Cyclic Voltammetry

Goals

The goals of this experiment are to:

- Learn how to set up a screen-printed electrode
- Learn how to operate the Gamry potentiostat
- Determine the redox potential of potassium ferricyanide
- Calculate the diffusion coefficient of potassium ferricyanide

Experimental Apparatus

- Gamry Instruments Interface 1000T
- Gamry Instruments Framework™ software package installed on a host computer
- Screen-printed electrode (SPE) cell stand (Gamry part number 990-00420)
- Platinum working screen-printed electrode (Gamry part number 935-00122)

Reagents and Chemicals

- 0.1 *M* potassium chloride, pre-purged to remove dissolved O_2
- 2 m*M* potassium ferricyanide in 0.1 *M* potassium chloride, pre-purged to remove dissolved O_2

The laboratory instructor has already purged the solutions of dissolved O_2. Purging the dissolved O_2 from these solutions prevents spurious peaks from appearing in your data.

CAUTION:

Cyanide-containing compounds can hydrolyze to form hydrogen cyanide gas, which is highly poisonous. Never pour potassium ferricyanide down the drain!

Background

Cyclic voltammetry is the most commonly used electroanalytical technique for obtaining rapid quantitative data about an electrochemical reaction. The importance of cyclic voltammetry is that it provides a quick result concerning the kinetics of a heterogeneous electron-transfer, diffusion coefficients, and thermodynamic information for a process. Cyclic voltammetry also can give data on subsequent chemical reactions or adsorption processes.

Cyclic voltammetry is usually the first experiment performed on an electroactive analyte because of its ability to provide the redox potential of that analyte. This technique also allows fast evaluation of the effect that a particular matrix may have on a redox process.

During a typical cyclic voltammetry experiment, a component of the solution is electrolyzed (oxidized or reduced) by placing the solution in contact with an electrode, and then applying a potential to that electrode that is sufficiently positive or negative with respect to a reference half-cell (e.g., calomel or Ag|AgCl). The electrode's voltage is adjusted higher or lower linearly, and finally, the voltage is returned to the original value at the same linear rate.

When the electrode becomes sufficiently negative or positive, a species in solution may gain electrons from the electrode's surface, or transfer electrons to that surface. As the potential is swept back and forth past the formal potential, $E°$, of an analyte, a current flows through the electrode that either oxidizes or reduces the analyte. Electron-transfer is a measurable current in the electrode's circuitry. The magnitude of this current is proportional to the concentration of the analyte in solution, which allows cyclic voltammetry to be used in an analytical determination of concentration.

The result is a **cyclic voltammogram** (or CV), in the form of a cycle between current and potential, where potential is plotted on the x-axis, and current is plotted on the y-axis.

Figure 1.1 shows a generic cyclic voltammogram. The potential is graphed along the x-axis with more positive (or oxidizing) potentials plotted to the right, and more

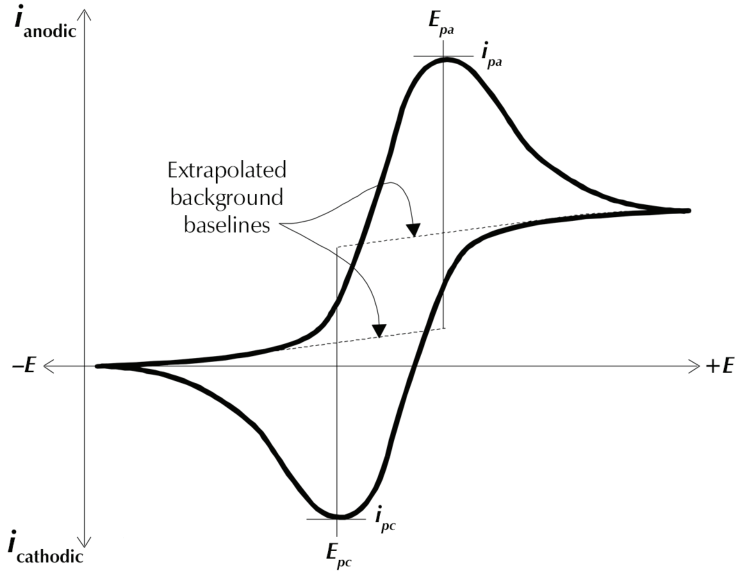


Figure 1.1. A generic CV. A CV plot reveals the reversibility of the redox couple. (Adapted from P. T. Kissinger and W. R. Heineman, *Laboratory Techniques in Electroanalytical Chemistry*, New York: Marcel Dekker, Inc., 1984, p. 88.)

