

Title: Cyclic Voltammetry

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Abstract

In this experiment, the conversion rate between $\text{Fe}(\text{CN})_6^{-4}$ and $\text{Fe}(\text{CN})_6^{-3}$ was found via the Randles-Sevcik equation. From the equation, the first method with the same scan rate but varying concentration yielded a diffusion coefficient of $3.11 \times 10^{-6} \text{ cm}^2/\text{sec}$. Using the second method with the same concentration but varying scan rate yielded a diffusion coefficient of $2.15 \times 10^{-6} \text{ cm}^2/\text{sec}$. After finding the diffusion rate, the unknown concentration in Run F was found to be 8.92mM or 0.00892M of $\text{Fe}(\text{CN})_6^{-4}$.

Keywords: Randles-Sevcik, diffusion coefficient, scan rate, concentration.

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Introduction

The purpose of this experiment was to determine the conversion reaction between Fe(CN)_6^{-4} and Fe(CN)_6^{-3} . The half reaction used in this experiment is $\text{Fe(CN)}_6^{-4} \leftrightarrow \text{Fe(CN)}_6^{-3} + e^-$. To do this, there is a three electrode system that is introduced that contains a working electrode, a counter electrode, and the reference electrode. The working electrode contains the half cell reaction that is being sought after, the counter electrode is the electrode that balances the charge in the system, and the reference electrode is where a known half cell reaction with a potential is contained. After acquiring data, cyclic voltammograms (CVs) can be plotted where information such as the anodic and cathodic peaks can be found.

From the CV, a lot of information can be obtained with the help of the Randles-Sevcik Equation where:

$$i_p = 269n^{3/2}AD^{1/2}v^{1/2}C^b \quad (1)$$

with i_p being the peak height in amperes, n being the number of electrons transferred in the half reaction, A being the area of the working electrode in cm^2 , D being the diffusion coefficient in cm^2/sec , v being the scan rate in V/sec and C^b being the bulk concentration of solution in M of the electroactive species.

To determine the reversibility of the redox reaction, this equation is used:

$$\Delta E = |E_{pa} - E_{pc}| = \frac{57\text{mV}}{n} \quad (2)$$

where E_{pa} is the anodic potential, E_{pc} is the cathodic potential, and n is the number of electrons transferred in the reaction. Because this reaction only transfers one electron in this experiment, the difference between these should be about 57mV. Another determination of reversibility is through the ratio of the anodic and cathodic current peaks where:

$$\frac{i_{pa}}{i_{pc}} \quad (3)$$

with i_{pa} being the peak anodic current and i_{pc} being the peak cathodic current. This ratio should be close to one for the reaction to be considered reversible.

Methods

Since the labs are cancelled, the data was provided by the professor so there will be no method explanation.

Results

Background CV (Run A)

