without a monolayer of octadecanethiol on the electrode surface.

Study of Reactions Mechanisms Using Cyclic Voltammetry

The last aspect of CV that we will discuss is its ability to provide information about the chemistry of redox couples. This is perhaps the most attractive feature of this technique. For example, if a redox couple undergoes two sequential electron-transfer reactions, you will see two peaks in the voltammogram. If either the reduced or oxidized species is unstable, you might see a voltammogram such as that shown in Figure 7. Such qualitative information is very useful.

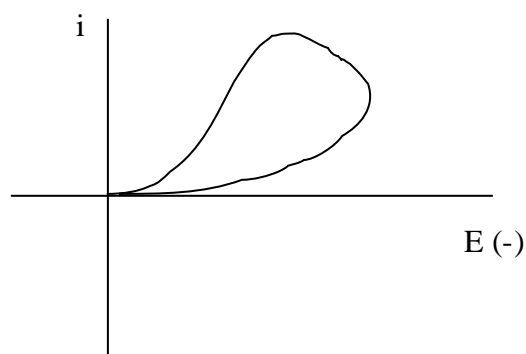


Figure 7. Cyclic voltammogram of a system where the reduced species is unstable.

Procedure

1. The first step is cleaning of the electrode in an effort to ensure that we will have good electron transfer. Place the gold electrode, the Ag/AgCl reference electrode, and the platinum wire counter electrode in a solution of 0.1 M HClO₄. (Make sure that you connect the reference electrode to the white clip, working to green, and counter to red.)
2. Cycle the electrode between 0.2 and 1.5 V for 10 minutes at 20 mV/sec. (Select these parameters in the cyclic voltammetry technique and simply put in a ridiculously large number of scans.) Stop the cyclic voltammograms after ten minutes. Steps 1 and 2 should give you a clean electrode.
3. First, run a voltammogram in 1 M Na₂SO₄, 0.005 M Fe(CN)₆³⁻. Make sure that you rinse electrodes very well between experiments. Run the CV from 0.5 to -0.1 V. Do the CV at three different scan rates to see how peak currents and peak splitting vary with scan rate. Use 0.5 V/sec, 0.1 V/sec, and 0.01 V/sec.
4. Next run the voltammogram in 1 M Na₂SO₄ without adding Fe(CN)₆³⁻. Run this voltammogram from 0.35 V to 0.00 V so that you are in regions where there is minimal Faradaic current. Run the CV's at 0.5 V/sec, 0.1 V/sec, and 0.01 V/sec. Note how capacitive current varies with scan rate.
5. To see an irreversible CV, run a cyclic voltammogram in 1 M Na₂SO₄, 0.005 M Co(NH₃)₆³⁺. Note the unusual shape of this voltammogram. Run the scan at 0.1 V/sec from 0.1 to -0.5 V vs Ag/AgCl. You don't need to vary the scan rate.
6. Rinse the electrode thoroughly and immerse it in 0.001 M octadecanethiol in EtOH for 30 minutes. Remove the electrode from the solution and rinse it thoroughly.
7. Make a plot of cathodic peak current versus the square root of scan rate for the voltammograms of Fe(CN)₆³⁻ at a clean gold electrode. Do you obtain the relationship between i_p and v that you expected?
8. Repeat step 4 with the monolayer-coated electrode.
9. Repeat step 3 with the monolayer-coated electrode.

CYCLIC VOLTAMMETRY REPORT

- (1) Write an introductory paragraph including the objectives of this experiment.
- (2) Determine the diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-}$ from your cyclic voltammograms at clean gold electrodes. Do this for the three different scan rates. What assumptions are you making when you do this calculation? Do the CV's justify this assumption? Why wouldn't you do this calculation at a monolayer-coated electrode. Which one of the scan rates would you expect to give you the most accurate value of the diffusion coefficient?
- (3) Approximate the formal potential of $\text{Fe}(\text{CN})_6^{3-}$ from its CV at bare gold. Convert this value to versus NHE and compare it with literature values.
- (4) Using the voltammograms in just Na_2SO_4 , calculate the capacitance/area of the bare gold system. Does the capacitance vary with scan rate? The diameter of the electrode is 3 mm.
- (5) From your capacitance, determine the dielectric constant at the interface. Assume a parallel plate capacitor with a separation between the plates of 3 Å.
- (6) Determine the capacitance/area of the electrode coated with the self-assembled monolayer. Determine a dielectric constant for the monolayer assuming that it is 25 Å thick. Does this value of dielectric constant seem reasonable?
- (7) Why does hexaamine(cobalt(III)) have an irreversible CV? You may need to consult an inorganic textbook to study the relative lability of cobalt(III) and cobalt(II) complexes.
- (8) Explain why the monolayer changed the CV of $\text{Fe}(\text{CN})_6^{3-}$.
- (9) Write a short paragraph stating your conclusions from this lab.