negative (or reducing) potentials to the left. The current is graphed on the *y*-axis of the voltammogram, with cathodic (i.e., reducing) currents plotted in the negative direction, and anodic (i.e., oxidizing) currents plotted in the positive direction.

The peaks in a voltammogram look something like those in a spectrum or chromatogram. Each peak denotes a particular electrolytic process in the analytical solution, and the height of a peak is proportional to the concentration of that analyte. The peaks in a cyclic voltammogram are asymmetrical, with the leading side steep and the trailing side showing a gradual fall-off. The peaks seen during the reverse scan have the same overall form as those in the forward sweep, but they are inverted because the current is flowing in the opposite direction.

The initial direction of the first sweep in a cyclic voltammetry experiment may be in either the positive (anodic) or negative (cathodic) direction, as determined by the characteristics of the analyte. For an oxidizable analyte, the first sweep starts in the positive direction, whereas for a reducible analyte, the first sweep begins in the negative direction.

Much quantitative information can be extracted from a high-quality cyclic voltammogram. First, the plot can serve as a test if a redox couple is actually electrochemically reversible. The peak potential for the anodic sweep, E_{pa}, and the peak potential for the cathodic peak, E_{pc}, can be read right from the voltammogram, and the difference between them, ΔE_{peak}, can be calculated. If the redox couple is reversible, then, based on the Nernst equation, $E = E° + 2.303\ (RT/nF)\ \log[\mathrm{Ox/Red}]$, the relationship between the ΔE_{peak} and the number of electrons involved in the redox couple is

$$n\, \Delta E_{peak} = 59\ \mathrm{mV} \tag{1.1}$$

where *n* is the number of electrons taking part in the redox couple.

In fact, for this particular experiment, ferricyanide ion undergoes a reversible one-electron transfer according to the following reaction:

$$\mathrm{Fe(CN)_6^{3-}}(aq) + \mathrm{e^-} \rightarrow \mathrm{Fe(CN)_6^{4-}}(aq) \tag{1.2}$$

The anodic peak current i_{pa} is equal to the cathodic peak current i_{pc}, so that the relationship,

$$\frac{i_{pc}}{i_{pa}} = 1 \tag{1.3}$$

also holds true. A ratio of the peak currents deviating from 1 is an indication of chemical or electrochemical irreversibly. If the ratio is <1 but a return peak is present, then the electrochemical reaction is said to be **pseudo-reversible**. The peak currents are not measured using the *x*-axis as a baseline. Rather, you must first extrapolate a background current baseline out to the peak potential (see Figure 1.1). Then, the peak current is measured vertically from the peak down to the extrapolated baseline.

The formal potential, $E°$, for a reversible redox couple is easily found as the average of the two peak potentials:

$$E^\circ = \frac{E_{pa} + E_{pc}}{2} \tag{1.4}$$

Quantitative information about concentration of the analyte can be determined from the voltammogram via the Randles-Ševićk equation (Eqn. 1.5). This equation calculates the peak current, i_p (either anodic or cathodic), in terms of the concentration C of the analyte.

$$i_p = 0.4463 nFAC\sqrt{\frac{nF\nu D}{RT}} \tag{1.5}$$

In this equation,

n is the number of electrons appearing in half-reaction for the redox pair,

v is the scan-rate for the potential sweep (V/s),

F is Faraday's constant (96 485 C/mol),

A is the electrode area (cm^2),

R is the gas constant (8.314 J mol^{-1} K^{-1}),

T is the absolute temperature (K), and

D is the diffusion coefficient of the analyte(cm^2/s).