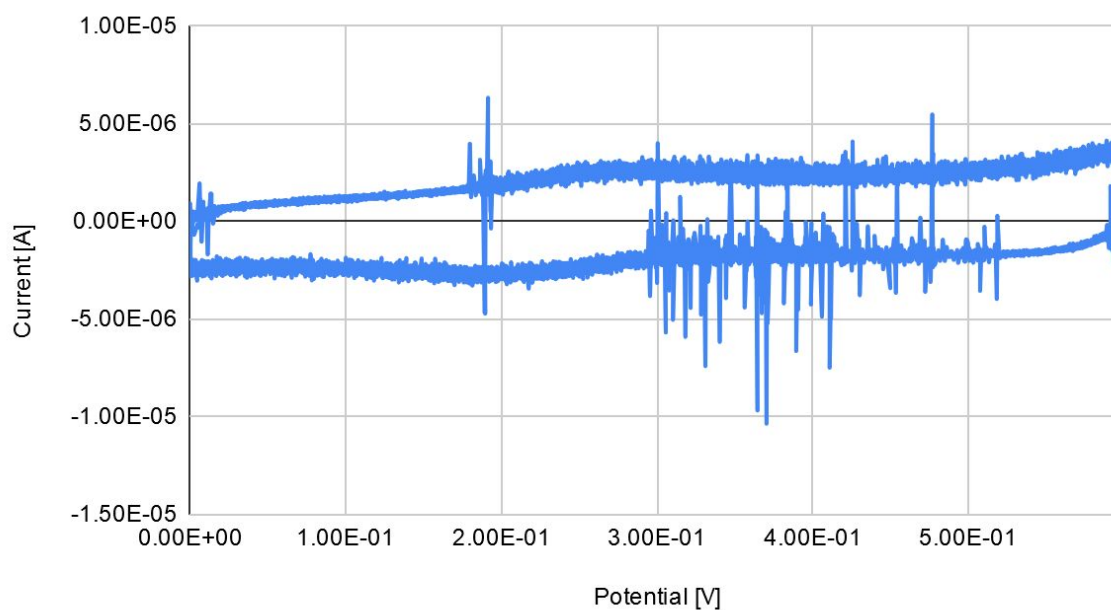


Figure 1. Background CV from Run A

Current [A] vs Potential [V] for Run B

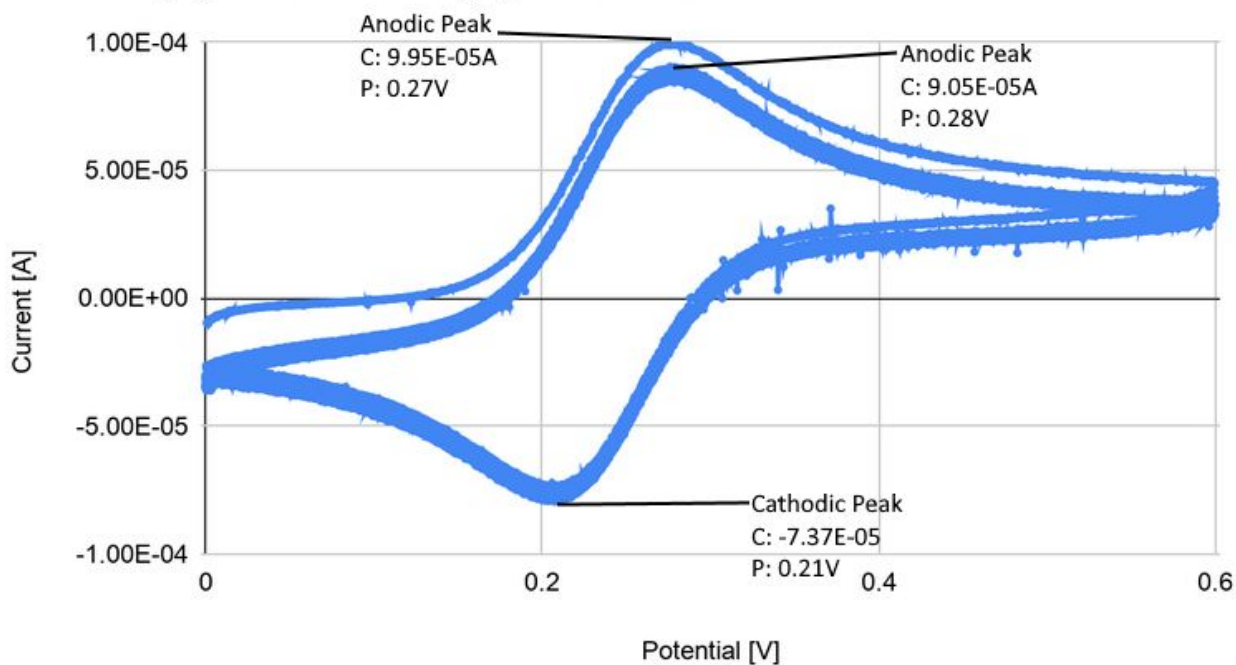


Figure 2. CV for Run B

Current [A] vs Potential [V] for Run C

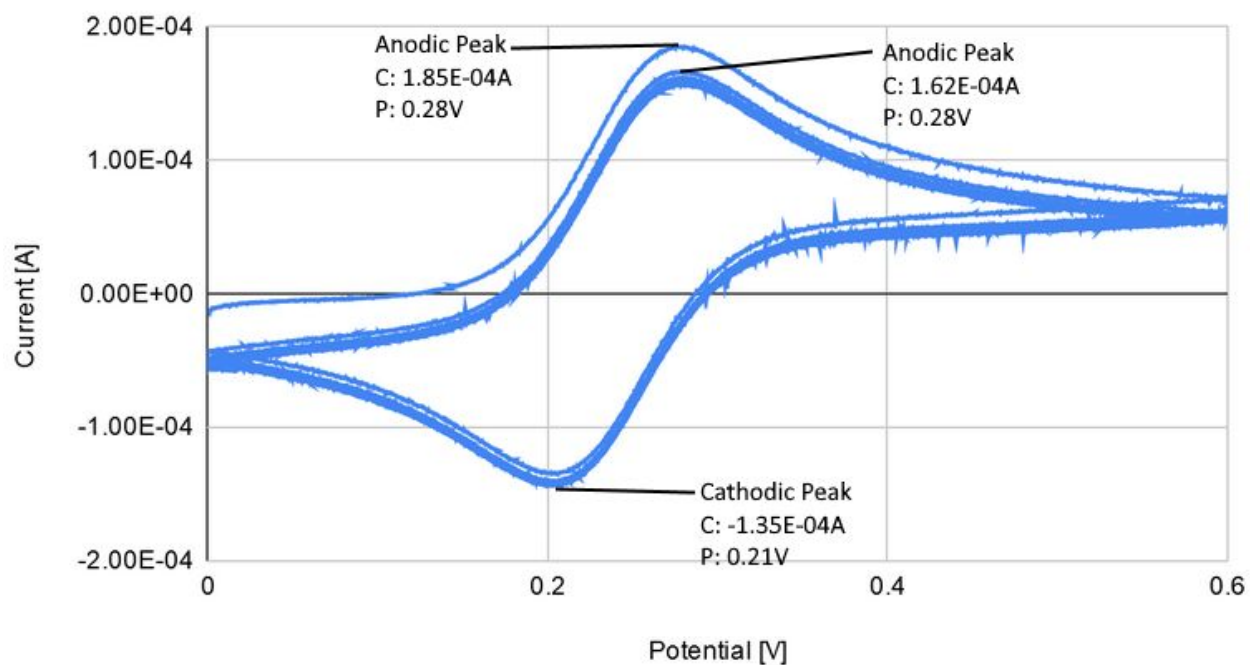


