Understanding the Basics of Electron Transfer and Cyclic Voltammetry of Potassium Ferricyanide - An Outer Sphere Heterogeneous Electrode Reaction

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Summary: Understanding and controlling the processes occurring at electrode/electrolyte interface are very important in optimizing energy conversion devices. Cyclic voltammetry is a very sophisticated and accurate electroanalytical method enables us to explore the mechanism of such electrode reactions. In this work, electrochemical experiments using cyclic voltammetry were performed in aqueous KCl solution containing potassium ferricyanide, $K_3[Fe(CN)_6]$ at a glassy carbon disc working electrode and the mechanism of the reactions is highlighted. The CV measurements shows that the ferricyanide $[Fe(CN)_6]^{3-}$ reduction to ferrocyanide $[Fe(CN)_6]^{4-}$ and the reverse oxidation process follows an outer sphere electrode reaction mechanism. Voltammetry analysis further indicates that the reaction is reversible and diffusion controlled one electron transfer electrochemical process. The peak currents due to $[Fe(CN)_6]^{4-}$ oxidation and the peak current due to $[Fe(CN)_6]^{3-}$ reduction increase with increase of concentration and scan rate increase. The diffusion co-efficient was determined by applying Randles-Sevcik equation. The report could be helpful for university students to understand the basics of electron transfer in redox processes and cyclic voltammetry.

Keywords: Cyclic Voltammetry; Diffusion; Electrochemical technique; Glassy carbon; Outer sphere.

Introduction

Electrochemistry involving heterogeneous electron transfers taking place at the electrode electrolyte interface, boundary between electrode electrolytes. This results in a chemical change where the electroactive specie undergoes oxidation or reduction at the electrode surface[1-3]. Understanding and controlling the processes occurring at the heterogeneous interface are very important in the optimization of energy conversion devices such as batteries, capacitors and fuel cells [4-6].

The transfer of electron (s) at the interface of electrode-electrolyte depends upon the energy gap of electrode's Fermi levels and the electroactive species molecular orbitals (MOs). The energy of electron is modulated by applying potential from the potentiostat that can change the rate of redox reactions by changing potential applied to the electrode. By applying negative potential to the electrode, the energy of the electron in Fermi level rises and eventually reaches a point where its energy is equal to that of the lowest unoccupied molecular orbital (LUMO). Hence at this point the electrons jump to LUMO of the redox specie resulting in its reduction. The energy of the Fermi level decreases below the energy of electron in the highest occupied molecular orbital (HOMO) of the species in solution by making the potential of electrode positive causing electron to

jump from the species HOMO to the electrode's Fermi level resulting in its oxidation [7,8]. The basic process is shown in Fig. 1.
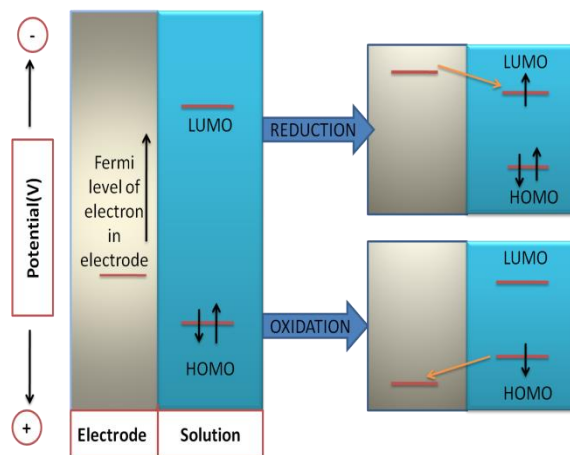

Fig. 1:   Illustration of the charge transfer energetic across the electrode/solution interface.

