Experiment 2

Cyclic Voltammetry Basics: Reduction of Ferricyanide

Cyclic voltammetry is an essential technique for a chemist. To use cyclic voltammetry effectively, you need to know how to assess a voltammogram and modify the operational settings to improve the quality of the data. Potential limits and sweep rate are two settings that are vital. In this experiment you will observe how changes in the settings alter the voltammogram. You will also explore fundamental aspects of a voltammogram, so you can glean information about the redox system from your data.

The redox couple you will use is ferrocyanide $[Fe(CN)_6]^{4-}$ and ferricyanide $[Fe(CN)_6]^{3-}$. You will use a cyclic voltammetry system to first scan the potential positively enough to oxidize ferrocyanide at the working electrode:

$$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$$

This results in an increase in the current to a peak, referred to as the anodic peak. At this point, the concentration of ferrocyanide at the electrode surface depletes and the current decays. The cyclic voltammetry system will then switch to scan the potential negatively, so that the ferricyanide that has been forming at the electrode surface will be reduced. The cathodic current will peak (referred to as the cathodic peak) and then decay as ferricyanide in the solution adjacent to the electrode is consumed.

In this experiment, you will explore how adjusting parameters of the Cyclic Voltammetry System affects your voltammogram. You will then use that information to obtain a desirable "duck" in your voltammogram.

OBJECTIVES

- Use an electrochemical technique called cyclic voltammetry.
- Explore how changes in the current, potential, and sweep rate affect a voltammogram.
- Generate a voltammogram for ferricyanide.

MATERIALS

One of the following
- Chromebook, computer, or mobile device with Vernier Instrumental Analysis app[1]
- LabQuest 2 (software is pre-installed; v2.8.7 or newer required)[2]
- LabQuest 3 (software is pre-installed; v3.0.6 or newer required)[2]

Go Direct Cyclic Voltammetry System and stand
screen-printed electrode (SPE)
scintillation vial(s)
2.5 mM potassium ferricyanide in 0.1 M potassium nitrate
0.1 M potassium nitrate
goggles and gloves

PROCEDURE

Part I Voltammogram of ferricyanide solutions

1. Set up the Cyclic Voltammetry System by following the directions for your equipment:

   Instrumental Analysis

   a. Launch Instrumental Analysis.
   b. Connect the Go Direct Cyclic Voltammetry System (CVS) to your device via USB or Bluetooth wireless technology. If using Bluetooth, click or tap Connect an Instrument, connect to your CVS, and click or tap Done.
   c. Click or tap Voltammetry. Then, set the CV Profile settings to the values in Table 1.

   LabQuest

   a. Connect the Go Direct Cyclic Voltammetry System (CVS) to your device via USB or Bluetooth wireless technology. If using Bluetooth, tap the Sensors menu and choose Wireless Device Setup►Go Direct. Select your instrument and tap OK.
   b. Choose Data Collection from the Sensors menu.
   c. Set the CV Profile settings to the values in Table 1. Make sure the Voltammetry mode is set to Cyclic Voltammetry.

Table 1	
Number of segments	3
Initial potential (mV)	0
Switching potential 1 (mV)	1200
Switching potential 2 (mV)	–600
Final potential (mV)	0
Sweep rate (mV/s)	100
Current range	High (±1000 μA)

[1] Instrumental Analysis v1.2 or newer required; download the most recent version for free at **www.vernier.com/ia**
[2] Download the most recent version of LabQuest software for free at **www.vernier.com/downloads**

2. Put on goggles and gloves.

3. Insert a screen-printed electrode (SPE) into the SPE connector on the Cyclic Voltammetry System (see Figure 1).

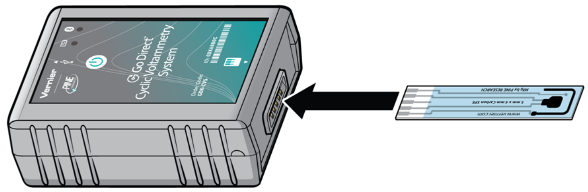

Figure 1

4. Obtain a background voltammogram.
   a. Fill the scintillation vial about halfway full (~10 mL) with your 0.1 M potassium nitrate solution. Insert the scintillation vial into the clip on the stand. Carefully guide the Cyclic Voltammetry System with SPE attached downward into the vial and snap the instrument into place, as shown in Figure 2. **Caution**: *Treat all laboratory chemicals with caution. Prudent laboratory practices should be observed*.

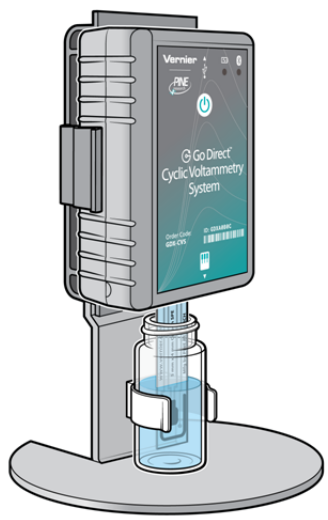

Figure 2

   b. Start data collection. When data collection is complete, examine the background cyclic voltammogram. The voltammogram should exhibit no significant peaks (other than random sub-microampere noise). The overall background current should be less than 500 nA. If significant peaks are apparent, then the buffer, the glassware, and/or the electrode surface are likely contaminated. Consult your instructor if excessive or unusual background current is observed.
   c. Name your sample appropriately.

