Cyclic Voltammetry of Ferrocyanide

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I.   Objective: To learn the fundaments and basic experiments involving electrochemistry.

II.   Introduction:

In Dr. Burgess' group I learned how to use a potentiostat to control my experiments. I learned how to set up an electrochemical cell. I had to use three electrodes for my experiment. The first electrode is called a working electrode. The working electrode is a platinum wire sealed in a black tube. The electrode is connected to the potentiostat. The reaction in solution occurs at the working electrode.
Below is the reaction observed:

Overall Reaction:

$$Fe^{+3} + e^{-} \;\rightleftharpoons\; Fe^{+2}$$
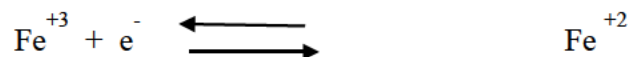
The second electrode I used was called a reference electrode for my electrochemical cell. The reference electrode is a silver silver chloride electrode. The electrode has a constant potential of 0.222V vs normal hydrogen electrode. The third electrode I used was called a counter electrode. The counter electrode acts as a source or sink for electrons. The overall reaction shows two arrows going in opposite directions. This means that the system or reaction is under equilibrium. When a system is under equilibrium as in this experiment, the Nernst equation can be used. Two conditions are met in this experiment:

Condition 1: Fast reactions taking place at electrode surface
Condition 2: Reversible
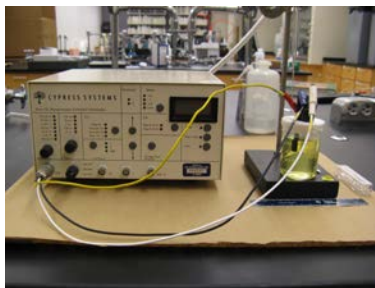
III.   Experimental Procedure

Figure 1.   (TOP)   Potentiostat   (Cypress Systems) and electrochemical cell.   (Bottom) Electrodes used in this experiment: (A) Pt counter electrode, (B) Reference electrode, and (C) Pt working electrode.

Experimental Procedure:
1. Polished working electrode with Alumina solution on polishing pad.
2. Prepared 1mM, 5mM, 10mM, 15mM, and 20mM potassium ferrocyanide and potassium ferricyanide solutions.
3. Electrolyte used in this experiment was 1M KCl.
4. Purged each solution for 10 minutes prior to start of experiment.
5. Blanketed the surface with nitrogen gas to prevent atmospheric oxygen dissolving into solution.
6. Potentiostat Controls:
    I.   Ferrocyanide Conditions vs Ag/AgCl:
        a. Initial Potential: -300mV
        b. First Vertex Potential: -300mV
        c. Second Vertex Potential: +600mV
        d. Final Potential: -300mV
    I.   Ferricyanide Conditions vs Ag/AgCl:
        a. Initial Potential: +500mV
        b. First Vertex Potential: +500mV
        c. Second Vertex Potential: -300mV
        d. Final Potential: +500mV
    I.   Scan Rates:
        a. 10mV/s, 30mV/s, 50mV/s, 70mV/s, 90mV/s
            100mV/s, 120mV/s, 140mV/s, 160mV/s,
        180mV/s, 200mV/s, 250mV/s, and 300mV/s.
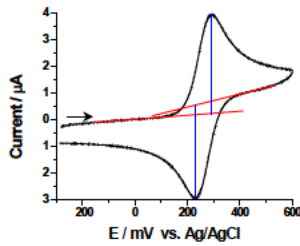
IV.   Results Discussion

Figure 2. Shows cV of 1mM ferrocyanide in 1M KCL scan rate of 10mV/s.

The y axis is the current and the X axis is the potential .The forward scan is oxidation and the backward scan is the reduction. The red lines are baselines. This helped me to get the peak currents. I looked at the peak current for oxidation and reduction by using origin software. When I divided the two peak currents I got a value of 0.91 which is very close to a value of 1.This means my experiment worked.
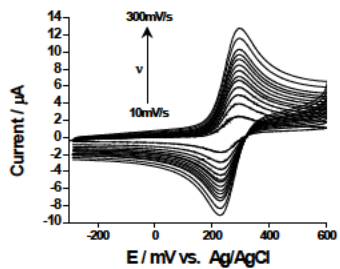

Figure 3. This figure shows the Different scan rates at 1mM ferrocyanide. I went through all the ferrocyanide from 10mV/s to 300mV/s .

The increase scan rates gave me larger currents. And the next figure I plotted the peak current vs. the square root of the scan rate.
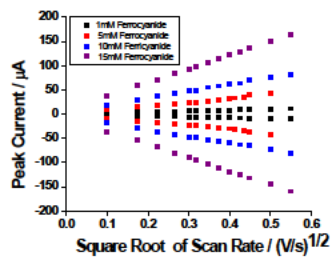

Figure 4. This is peak current and square root of scan rate V/s. First I took the slope and then I took thae concentration times 10^{-6}. I used the following equation:

$$I = 2.69x10^5 * n^{3/2} * A *C* D^{1/2}$$

In the above equation n is equal to the number of electrons in the reaction I'm looking at n is equal to 1. The next variable a is the area the unites for the area in the equation cm^2. I used the area of a circle = pi*r^2. The next variable c is the moles of cm^{-3}. The next variable d is the diffusion coefficient that tell me how fast it moves.

For example, a 20mM of ferrocyanide my slope was $-1269.68.221*10^{-6}$, the area that I calculated was 0.0314cm, the concentration I used was $0.20*10^{-6}$mol cm^{-3}. From using the above equation I calculated D is equal to $5.65*10^{-5}$ $cm^{2/}s$ this was for the cathodic. I did the similar thing for oxidation and I got diffusion coefficient of $6.26*10^{-5}$ cm^2/s. I did statistics on the diffusion coefficient for ferri and ferro and I got these values

Do = $4.70x10^{-6}$ +/- $1.34x10^{-6}cm^2/s$

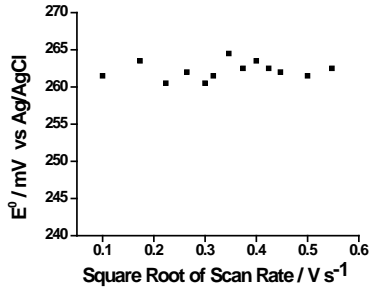Dr = $4.28x10^{-6}$ +/- $1.14x10^{-6}cm^2/s$

Figure 5. No change in formal reduction potential with scan rate.

The formal reduction potential was calculated by taking the peak potentials of the oxidation and reduction and dividing by two. So it doesn't change. This means my experiment worked.
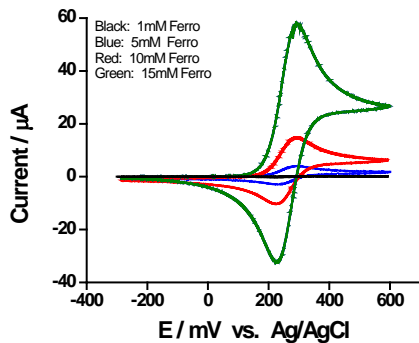

Figure 6. It shows 1mM 5mM 10mM and 15mM of ferrocyanide at one scan rate.

When the concentration was changed the current increased.

IV.   Conclusion

      Throughout my experience at Case University I have learned a lot of things. I have learned how to measure out powder for my experiment. I've also learned how to do scan rates, purged my solution, tell which scan rate is oxidation and which scan rate is reduction. I also learned that oxidized mean loss of electrons and reduced mean gain of electrons.