By partly immersing electrode in an electrolyte, an electrical double layer (EDL) formation takes place which is the structure of charge accumulation and charge separation at electrode surface [9]. Two types of heterogeneous redox reactions occur across EDL. The redox reactions in

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which the transfer of electron between electroactive species and electrode takes place by tunneling across a monolayer of solvent attracted to the electrode is called outer sphere electrode reaction (OSER) (Fig. 2 left). The rate of such type electrode reactions does not depend on the nature and composition of the electrode and depend on the reorientation of the solvent shell. The other type of electrode reaction is called inner sphere electrode reaction (ISER) in which the identity of the electrode play a decisive role. Here the reactant, product and/or intermediate species are strongly bound (specifically adsorbed) through which transfer of electron occur between the electrode and electroactive substance in solution (Fig. 2 right). The rate of these reactions may be enhanced by using different electrodes and/or electrolytes, or by even modifying the electrode surface [10].
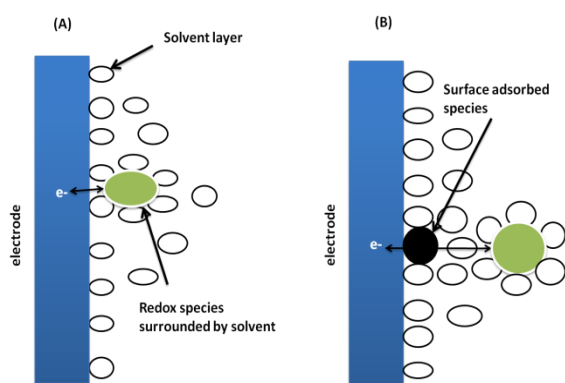

Fig. 2:   Schematic illustration of (left) outer-sphere and (right) inner-sphere electrode reactions.

Cyclic voltammetry is an important potential sweep voltammetric method to measure the response of current, I (A or μA) obtained during oxidation or reduction process occurring at an electrode with certain applied potential, E (V) at constant 'sweep or scan rate'(V s^{-1}). The current of the working electrode for the reaction of interest (either oxidation or reduction) is measured during the forward and reverse potential sweeps. The resulting plot of the potential (*x-axis*) versus current (*y-axis*) is known as a *cyclic voltammogram (CV)* [11,7]. Cyclic voltammetry is a very sophisticated and accurate electrochemical method employed during analysis of redox processes in any laboratory experiment. This technique can be used to differentiate between electrochemically reversible and irreversible reactions, inner sphere and outer sphere reactions and probe the mechanism of an electrochemical reaction [12,13] and extract sound information about understanding various oxidation-reduction reactions

taking place at the electrode/electrolytes interface [14].

Potassium ferricyanide, $K_3[Fe(CN)_6]$ is a bright red colour coordination compound and is used as an oxidizing agent in dot etching process and mutual colour correction in photography [7]. In electrochemistry, it can be used in cyclic voltammetry as standard like ferrocene and cobaltecene [15-19].

The aim of this work is to study heterogeneous electron-transfer reaction through cyclic voltammetry (CV) involving aqueous potassium ferricyanide electrolyte and determine the influence of concentration and sweep rate on its cyclic voltammogram and find out its diffusion co-efficient at a glassy carbon (GC) working electrode. The study will be helpful for undergraduate level university students to understand the basics of electron transfer reactions described in the introduction section of this manuscript and about the practical aspect of the cyclic voltammetry technique described in the experimental and results & discussion sections below.

Experimental

Reagents and Apparatus

$K_3[Fe(CN)_6]$ (98%) and KCl (≥ 95%) were from sigma-Aldrich. A computer-controlled Autolab Potentiostat (Netherland) was used for electrochemical analysis in this work.

Solution preparation

The electrochemical measurements were performed in aqueous $K_3[Fe(CN)_6]$ using KCl as supporting electrolyte. For this purpose, 3.7g KCl was dissolved in doubly distilled water to make 100 ml solution. This was 1 M KCl solution. Then, 2.5 mmol (millimole), 5 mmol and 7.5 mmol solutions of $K_3[Fe(CN)_6]$ in 1 M aqueous KCl were prepared by dissolving 0.008 g, 0.016 g and 0.024 g $K_3[Fe(CN)_6]$/10 mL 1 M aqueous KCl, respectively.