Figure 3. CV for Run C

Current [A] vs Potential [V] for Run D

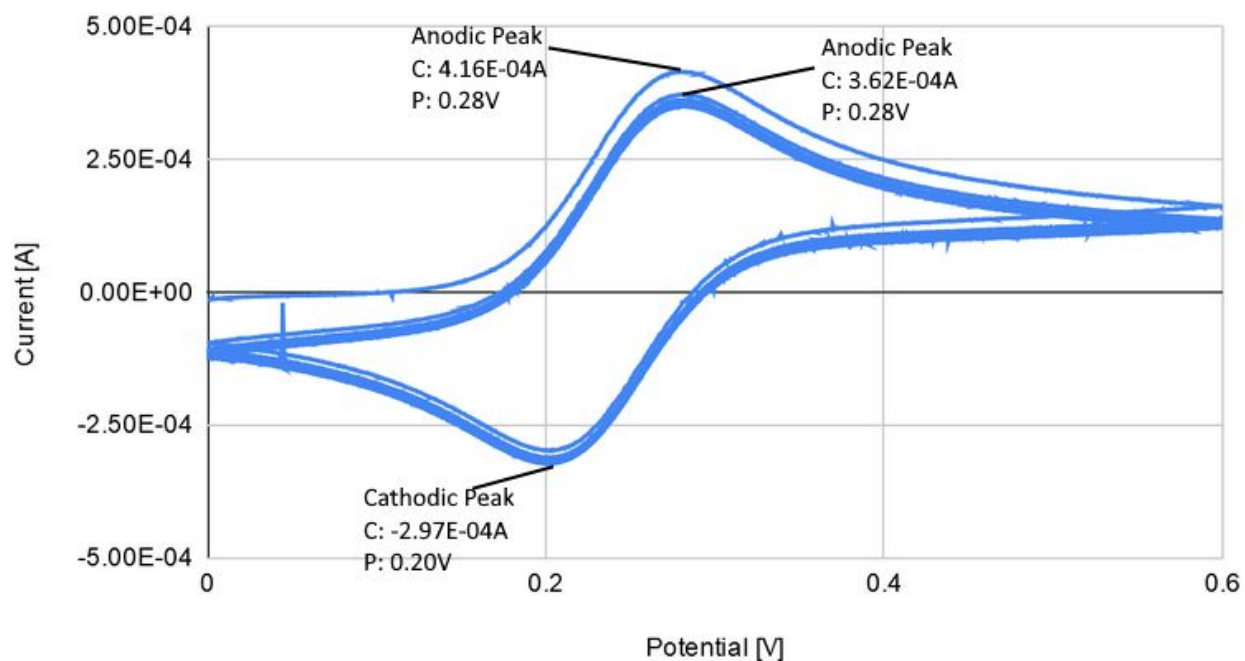


Figure 4. CV for Run D

Current [A] vs Potential [V] for Run E

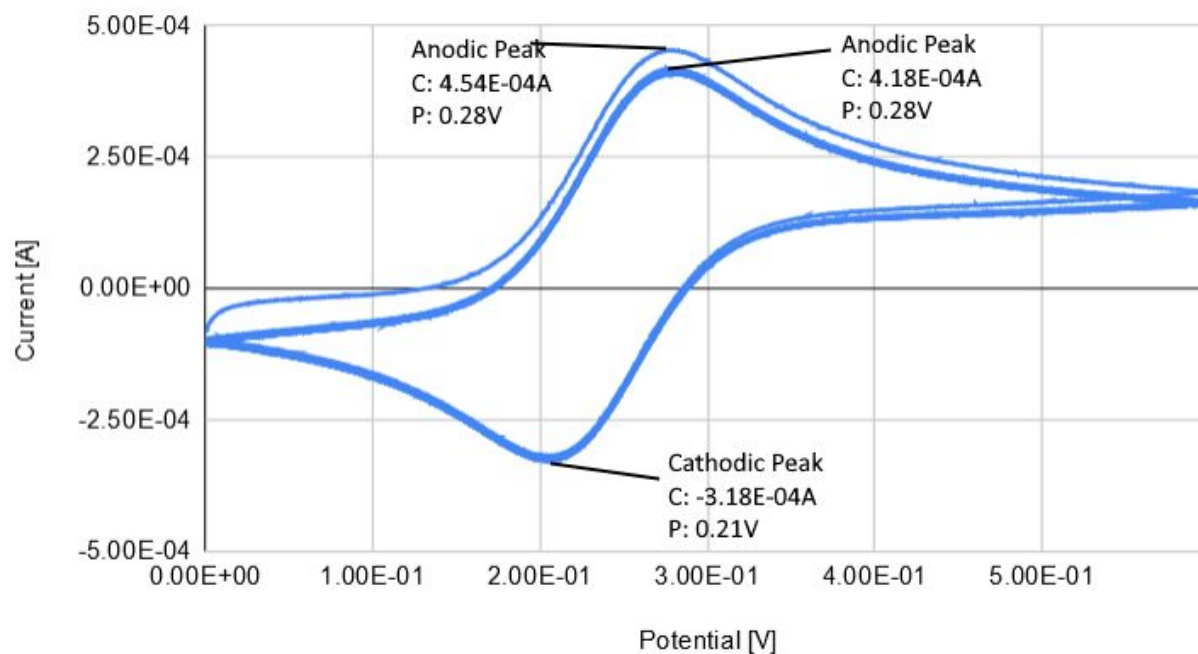


Figure 5. CV for Run E under a sweep rate of 0.05 V/s

