Electrochemical Reduction of Ferricyanide at a Platinum Electrode

Cyclic Voltammetry (CV) is an electrochemical technique which provides a thorough variety of information using a three electrode system. CV allows for the reversibility of the reaction to be determined using a range of different conditions. A reversible reaction is that of which is controlled by diffusion, and an irreversible reaction is controlled by charge. A quasi reversible reaction is a reaction that is reversible but with slow kinetics. In an irreversible reaction's peak potential changes with the scan rate and is characterised by widely separated peaks[1]. In this experiment the reversibility of the reduction of ferricyanide is determined using CV. It is hypothesised that the electrochemical reduction of ferricyanide is always reversible[2]. The reaction is a one electron reduction of Ferricyanide:

$[Fe^{III(}(CN)_6]^{3-} + e^- <> [Fe^{II(}(CN)_6]^{4-}$

The CV allows provides a range of parameter including current, voltage, time, scan rate, and concentration. These can be plotted against each other to analyse the reversibility of the reaction. Some of the conditions required for a reaction to be considered reversible include and linear relationship between the current and time. Peak potential to be independent of the scan rate and a difference between the peak potentials of the cathode and anode to be within 59mV/n.

Materials and Method[2]:

- 1.6mm Pt working electrode
- Pt wire auxiliary electrode
- Ag/AgCl reference electrode
- Polishing Kit
- Potentiostat
- AfterMath Software
- KNO_3
- 100mM Potassium Ferricyanide
- Distilled water

Group A Solutions;
- 250mL of 0.1M KNO_3: 2.528g used, diluted to 250mL
- 100ml of 100mM potassium Ferricyanide in 0.1. 2,5,8mM: 0.2mL, 0.5mL, 0.8,mL used.

Method as shown in Torriero, A. A. J., Practical Class 2: Electrochemical Reduction of Ferricyanide at a Platinum Electrode. In SLE338 Electrochemistry for a Sustainable Future – laboratory instructions[2].

Results and Discussion:

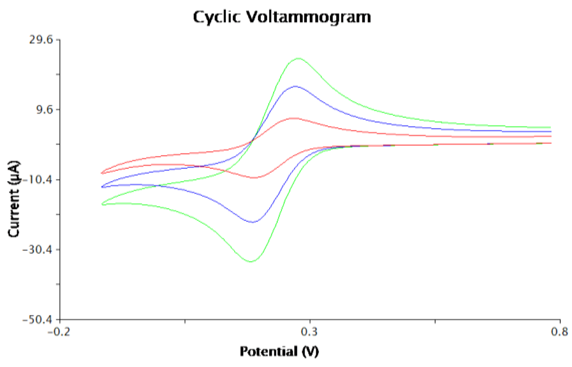

Figure 1: *Cyclic Voltammogram from AfterMath software plotting potential against current. Overlay of electrolyte concentrations of 2mM, 5mM and 8mM at a scan rate of 0.1V/s, initial and final potential of 0.8V and a vertex potential of -0.1V.*

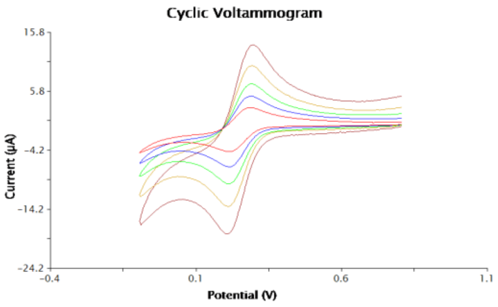

Figure 2: *Cyclic voltammogram from AfterMath software plotting potential vs current. Overlay of 2mM electrolyte concentration at scan rates 0.02, 0.05, 0.1,0.2,0.4. initial and final potential of 0.8V and a vertex potential of -0.1V.*

v1/2	V	Epa (mV)	Epc (mv)	ipa (uA)	Ipc (uA)	ipa/ipc (uA)	epa-epc (mV)	E^0	D
0.141	0.02	278.19	206.7	3.6418	-4.1765	-0.87197	71.49	242.445	5.74241E-06
0.224	0.05	283.35	202.16	5.4691	-6.3994	-0.8546	81.19	242.755	5.18028E-06
0.316	0.1	282.7	202.2	7.4441	-8.8027	-0.84566	80.5	242.45	4.79862E-06
0.447	0.2	277.87	206.67	10.5463	-12.2826	-0.8586	71.2	242.27	4.81573E-06
0.632	0.4	288.83	196.69	12.8558	-15.9943	-0.80378	92.14	242.76	3.57791E-06

Table 1: *Information obtained from figure 2 using peak current and peak potential to analyse the effect of different scan rate on the same electrolyte concentration (2mM).*

		peak potential mV		peak current uA				
conc. (mM)	scan rate (V/s)	Epa	Epc	ipa uA	ipc	ipa/ipc	epa-epc (mV)	E^0
8	0.1	293.7	197.7	29.5623	-32.7697	-0.902	96	245.7
5	0.1	287.5	202.8	19.4979	-21.3953	-0.911	84.7	245.15
2	0.1	282.7	202.2	7.4441	-8.8027	-0.84566	80.5	242.45

