

Electrochemistry: Cyclic Voltammetry

This document contains a list of tasks to complete, after which you should be fairly comfortable with the common electrochemical technique, cyclic voltammetry which is one of the workhorses of electrochemical measurements. In cyclic voltammetry, a linear potential sweep is applied to an electrode, in an effort to drive a redox reaction at the electrode surface. Throughout the experiment, the current that results from the redox process is recorded and plotted as a function of potential as a cyclic voltammogram. Such data is capable of providing a wealth of insight into the electrochemical system. Information related to analyte concentration, electrode reaction kinetics, and diffusional contributions is all contained in a cyclic voltammogram.

NOTE: all experiments described in this document should use a platinum wire auxiliary electrode and silver/silver chloride reference electrode.

I. Electrode Preparation:

The response of a species at an electrode surface is strongly dependent on how the electrode has been prepared prior to running the experiment. Typically, electrodes are polished and rinsed before the start of the experiment.

Solution(s) Needed: 10 mM Potassium Ferricyanide ($K_3Fe(CN)_6$) in 0.10 M Potassium Chloride (it is easiest to prepare the KCl solution first). Prepare some extra 0.1 M KCl (~200 mL) for use in the rest of the experiment.

1. Locate a gold electrode. This will be your *working* electrode.
2. Immerse the working, reference, and auxiliary electrodes in a small vial and add a few mL of your KCl solution, without ferricyanide (you only need enough solution to cover the ends of the electrode (~1/2 inch in the bottom of the vial)).
3. Connect the leads follows: the gold electrode to Working Electrode, the platinum wire to Auxiliary Electrode and the silver/silver chloride electrode to Reference Electrode.
4. Perform a cyclic voltammetry experiment using the following conditions: (This will be a *Background* scan containing no electroactive material)

Initial E	800 mV		Scan Rate	100 mV/s
High E	800 mV		Initial Direction	Negative
Low E	-100 mV		Sensitivity	10 $\mu A/V$

NOTE: You may need to adjust the sensitivity throughout the course of the experiment to maximize S/N for each voltammogram.

5. Save the CV.
6. Disconnect and remove the electrodes from the cell, and rinse them with deionized water.
7. Immerse the working, reference, and auxiliary electrodes in a small vial and add a few mL of your ferricyanide solution.
8. Perform a cyclic voltammetry experiment using the conditions in step 4. Following completion of the CV, disconnect and remove the electrodes and rinse them.
9. Polishing procedure:

- a. Affix three small pieces of polishing felt to a glass plate.
 - b. Deposit a pea-sized drop of 1-micron polishing compound on one of the pieces of felt.
 - c. Polish the gold electrode by applying moderate pressure while moving the electrode in a figure-eight pattern on the felt. Polish for about 30 seconds.
 - d. Rinse the electrode well with distilled-deionized water.
 - e. Repeat steps b-d using 0.30 micron, then 0.05 micron polishing compound, rinsing well after each step.
10. Rinse the electrode again and return it to the KCl solution and collect a scan.
 11. Transfer the electrodes to the ferricyanide solution and collect a CV using the conditions in step 4.
 12. Disconnect and remove the gold electrode and immerse it in a dilute solution of decanethiol (or other long chain alkanethiol) for ~5 minutes (do this in the hood, it stinks!). After 5 minutes remove the electrode, and rinse it well with ethanol and water.
 13. Collect a *Background* CV using the KCl solution.
 14. Collect a CV in the ferricyanide solution
 15. Repeat the entire polishing series using a glassy carbon working electrode instead of gold.

What changes in do you notice in the CV's collected following various electrode treatments? Suggest a reason for the differences between the polished, unpolished, and thiol-treated electrodes.

II. Scan Rate Dependence

The response observed during a voltammetry experiment depends strongly on the rate that material approaches the electrode surface. This task will introduce you to this dependence.

Solution Needed: 10 mM Potassium Ferricyanide ($K_3Fe(CN)_6$) in 0.10 M Potassium Chloride

1. Polish the gold electrode as described in the *Electrode Preparation* task above.
2. Immerse the working, reference, and auxiliary electrodes in a small vial and add a few mL of your ferricyanide solution.
3. Connect the leads follows: the gold electrode to Working Electrode, the platinum wire to Auxiliary Electrode and the silver/silver chloride electrode to Reference Electrode.
4. Prepare to perform a cyclic voltammetry experiment using the following conditions:

Initial E	800 mV		Initial Direction	Negative
High E	800 mV		Sensitivity	10 $\mu A/V$
Low E	-100 mV			

5. Run a series of CV's at scan rates ranging from 10 mV/s to 500 mV/s, save each CV. *NOTE: the **Sensitivity** may need to be adjusted as the scan rate changes in order to observe a reasonable CV.*
6. Determine the peak potential and peak current for each peak on each CV. *Do you observe any trends in the data? Make plots of peak current for the anodic and cathodic peaks as a function of scan rate and as a function of square root of scan rate. Which plots are linear? Which plots should be linear?*

III. Concentration Dependence

The concentration of electroactive species present in a solution also plays a major role in determining the response observed in a voltammetric experiment.

Solutions Needed: Solutions of 1, 2, 5, and 10 mM Potassium Ferricyanide ($K_3Fe(CN)_6$) in 0.10 M Potassium Chloride. These can be prepared by first making the 10 mM solution and diluting aliquots of this solution with 0.10 M KCl to make the appropriate concentrations. You will also need to bring your instructor your 10 mM ferricyanide solution, your 0.1 M KCl solution, and a clean 25 mL flask to be used for an unknown.

1. Polish the gold electrode as described in the *Electrode Preparation* task above.
2. Immerse the working, reference, and auxiliary electrodes in a small vial and add a few mL of your ferricyanide solution.
3. Connect the leads follows: the gold electrode to Working Electrode, the platinum wire to Auxiliary Electrode and the silver/silver chloride electrode to Reference Electrode.
4. Prepare to perform a cyclic voltammetry experiment using the following conditions:

Initial E	800 mV		Scan Rate	100 mV/s
High E	800 mV		Initial Direction	Negative
Low E	-100 mV		Sensitivity	10 $\mu A/V$

5. Run series of CVs for each of the four concentrations you prepared, as well as your unknown. Save each CV.
6. Determine the peak potential and peak current for each peak on each CV. Do you observe any trends in the data? Plot anodic and cathodic peak current as a function of concentration. Is the response what you would expect? Based on your results, determine the ferricyanide concentration in your unknown.

Based on your observation in the above experiments; is the ferri/ferrocyanide couple electrochemically reversible? Chemically reversible? Are we operating under diffusion controlled conditions?