Current [A] vs Potential [V] for Run E

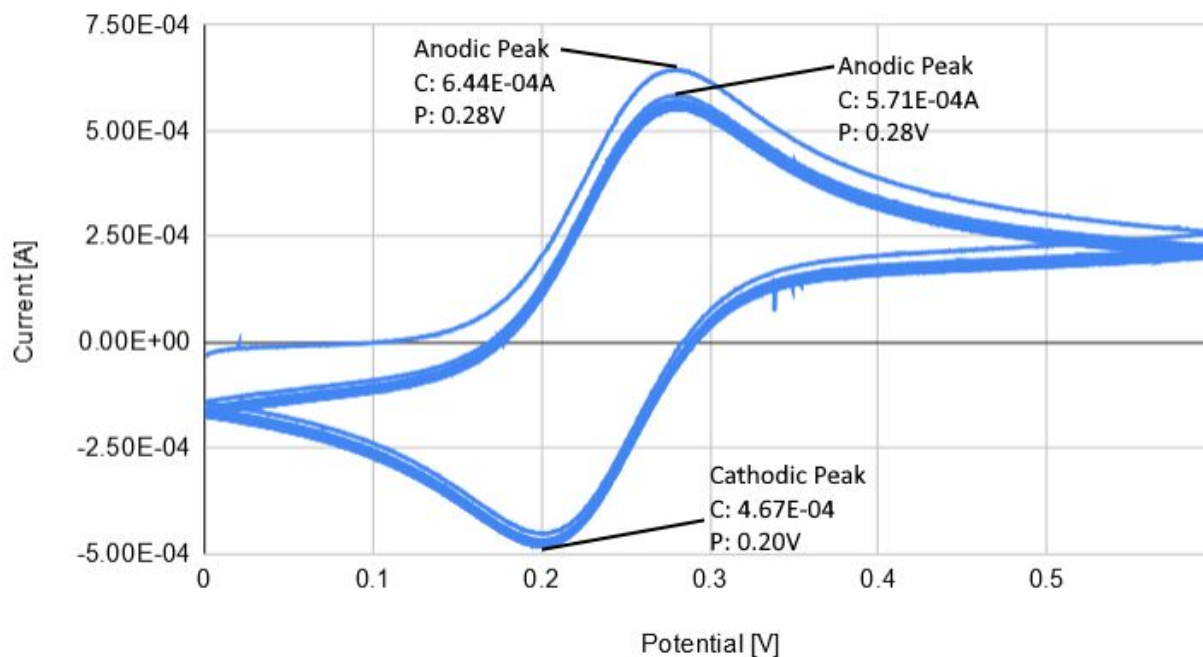


Figure 6. CV for Run E under a sweep rate of 0.1 V/s

Current [A] vs Potential [V] for Run E

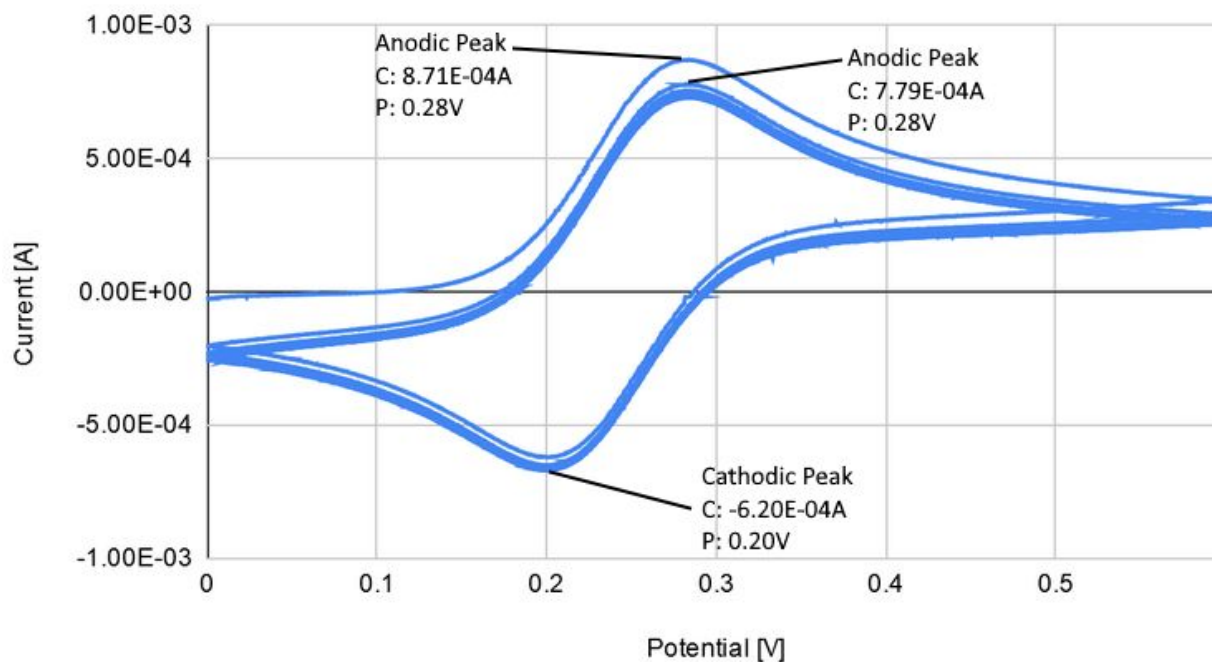


Figure 7. CV for Run E under a sweep rate of 0.2 V/s

