Introduction:

Cyclic voltammetry (CV) is a widely used electrochemical technique that involves the cyclical scanning of the potential (i.e., scanning from a starting to an ending potential and back again at a constant rate) and measuring the resultant current. The resulting "cyclic voltammogram" relays information about the reodx potential of the analyte, the number of electrons transferred in the reduction or oxidation, the reversibility and speed of the electrochemical process, the stability of the oxidized or reduced form of the analyte, and (though rarely used) the concentration of analyte.

In a typical setup, a three electrode cell (working, reference, and counter) is used, with the measured current passing between the working and counter electrodes. The analyte solution must be made to contain a supporting electrolyte, and thus care should be taken to choose an electrolyte that will not react with the analyte or be electroactive within the scan range. Prior to the scan, the solution is degassed with N\textsubscript{2} to remove dissolved O\textsubscript{2}. The solution is not stirred during the analysis.

CV is analogous to spectroscopy in that the system is excited by an energy scan, and the response is recorded. A typical excitation signal for CV is a triangular waveform, when plotted as potential versus time (Figure 1). The scan direction may be either in the negative or positive direction, depending on whether a reductive or oxidative process is being studied. Figure 2 shows a typical cyclic voltammogram for a reversible reduction (note that the potential was first swept in the cathodic direction, resulting in a positive current, and then in the anodic direction, resulting in a negative peak with approximately the same area). The important parameters of a cyclic voltammogram are the magnitudes of the anodic and cathodic peak currents (i\textsubscript{pa} and i\textsubscript{pc} respectively) and of the anodic and cathodic peak potentials (E\textsubscript{pa} and E\textsubscript{pc} respectively), which are labeled in Figure 2 (note the extrapolations of the baselines to determine the peak currents).

An "electrochemically reversible couple" refers to a redox process in which both the oxidized and reduced form of the analyte rapidly exchange electrons at the electrode. The cyclic voltammogram in Figure 2 shows the result of a CV analysis of such a species, wherein the cathodic and anodic peaks are
symmetric, but occur at slightly offset potentials. (Semi-reversible couples occur when the rates of
electron exchange for the oxidized and reduced species are substantially different, such as may happen
if one of them is a solid or a liquid; irreversible couples occur when the species decomposes after
electron exchange, and therefore is not available for the reverse electron exchange). For reversible
couples, the formal reduction potential is centered between \( E_{pa} \) and \( E_{pc} \), found mathematically by:

\[
E = \frac{E_{pa} + E_{pc}}{2}
\]

the number of electrons transferred in the reaction at the electrode is given by:

\[
\Delta E = |E_{pa} - E_{pc}| \approx \frac{0.059}{n}
\]

and the ratio of the peak currents is unity:

\[
\frac{i_{pa}}{i_{pc}} \approx 1
\]

Finally, the peak current is given by:

\[
i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C \nu^{1/2}
\]

where \( n \) is the number of electrons, \( A \) is electrode area, \( D \) is the diffusion coefficient, \( C \) is the
concentration, and \( \nu \) is the scan rate (e.g. V/s). Thus, a great deal of information can be learned about
the system by varying known parameters, such as concentration and scan rate.

In this lab, you will be given a compound known to undergo a reversible redox couple. You will
begin by sweeping through the usable range of potentials, as governed by the instrumental setup (in this
case, the working electrode will be mercury) to find the approximate redox potential of the analyte.
You will then perform a series of cyclic voltammetry analyses, varying the scan rate and concentration,
so determine the effects of these parameter changes on the analysis.

**Equipment**: Read through the procedures and make a list of the equipment you will need.

**Safety Considerations**: Read through the procedures and note any safety considerations.

**Procedure**

**A. Solution preparation**

1. You will be supplied with a 1M KCl solution. Use this solution to prepare 2, 4, 8, and 16 mM
   solutions of the analyte. (note: less than 10 mL of solution is needed for an analysis; you will
   use the 4 mM solution for several analyses and the others only one)
2. Prepare two 4 mM solutions of the analyte, one in 1 M KNO_3 and one in 1M Na_2SO_4.

**B. Electrochemical Analysis**

1. Clean the Pt counter electrode with an abrasive substance.
2. Fill the Ag/AgCl reference electrode with filling solution (saturated KCl) and assemble.
3. Place a sample of 4 mM sample in 1 M KCl in the cell and purge for several minutes with N_2.
4. The working range of a mercury electrode is roughly 0.25 V to -1.1 V. Set up a CV to scan this
   range at 100 mV/s.
5. After waiting a few minutes for the solution to settle, run the scan.
6. Determine the approximate potential for the redox couple. Set up and perform scans through
   this potential ±0.3V at a scan rates of 20, 50, 75, 100, 125, 150, 175, and 200 mV/s. Between
   scans, stir the solution very briefly and allow a minute or two for the system to come to rest.
7. Set up and perform a series of scans on the 2, 8, and 16 mM samples in 1 M KCl, and the 4 mM samples in 1 M KNO₃ and one in 1M Na₂SO₄ using the same scan range as in Step B6 and a scan rate of 20 mV/s.

Analysis

1. Make a table of $i_{pa}$, $i_{pc}$, $E_{pa}$ and $E_{pc}$ for each scan.
2. Determine $E$ and $n$ (see equations in Introduction) for the 4mM solutions in 1 M KCl, KNO₃ and Na₂SO₄ at scan rate of 20 mV/s.
3. Determine the effect of scan rate on peak height calculating $i_{pa} / i_{pc}$ for each of the scans of 4mM sample in 1 M KCl at different scan rates (Step B6) and by plotting the anodic peak current versus square root of scan rate ($i_{pa}$ vs $v^{1/2}$).
4. Determine the effect of scan rate on $\Delta E$ by plotting $\Delta E$ vs $v$ using the the scans of 4mM sample in 1 M KCl at different scan rates (Step B6).
5. Determine the effect of concentration on peak current by plotting $i_{pa}$ versus concentration of analyte from the scans of various analyte concentrations in 1 M KCl.

Conclusions

1. In the initial wide scan, what happened at the ends of the scan? Why?
2. Discuss the various effects of scan rate, concentration, and supporting electrolyte on CV analysis.
3. What would a cyclic voltammogram look like if the solution were stirred constantly through the analysis?