Cleaning of Glassware

Before use, all the glassware required in the experiments including the three-necked electrochemical cell were thoroughly cleaned and dried. They were first rinsed with aqueous dilute nitric acid solution, then with distilled water and finally with acetone and then dried in an oven at 100ºC.

Electrochemical Measurements

Cyclic voltammograms were taken using a potentiostat and a three-necked glass cell containing a glassy carbon (GC) as working, gold flag as counter and saturated Ag/AgCl as reference electrodes. Before using, the GC working electrode was cleaned. The cleaning of the GCE was carried out on a small polishing pad (Buehler, Lake Bluff, Illinois) by applying to its surface an aqueous 0.05 μm alumina and thoroughly polished by smoothly rubbing the electrode surface for 2 minutes. The electrode surface was then rinsed with distilled water, sonicated for 2min in an ultrasonic bath, again rinsed with distilled water and then dried in a stream of N_2. This polished electrode was then used for electrochemical measurements.

For electrochemical measurements, 10ml of the electrolyte solution was taken in the electrochemical cell. Prior to each measurement, the electrolyte was deaerated with high-purity N_2 for 20-30 minutes and a blanket of N_2 was maintained above the electrolyte during the measurements. The same procedure was adopted for cleaning the working electrode and for removing dissolved O_2 from the electrolyte solution in all of the measurements. During measurement of the reaction of interest all the three electrodes were inserted in the three necked flask and were connected to the crocodile clips of the potentiostat and the potentiostat was turn on and the respective CVs obtained.

Results and discussion

Electrochemical response of potassium ferricyanide at glassy carbon electrode

In this experiment, electrochemical reduction of ferricyanide ions to ferrocyanide and the reverse oxidation process was carried out at a 3 mm diameter GC electrode at a 50 mV s^{-1} using cyclic voltammetry. A typical CV response for the redox couple is shown in Fig. 3 for 5 mM potassium ferricyanide in 1 M aqueous KCl. In the CV, the forward sweep (anodic sweep) is shown from A to C and reverse sweep (cathodic sweep) from C to F. In the forward sweep, before point A i.e. 0.0 V there is no electrolysis. After point A (0.0 V) oxidation process starts and oxidation increases until reaches to maximum value shown by point B in the CV. At this stage the graph acquires a peak shape that shows that the oxidation process is diffusion limited. After point B the oxidation process continue with the decreasing rate of the process until at point C. In this whole process from A to C ferrocyanide is converted into

ferricyanide. At point B, the oxidation current reaches to maximum value and is called anodic peak current, i_{pa} and the potential of maxima as anodic peak potential, E_{pa}. The E_{pa} and i_{pa} in the CV are found to be 0.349 V and 1.82×10^{-5} A, respectively.

In the reverse sweep or the cathodic sweep, from point C to D the oxidation process still happen and after point D, the reduction of $[Fe(CN)_6]^{3-}$ takes place that reaches to maximum at point E where the CV again adopt a peak shape. At point E the reduction process reaches to diffusion limited. The E_{pc} is 0.195 V and i_{pc} is 3.22×10^{-5} A, and the reduction continued after point E to point F. The CV shows that ferricyanide/ ferrocyanide redox reaction is a single electron transfer process.
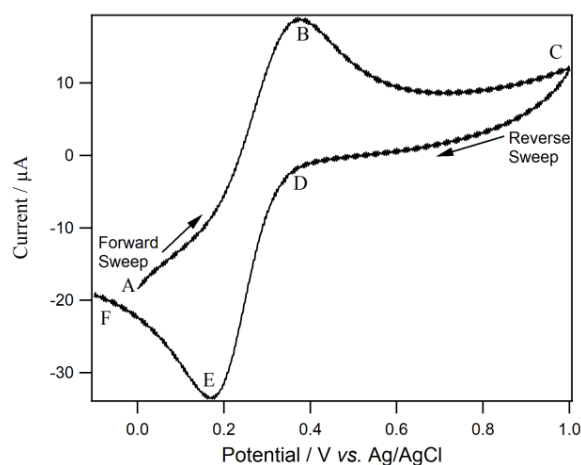

Fig. 3:   CV of 5 mM K$_3$[Fe(CN)$_6$] solution at 3 mm diameter GC vs. Ag/AgCl at 50 *mV s^{-1}*.