Table 2: *Information obtained from figure 1 showing effect of electrolyte concentration on peak potential and peak current using the scan rate (0.1V/s).*

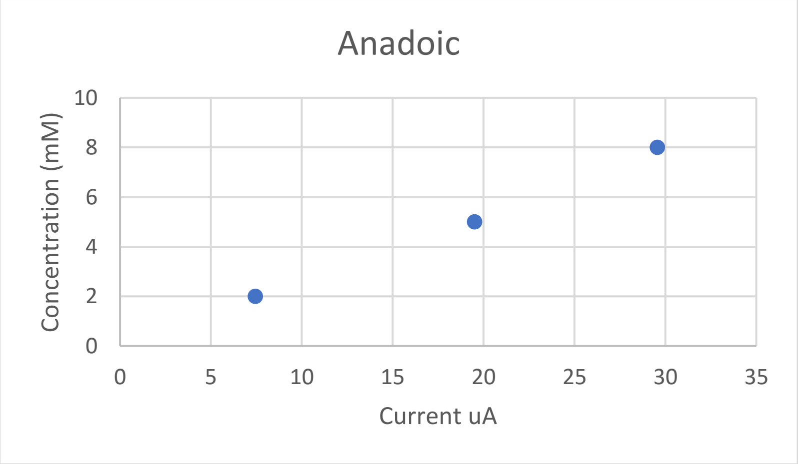

Figure 3: *Plot of concentration vs current for the anadoic peak to show linear relation of concentration on peak current using information from table 2.*

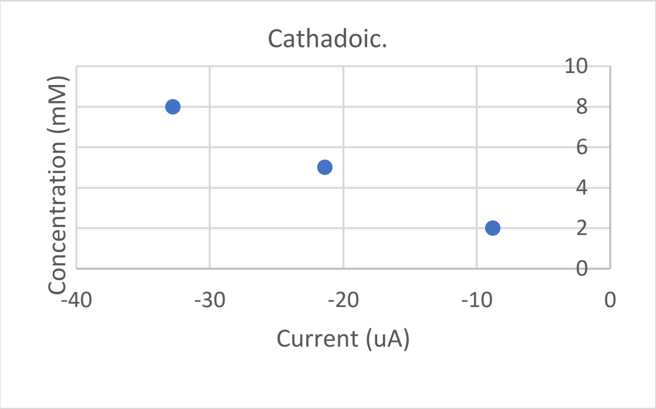

Figure 4: *Plot of concentration vs current for the cathadoic peak to show linear relation of concentration on peak current using information from table 2.*

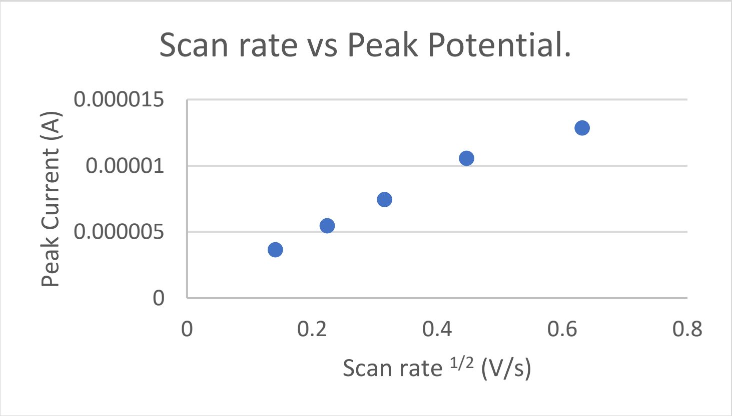

Figure 5: *scan rate* $^{1/2}$ *vs peak current plotted to determine diffusion coefficient from slope of linear equation, shown in table 1.*

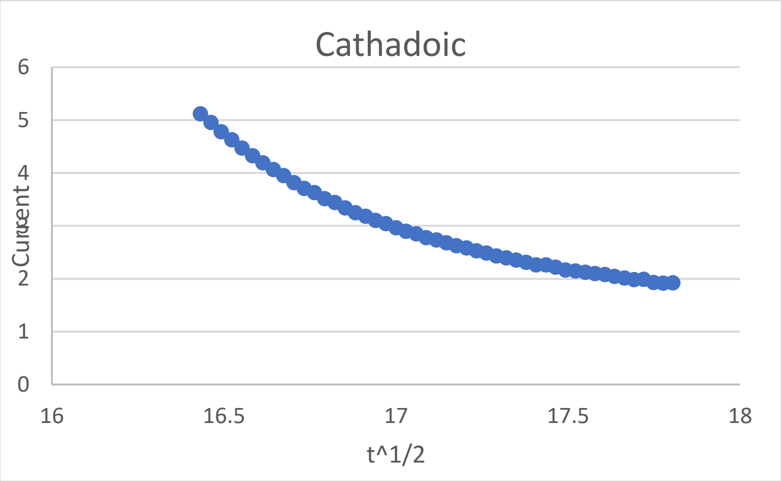

Figure 6: *current vs time*$^{1/2}$ *at the cathode. As concentration of* Fe^{3-} *decreases at the electrode, current also subsequently drops.*