If we assume standard temperature (25°C, 298.15 K), the Randles-Ševićk equation can be written concisely as

$$i_p = 2.686 \times 10^5 n^{\frac{3}{2}} AC\sqrt{\upsilon}\sqrt{D} \tag{1.6}$$

where the constant has units of 2.686×10^5 C mol^{-1} $\text{V}^{-1/2}$.

The peak current is directly proportional to the concentration of the analyte. If the analyte concentration is known, then cyclic voltammetry can be used to find the analyte's diffusion coefficient. The diffusion coefficient shows how fast the analyte moves through the solution because of random collisions with other molecules.

Procedure

NOTE: Ensure that all glassware is as clean as possible. The solvents and reagents used to make solutions should be as pure as possible. We recommend that you use deionized, ultrafiltered (DIUF) water, "conductivity water," or "HPLC-grade water" for the final rinsing of glassware and to prepare all solutions.

Prepare the cell.

1. Connect the banana pins for the green (working), blue (working sense), white (reference), red (counter), and orange (counter sense) to the banana jacks indicated on the SPE cell stand. Leave the black (ground) pin unconnected.
2. Insert the screen-printed electrode horizontally into the connector on the SPE cell stand.

   The apparatus should be set up like that shown in Figure 1.2.

Screen-printed electrode

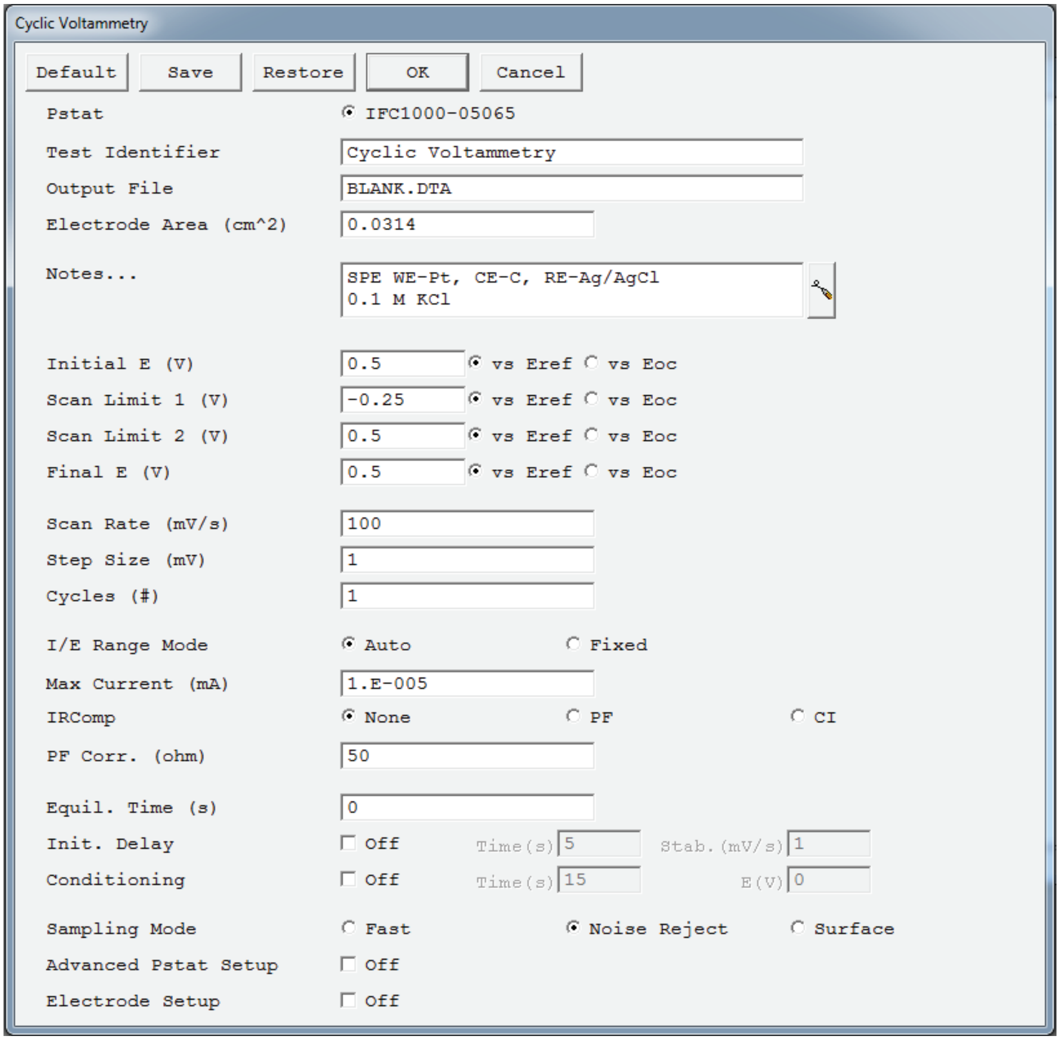
Figure 1.2. Left: Screen-printed electrode inserted into SPE cell stand. Right: Complete set-up.