Effect of concentration on oxidation and reduction peak currents

Fig. 4 shows CVs of 5mM K$_3$[Fe(CN)$_6$] (Black) and 10 mM K$_3$[Fe(CN)$_6$] (Blue) at the GC recorded at 50 mV s^{-1} scan rate. The anodic peak potential is same for both the CVs. While anodic peak currents were 1.82×10^{-5} A and 2.39×10^{-5} A and cathodic peak currents were 3.22×10^{-5} A and 5.15×10^{-5} A in 5 mM and 10 mM potassium ferricyanide solutions, respectively. From the two CVs and the values of peak currents, it is evident that with the increase of concentration, the i_{pa} and i_{pc} increases. This response shows a direct relationship between peak current and concentration of the electroactive specie in solution which confirms the relation in the Randles-Sevcik equation (Eqn.1) [1].

$$i_p = (2.69 \times 10^5) A C D^{\frac{1}{2}} n^{\frac{3}{2}} \vartheta^{\frac{1}{2}}$$

(Eq. 1)

where i_p, C, A, υ , n, and D represents the peak current, concentration, the working electrode surface area, the scan rate, electron involved during reaction, and diffusion coefficient of analyte, respectively.
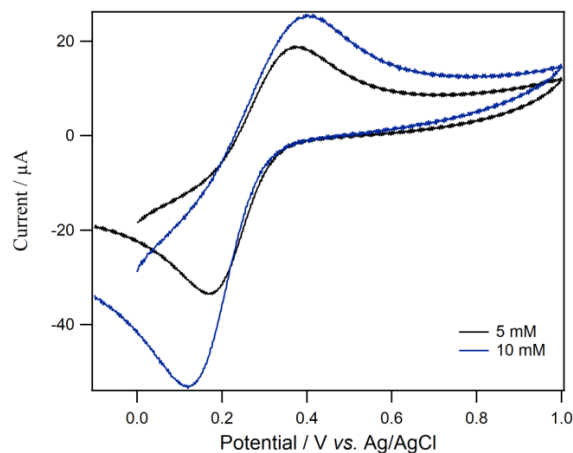

Fig. 4: CV obtained at GC *vs.* Ag/AgCl at 50 mV s^{-1}, showing the effect of K$_3$[Fe(CN)$_6$] concentration at 25 $^\circ$C.

The dependence of oxidative and reductive currents on scan rate

Fig. 5 shows CVs obtained in 5 mM K$_3$[Fe(CN)$_6$] at 50, 100, 200, 300 and 400 mV s^{-1} on GC electrode *vs.* Ag/AgCl. In each case, a well-defined anodic peak and a corresponding cathodic peak was nticed. The figure indicates that both E$_{pa}$ and E$_{pc}$ are independent on sweep rate where the i$_{pa}$ and i$_{pc}$ varies with rise in the sweep rate. The i$_{pa}$ for 50, 100, 200, 300 and 400 mV are 2.50×10^{-5}, 3.08×10^{-5}, 4.40×10^{-5}, 5.84×10^{-5}, and 6.90×10^{-5} respectively. Similarly the i$_{pc}$ for 50, 100, 200, 300 and 400 mV are 3.3×10^{-5}, 4.3×10^{-5}, 5.71×10^{-5}, 6.85×10^{-5} and 7.68×10^{-5}, respectively. Both i$_{pa}$ and i$_{pc}$ showing increasing trend with the sweep rate. The ratios between i$_{pa}$ and i$_{pc}$ are close to 1, indicating the reversible character of potassium ferricyanide 1 M aqueous KCl. The difference in peak potential (i.e. $\Delta E_p = E_{pa} - E_{pc}$) at 50 mV s^{-1} is 0.183 V for potassium ferricyanide in 1 M KCl $_{(aq)}$. The expected ΔE_p for one electron diffusion limited redox process is 0.059 V at 298 K. The high peak potential difference value compared to the ideal value is due to slow electron transfers and solution resistance which could be attributed to the grimmy and resistive nature of our electrode available in the laboratory.
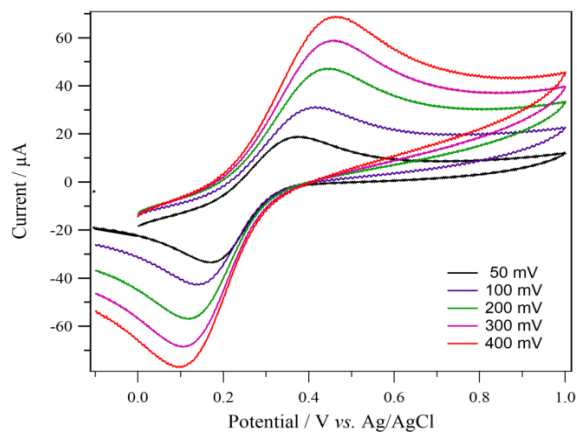