Current [A] vs Potential [V] for Run E

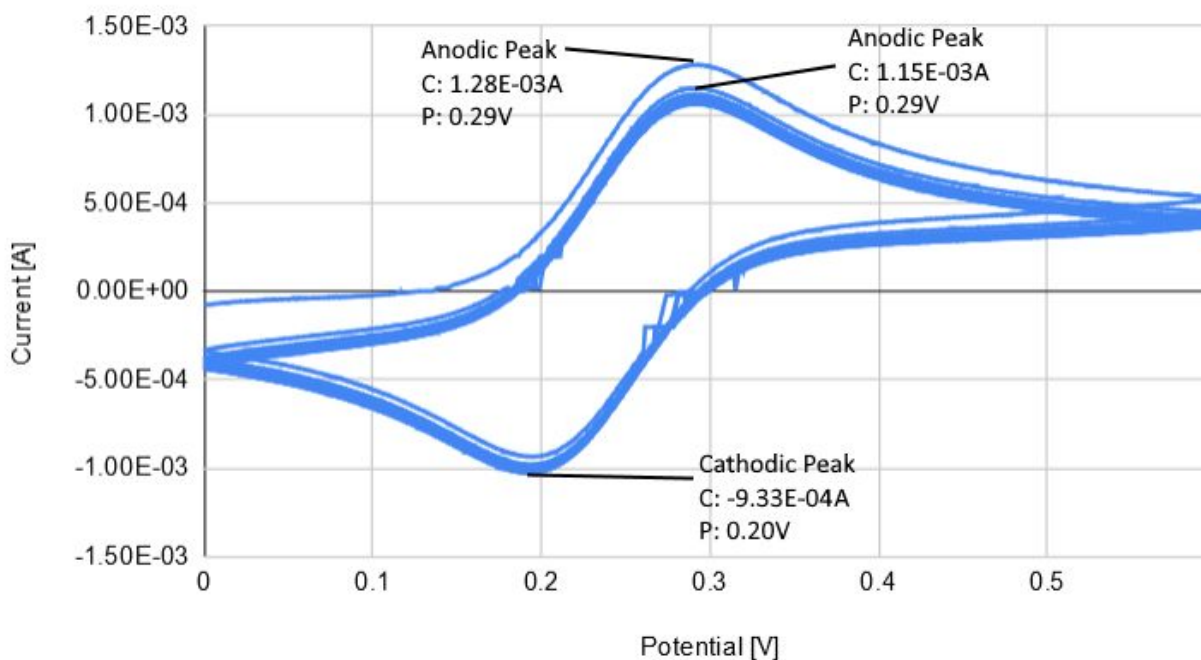


Figure 8. CV for Run E under a sweep rate of 0.5 V/s

Current [A] vs Potential [V] for Run E

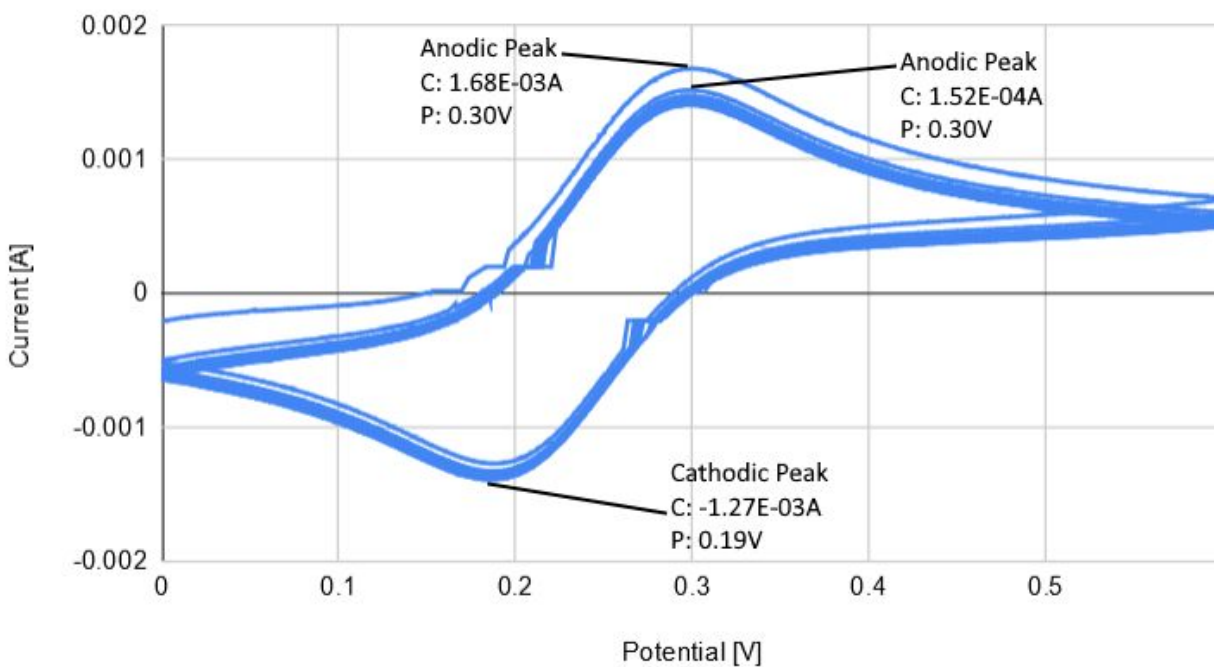


Figure 9. CV for Run E under a sweep rate of 1.0 V/s