NOTE: When you add a drop of reagent, you only need enough to completely cover all three electrodes on the face of the screen-printed electrode. More reagent is uncessary.

Perform a background scan.

1. Turn on the potentiostat, and, on the host computer's Windows® desktop, open the Gamry Framework™ software.
2. When the host computer detects the potentiostat, choose **Experiment** > **Physical Electrochemistry** > **Cyclic Voltammetry**. The **Cyclic Voltammetry** window opens.

3. Set the experimental fields in the **Cyclic Voltammetry** window to those shown in Figure 1.3, with the file name as **blank**.



Pstat	● IFC1000-05065		
Test Identifier	Cyclic Voltammetry		
Output File	BLANK.DTA		
Electrode Area (cm^2)	0.0314		
Notes...	SPE WE-Pt, CE-C, RE-Ag/AgCl 0.1 M KCl		
Initial E (V)	0.5	● vs Eref	○ vs Eoc
Scan Limit 1 (V)	-0.25	● vs Eref	○ vs Eoc
Scan Limit 2 (V)	0.5	● vs Eref	○ vs Eoc
Final E (V)	0.5	● vs Eref	○ vs Eoc
Scan Rate (mV/s)	100		
Step Size (mV)	1		
Cycles (#)	1		
I/E Range Mode	● Auto	○ Fixed	
Max Current (mA)	1.E-005		
IRComp	● None	○ PF	○ CI
PF Corr. (ohm)	50		
Equil. Time (s)	0		
Init. Delay	☐ Off	Time(s) 5	Stab.(mV/s) 1
Conditioning	☐ Off	Time(s) 15	E(V) 0
Sampling Mode	○ Fast	● Noise Reject	○ Surface
Advanced Pstat Setup	☐ Off		
Electrode Setup	☐ Off		

Figure 1.3. Cyclic Voltammetry window, with fields set to run a blank.

4. Place a drop of the blank solution, 0.1 *M* KCl, onto the electrodes of the SPE. (See Fig. 1.4.)

5. Click the **OK** button to run the experiment.

Perform scans using sample solution.

1. Rinse the SPE with de-ionized water into a waste container. Then dab the SPE with a laboratory wiper to remove the rinsing solution.

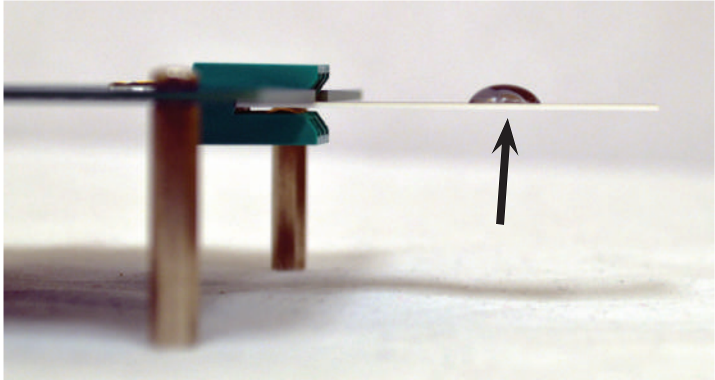


Figure 1.4. Single drop of fluid on the SPE's electrodes.