Fig. 5: CV obtained at different scan rates in 5 mM K$_3$[Fe(CN)$_6$] at GC *vs.* Ag/AgCl.

Diffusion coefficient determination for the redox couple

As evident from CVs in Fig. 5, both i$_{pa}$ and i$_{pc}$ rises with rise in the scan rate. Figure 6 is a plot of i$_{pa}$ vs. $\upsilon^{1/2}$ from which it is shown that when the scan rate increases, the i$_{pc}$ value in each case also increases showing that both i$_{pa}$ and i$_{pc}$ are proportional to $\upsilon^{1/2}$. This response is according to Randles-Sevcik equation (1) and indicating that mass transfer of K$_3$[Fe(CN)$_6$] is diffusion limited. The obtained linear relationship indicates clear diffusion character. From the slope of the plot, the diffusion coefficient D was calculated for the redox couple and the value obtained was 9.9513×10^{-8} cm^2/s. Compared to the literature value of D for the redox couple 7.63×10^{-6} cm^2 s^{-1} [20] our results show lower D value showing a slow mass transport mainly due to the roughness of the available electrode surface.

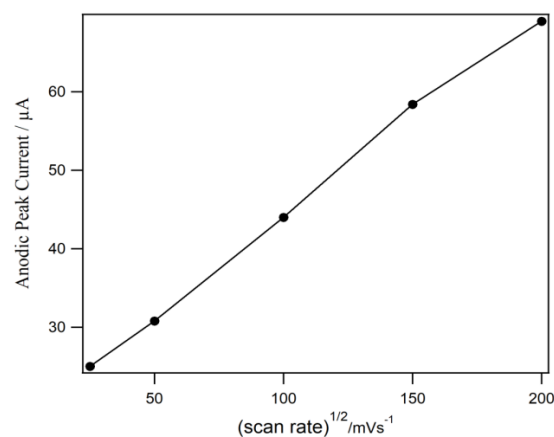Fig. 6: A plot of i$_{pa}$ *vs.* $\upsilon^{1/2}$ for 5 mM K$_3$[Fe(CN)$_6$].

Conclusions

Cyclic voltammetry measurements of potassium ferricyanide carried out at glassy carbon working electrode shows that the redox couple ($[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$) follows Randle-Sevcik equation. The peak currents due to oxidation (i_{pa}) as well as reduction (i_{pc}) of the electroactive specie enhances with enhancement of both the scan rate and bulk electrolyte concentration. This indicates that the redox process is a one electron reversible and diffusion-controlled electrochemical process. In addition, the process is an outer-sphere electrode reaction and independent on the electrode nature. The diffusion coefficients of ferricyanide determined was low compared to literature value which could be attributed to poor response of the grimy electrode surface.

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