Current [A] vs Potential [V] for Run F

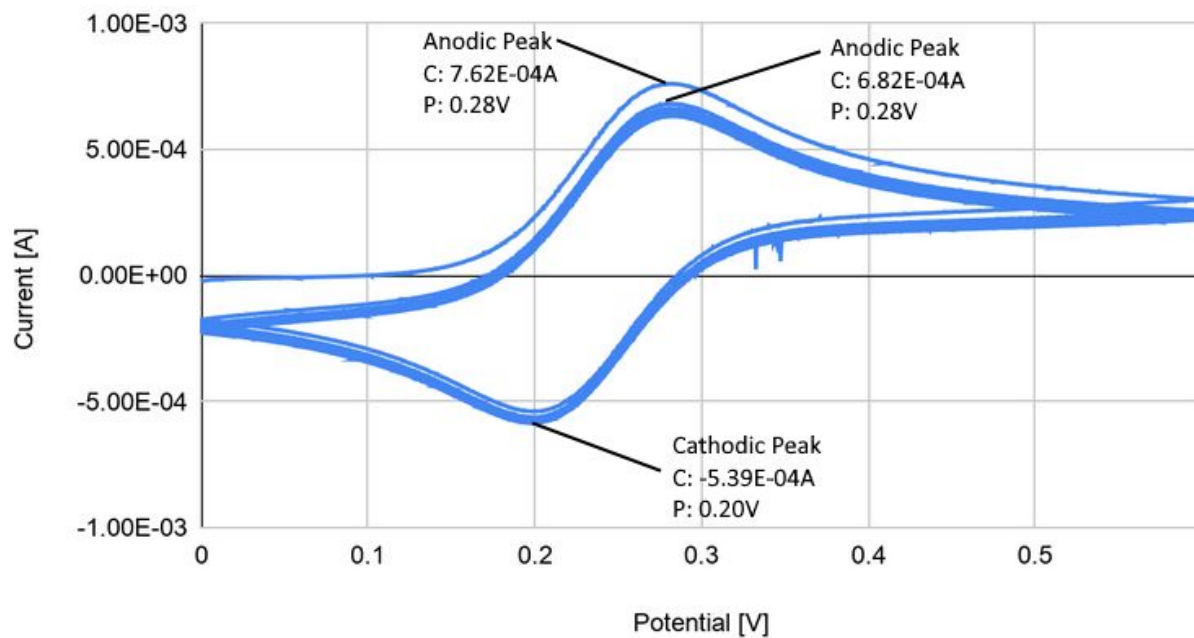


Figure 10. CV for Run F

Table I. Data for Figure 11

Concentration (M)	Peak Anodic Current (A)
0.001	9.05×10^{-5}
0.002	1.62×10^{-4}
0.005	3.62×10^{-4}
0.01	7.79×10^{-4}