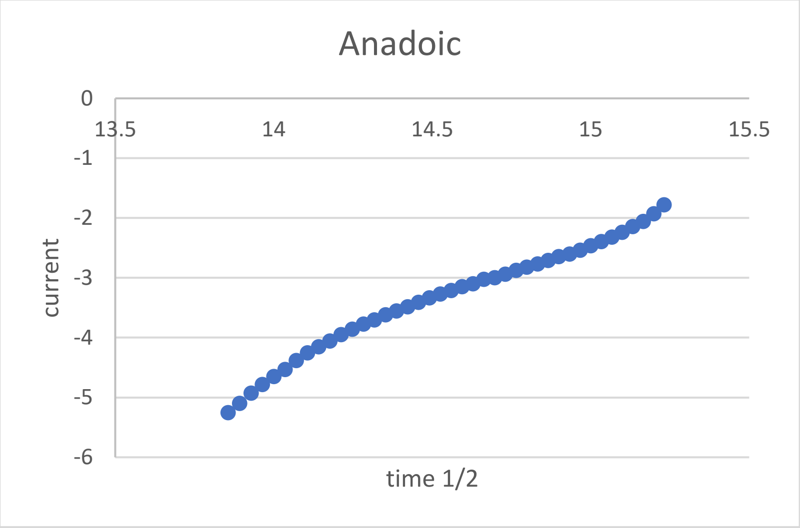

Figure 7: *current vs time$^{1/2}$ at the anode. As the concentration of Fe^{4-} increases at the electrode the current increases.*

The cyclic voltammogram provides a huge variety of information for the redox reaction occurring. By creating an overlay of the graphs at different concentrations or different scan rates as seen in figure 1 and 2, the effect of these variables can be observed. As seen in figure 1,3,4 the higher the concentration the results in a higher peak current. Figure 3 and 4 show a linear relationship indicating that as concentration increases so does the peak current this is due to the higher concentration of electrons and ions at the electrode, which therefore results in an increased current, this suggests that the reaction is diffusion controlled. The overlay also makes evident that both the reduction and oxidation reactions are occurring as there a two peaks present in the graphs. When the peak current of the cathode and the anode were divide by each other as seen in table 1 and 2 the result is quite close to one (0.8mA). This indicates that no other reactions are present within the system.

The formal potential $E^{0\prime}$ is ~242mV for all concentrations and scan rates. The formal potential for the ferricyanide/ferrocyanide reaction at 0.1M if KNO^3 is 400mV. The concentrations used in this experiment are all less than 0.1M and therefore it is expected for the $E^{0\prime}$ to be less than 400mV.

The difference between the peak potentials of the cathode and anode reactions is greater than 59V/n suggesting that the reaction is not reversible. However, the presence of two peaks in figure 1 and 2 indicate that both reactions do occur. A possible reason for the varying results may be due to uncompensated resistance, a resistance that is already present within the system. This would result in the peak potentials appearing further apart than they really are, therefore the difference in peak potential of around 80mV may not actually suggest an irreversible reaction. The peak potentials also do not vary with a change in scan rate as seen in figures 1 and 2 which is another condition which indicates the reaction is reversible. This is due to the Nerst equation which requires the potential to be independent of the scan rate.

Figures 6 and 7 show the relationship between time and current. A linear relationship indicates a diffusion-controlled reaction. However, the relationship is not completely linear suggesting that the reaction may not be completely controlled by diffusion.

The diffusion coefficient shown in table 1 show a decrease in the diffusion coefficient as the scan rate increase. The diffusion coefficient for the scan rate 0.02V/s is only slightly off (by 1.3) the literature value[2] of 0.63×10^{-5} cm^2/s this is due to the diffusion coefficient greatly depending on the concentration of the supporting electrolyte.

Conclusions:

Much of the data analysis shows that the reversible reaction is possible however the large peak potentials and the non-linear relationship between the time and current indicate that the reaction may only be quasi reversible. The hypothesis is therefore incomplete and requires further analysis under a wider variety of conditions.

References:

Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L.. A Practical Beginner's Guide to Cyclic Voltammetry, 2017.

Torriero, A. A. J., Practical Class 2: Electrochemical Reduction of Ferricyanide at a Platinum Electrode. In SLE338 Electrochemistry for a Sustainable Future – laboratory instructions, CloudDeakin, Deakin University, 2017.