NOTE: Do not get water on the SPE board.

2. Place a drop of the 2 m*M* potassium ferricyanide in 0.1 *M* potassium chloride solution onto the screen-printed electrode (Fig. 1.4).
3. In the experimental window, change the file name to **FeCN6 10mVs-1.dta**.
4. Run the experiment.
5. Redo steps 1 through 4, changing the scan rate to 20 mV/s and the file name to **FeCN6 20mVs-1.dta**.
6. Redo steps 1 through 4, this time changing the scan rate to 30 mV/s, then 40, 50, 60, 70, 80, 90, and 100 mV/s, simultaneously adjusting the file name appropriately.
7. Remove the screen-printed electrode from the connector, and discard it in the waste can.
8. Discard the analyte solution into the appropriate waste container (NEVER DOWN THE DRAIN!).

Reference

J.J. van Benschoten, J.Y. Lewis, W.R. Heineman, D.A. Roston, and P.T. Kissinger, *J. Chem. Ed.*, 1983, **60**(9), 772.

Data Analysis

Determine cathodic and anodic peak currents and voltages.

1. On the host computer's desktop, open Gamry Echem Analyst™ software.
2. Use Echem Analyst to determine the potential of cathodic and anodic peaks and cathodic and anodic peak currents.
   a. Open the CV file you want to evaluate.
   b. Using the mouse icon 🖱, select the region for the peak, and choose **Cyclic Voltammetry** > **Peak Find**, then choose **Cyclic Voltammetry** > **Automatic Baseline**. The **@ Vf (V vs. Ref)** is the potential, and the **Height (A)** is the peak current.
   c. Repeat for both cathodic and anodic peaks.
   d. Fill in the appropriate column in the table below.
3. Repeat step 2 for all the other scan rates.

Scan Rate (mV/s)	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**
E_{pc} **(mV)**										
E_{pa} **(mV)**										
I_{pc} **(μA)**										
I_{pa} **(μA)**										

Print graphs.

1. Print a graph of the ten different scan-rates overlaid onto one plot.
   a. Open the **FeCN6 1000mVs-1.DTA** file.
   b. Choose **File** > **Overlay**.
   c. Select the other graphs to be overlaid.
   d. Print the complete plot.
   e. Include this plot in your laboratory report.
2. Using software designated by your laboratory instructor, create plots of i_{pc} versus scan rate$^{1/2}$, and i_{pa} versus scan rate$^{1/2}$.
3. Print these two plots.
4. Include these two plots in your laboratory report.

Calculate your results.

1. From your scan-rate data, calculate ΔE_p, $E_{1/2}$, and i_{pc}/i_{pa}, then fill in the table below with your results.

Scan Rate (mV/s)	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**
ΔE_p (mV)										
$E_{1/2}$ (mV)										
i_{pc}/i_{pa}										

2. From the plots of the i_p versus scan rate$^{1/2,}$ determine the slope of the best-fitting line.
   a. Slope of the graph i_{pc} versus scan rate$^{1/2}$ = ____________________
   b. Slope of the graph i_{pa} versus scan rate$^{1/2}$ = ____________________
3. Using the Randles-Ševćik equation and the slope from the graph of i_{pc} versus scan rate$^{1/2}$, calculate the diffusion coefficient for potassium ferricyanide.

▶ Questions

1. Based on the Randles-Ševćik equation, would you expect the peak current to increase or decrease as the temperature increases? Why?

2. The average distance that molecules move in solution is expressed by the formula

$$l = \sqrt{2Dt}$$

where

l is distance (cm),

D is diffusion coefficient (S·m^2/s), and

t is time (s).

Using your calculated diffusion coefficient, how long would it take for the analyte to diffuse 1 mm?

3. (*Bonus question*) Calculate the ratio of slopes i_{pc} and i_{pa}. Based on this number, is the reaction of ferricyanide reversible, pseudo-reversible, or non-reversible? Why?