Peak Anodic Current (A) vs. Concentration (M)

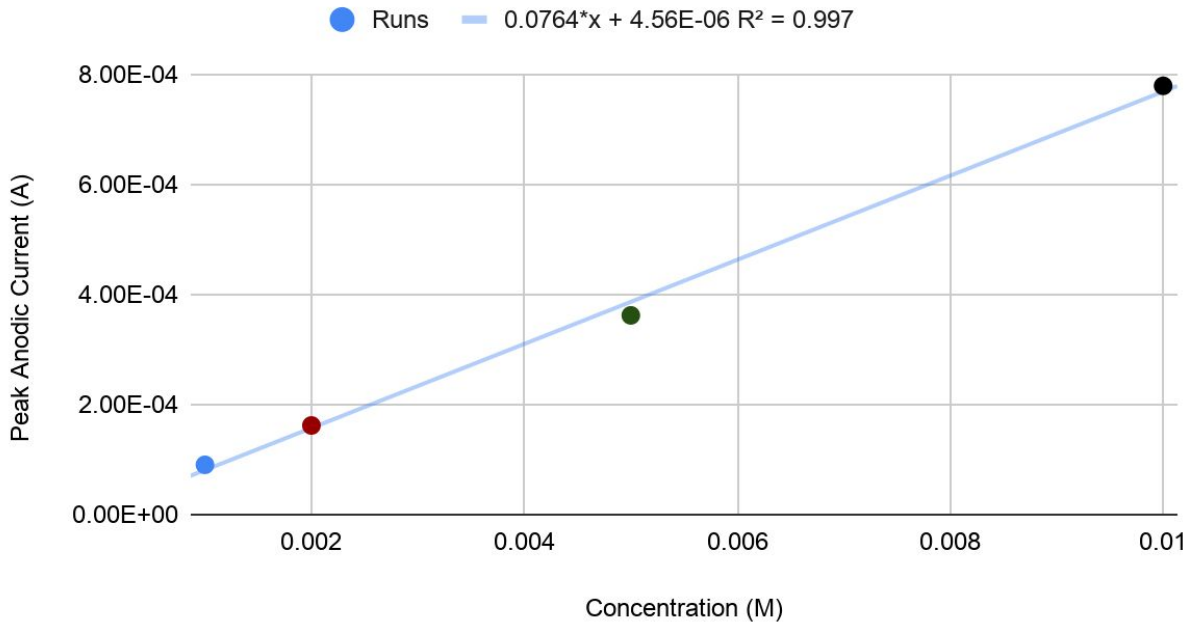


Figure 11. Known Concentrations of Runs B-E fit with a line of best fit. Blue is Run B, Red is Run C, Green is Run D, Black is Run E.

Using the equation 1 from the introduction:

$$i_p = 269n^{3/2}AD^{1/2}v^{1/2}C^b$$

From Figure 1, the slope is 0.0764x where x is equal to C^b .

So slope = $269 \cdot n^{3/2} \cdot A \cdot D^{1/2} \cdot v^{1/2}$

$$0.0764 = 269 \cdot 1 \cdot 0.36 \text{ cm}^2 \cdot D^{1/2} \cdot \sqrt{0.2 \frac{\text{V}}{\text{sec}}}$$

$$D = 3.11 \times 10^{-6} \text{ cm}^2/\text{sec}$$

Using this, the concentration for figure 10 can be found where:

$$6.82 \times 10^{-4} \text{ A} = 269 \cdot 1 \cdot 0.36 \text{ cm}^2 \cdot \sqrt{0.2 \frac{\text{V}}{\text{sec}}} \cdot \sqrt{3.11 \times 10^{-6} \frac{\text{cm}^2}{\text{sec}}} \cdot C^b$$

$$C^b = 0.00892 \text{ M} = 8.92 \text{ mM Fe(CN)}_6^{-4}$$

Table II. Data for Figure 12

Square Root of Sweep Rate (V/s)	Peak Anodic Current (A)
0.22	4.18×10^{-4}
0.32	5.71×10^{-4}
0.45	7.79×10^{-4}
0.71	1.15×10^{-3}
1.00	1.52×10^{-3}

Peak Anodic Current (A) vs. Square Root of Sweep Rate (V/s) for Varying Runs of E