5. Obtain a voltammogram of your ferricyanide solution.
   a. Carefully remove the Cyclic Voltammetry System from the holder by pulling back on the top tab. With the SPE still inserted, rinse the SPE with 0.1 M KNO_3 solution, and dry it by gently blotting the electrode surface with a piece of paper towel.
   Important: Do not invert the Cyclic Voltammetry System with a damp SPE attached. You want to avoid getting liquid inside the SPE connector.
   b. Discard the potassium nitrate solution from the scintillation vial. Fill it halfway full with the 2.5 mM ferricyanide solution. **Caution**: *Treat all laboratory chemicals with caution. Prudent laboratory practices should be observed*.
   c. Replace the vial in the holder. Replace the Cyclic Voltammetry System with the SPE attached in the holder.
   d. Start data collection. When data collection is complete, name your sample appropriately.
   e. In Table 5, record your observations of the voltammogram and sketch a drawing of voltage *vs*. time that adequately portrays the parameters set.

6. Adjust the current setting, and repeat the voltammogram of ferricyanide.
   a. To adjust the settings, follow the directions for your equipment:
      - Instrumental Analysis: Click or tap Voltammetry Settings, ⚙, and set the parameters to the values in Table 2. **Note**: Only the current range needs to be adjusted.
      - LabQuest: Choose Data Collection from the Sensors menu. Set the CV Profile settings to the values in Table 2. **Note**: Only the current range needs to be adjusted.

Table 2	
Number of segments	3
Initial potential (mV)	0
Switching potential 1 (mV)	1200
Switching potential 2 (mV)	–600
Final potential (mV)	0
Sweep rate (mV/s)	100
Current range	Medium (±100 μA)

   b. Start data collection. When data collection is complete, name your sample appropriately.
   c. In Table 5, record your observations of the voltammogram, particularly as they apply to variation from the previous voltammogram, and sketch a drawing of voltage *vs*. time that adequately portrays the parameters set.

7. Adjust the number of segments and the potentials, and repeat the voltammogram of ferricyanide.
   a. To adjust the settings, follow the directions for your equipment:
      - Instrumental Analysis: Click or tap Voltammetry Settings, ☰, and set the parameters to the values in Table 3.
      - LabQuest: Choose Data Collection from the Sensors menu. Set the CV Profile settings to the values in Table 3.

Table 3	
Number of segments	2
Initial potential (mV)	600
Switching potential 1 (mV)	–600
Final potential (mV)	600
Sweep rate (mV/s)	100
Current range	Medium (±100 μA)

   b. Start data collection. When data collection is complete, name your sample appropriately.
   c. In Table 5, record your observations of the voltammogram, particularly as they apply to variation from the previous voltammogram, and sketch a drawing of voltage *vs*. time that adequately portrays the parameters set.

8. Adjust the sweep rate, and repeat the voltammogram of ferricyanide.
   a. To adjust the settings, follow the directions for your equipment:
      - Instrumental Analysis: Click or tap Voltammetry Settings, ☰, and set the parameters to the values in Table 4.
      - LabQuest: Choose Data Collection from the Sensors menu. Set the CV Profile settings to the values in Table 4.

Table 4	
Number of segments	2
Initial potential (mV)	600
Switching potential 1 (mV)	–600
Final potential (mV)	600
Sweep rate (mV/s)	25
Current range	Medium (±100 μA)

   b. Start data collection. When data collection is complete, name your sample appropriately.
   c. In Table 5, record your observations of the voltammogram, particularly as they apply to variation from the previous voltammogram, and sketch a drawing of voltage *vs*. time that adequately portrays the parameters set.

9. With the knowledge you have from the previous steps, adjust any of the values to obtain an optimal voltammogram. Add any additional parameter changes to Table 5 and record your observations.

10. When you are finished collecting all of your data, save or export your data as instructed.

11. Carefully remove the Cyclic Voltammetry System from the stand by pulling back on the top tab. Remove the SPE and discard as instructed. **Important**: Do not invert the Cyclic Voltammetry System with a damp SPE attached. You want to avoid getting liquid inside the SPE connector.

DATA TABLE

Table 5		
Parameter modification	Observation	Sketch of voltage *vs*. time graph
Default parameters		
Current change		
Segment and voltage change		
Sweep rate change		

DATA ANALYSIS

1. Complete Table 5. What set of parameters resulted in the best voltammogram?

2. Label your best voltammogram with the following: anodic peak, cathodic peak, and switching potential. In Instrumental Analysis, this can be done using the Add Annotation feature found in Graph Tools, . If using LabQuest, print out your graph and label it accordingly.