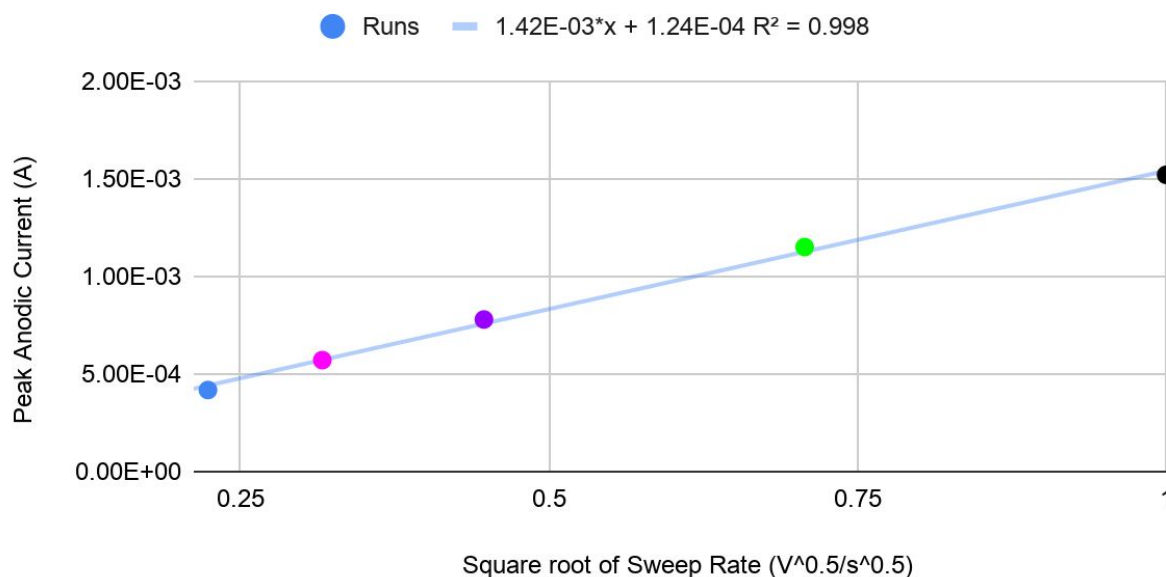


Figure 12. Fixed concentrations of Run E under varying sweep rates. Blue is a sweep rate of 0.05 V/s, Pink is a sweep rate of 0.1 V/s, Purple is a sweep rate of 0.2 V/s, Green is a sweep rate of 0.5 V/s, and Black is a sweep rate of 1.0 V/s.

From Figure 12, the slope is $1.42 \times 10^{-3}x$ where x is equal to $v^{1/2}$.

$$\text{So slope} = 269 \cdot n^{3/2} \cdot A \cdot D^{1/2} \cdot C$$

$$1.42 \times 10^{-3} = 269 \cdot 1 \cdot 0.36 \text{ cm}^2 \cdot D^{1/2} \cdot 0.01 \text{ M}$$

$$D = 2.15 \times 10^{-6} \text{ cm}^2/\text{sec}$$

Conclusion

Using the two different methods, one being varying concentrations and the other being varying scan rates, the two diffusion coefficients found are different between each other. The one

from varying concentrations yielded $3.11 \times 10^{-6} \text{ cm}^2/\text{sec}$ while the one with varying scan rates yielded $2.15 \times 10^{-6} \text{ cm}^2/\text{sec}$. Using the varying concentration diffusion coefficient to find the unknown concentration, it yields 8.92mM or 0.00892 M of $\text{Fe}(\text{CN})_6^{-4}$. This was used because the scan rate was the same, as well as the independent variable standing for concentration.

Each calculation was done using the second greatest peak due each of the CVs showing a different first cycle compared to everything else in the CV. About all the gaps in the CVs from the first cycle to the rest of the cycles had a gap the size of the rest of the cycles, excluding the first one, combined.

Acknowledgements

I used the lecture video and the lecture slides that the professor posted.

Discussion Questions

1. Is a reversible redox reaction occurring at the working electrode? Give at least three reasons.

There is a reversible redox reaction occurring at the working electrode because both E_{pa} and E_{pc} , the anodic and cathodic peaks, don't change between the scan rates as shown in figures 5-9 in the Run E trials and that the two peaks are shown. In each figure of a CV, there is also a difference between the location of the two peaks which means that it is also a reversible reaction. Another reason that the reaction is reversible is that all of the ratios between the anodic and cathodic peak currents are close to 1. The only issue is due to the difference between the E_{pa} and E_{pc} being not close to 57 mV which can be caused by electrode surface contamination or high solution resistance.

2. Write out the reaction that occurs at the anodic peak and cathodic peak.

At the anode: $\text{Fe}(\text{CN})_6^{-4} \rightarrow \text{Fe}(\text{CN})_6^{-3} + e^-$

At the cathode: $\text{Fe}(\text{CN})_6^{-3} + e^- \rightarrow \text{Fe}(\text{CN})_6^{-4}$

3. Describe the direction of electrons flow at the surface of the working, counter, and reference electrodes at the anodic peak and cathodic peak.

At the anodic peak at the surface of the working electrode, electrons flow from anode to cathode and the counter electrode would have electrons flowing the opposite way to counter the change.

At the cathodic peak at the surface of the working electrode, electrons flow from cathode to anode and the counter electrode would have electrons flowing the same way. For both peaks, the reference electrode does not pass current which means there is no flow of electrons.

References

Professor's lecture slides and lecture video.