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PRETREATMENT OF GLASSY CARBON ELECTRODE LEADING TO SURFACE MODIFICATION IN FERRO/FERRICYANIDE IN POTASSIUM CHLORIDE MEDIUM

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Potentiostatic and potential cycling pretreatments given to glassy carbon were found to accelerate the rate of ferro/ferricyanide electrode reaction in KCl medium. Interesting observations were made when these pretreatments were carried out in presence of the redox species leading to a sort of surface modification. The results of the same are discussed communication.

Key words: Glassy carbon electrode (GCE), pretreatment in ferro/ferricyanide redox medium, surface modification

INTRODUCTION

Carbon electrodes are frequently used for electroanalytical studies of oxidizable compounds [1]. However for many compounds heterogeneous charge transfer rates are very slow at carbon electrodes, leading to ill defined voltammograms [1] for which various surface treatments are recommended. While using carbon electrodes, the rich chemistry of the electrode surface also should be taken into consideration [2-4]. There are several factors which could affect the electron transfer rates based on previous history and pretreatment given to the carbon surface [4-11]. The degree of activation of the electrode surface is also an important parameter for the activity of the carbon electrode surface [12]. Controversies exist regarding the pretreatment procedures. A study of voltammetric behaviour of a simple and well known redox reaction when performed on a GC electrode subjected to different pretreatment procedures can be expected to give useful information in this regard. An investigation made in this direction did provide interesting observations which are peculiar to this system [13] and which are hitherto unreported. Moreover kinetic parameters could be evaluated and the results are reported for this system wherever possible.

EXPERIMENTAL

A three compartment cell fixed with stoppers in between each compartment and provision for introducing the working, counter and reference electrodes along with suitable luggin capillary was employed. Normal calomel electrode (NCE) was used as reference electrode. All cyclic voltammetric experiments were carried out with a potentiostat (Wenking LB 75(M) Laboratory Model) coupled to a Wenking voltage scan generator and a Rikadenki RW 201 X-Y recorder.

Electrochemical pretreatment involved (i) Potentiostatic polarization of the glassy carbon electrode at +1.5V for 30 min in H_2SO_4 or KCl containing ferro/ferricyanide as the case may be and (ii) cycling the electrode potential between +1.6 to −0.4 V at a scan rate of $1V.s^{-1}$ for 30 minutes in H_2SO_4 or KCl containing ferro/ferricyanide as the case may be.

Working solutions were prepared from pure chemicals using triple distilled water. The reactions were carried out at room temperature. The working solutions were deaerated by purging nitrogen.

RESULTS AND DISCUSSION

Emery polished glassy carbon in 1 mM ferro/ferricyanide in 0.5M KCl

The cyclic voltammetric behaviour of emery polished glassy carbon in 1 mM ferro/ferricyanide in 0.5M KCl at different scan rates (50-300 $mV.s^{-1}$) are represented in Figs. 1-3.

The cyclic voltammograms exhibit peaks in the forward as well as in the reverse scan corresponding to the oxidation of ferrocyanide and reduction of ferricyanide respectively. Peak separation, ΔEp varies from 90 mV to 160 mV over the range of scan rates employed. The cv represents a quasireversible electron transfer with large peak separation even at a slow sweep rate of $5mV.s^{-1}$ (Fig. 3 curve(a).).

Peak separation values of 70 mV at platinum, 170 mV at glassy carbon, 190 mV on edge plane of pyrolyte graphite and 380 mV for ferrocyanide reduction at carbon paste in neutral pH at a scan rate of 100 $mV.s^{-1}$ have been reported [14].

This disagreement of data on glassy carbon electrodes only indicates that GC electrodes of different origins may be different in their activity as well as in surface characteristics. The extent of polishing may also have influence on the electrode activity. E_{av} shifts to slightly positive values with increasing scan rate as the redox reaction becomes more and more irreversible with scan rate. The ratio of anodic peak current to cathodic peak current is exactly unity only at slow scan rate.

The sum of the transfer coefficients of anodic and cathodic reactions is almost equal to unity and α was calculated from the equation

$$E_p - E_{p/2} = \frac{4.8}{\alpha n} \text{ mV at 298K}$$

where E_p = peak potential, $E_{p/2}$ = half peak potential, α = transfer coefficient and n = number of electrons transferred. Diffusion coefficient values for the oxidation reaction is 1.03×10^{-5} $cm^2.s^{-1}$ and for reduction, the value is 1.15×10^{-5} $cm^2.s^{-1}$. This is in close agreement with the value reported in literature [16].

Average value of heterogeneous rate constant for oxidation is 0.68×10^{-3} cm.s^{-1} and for reduction it is 0.52×10^{-3} cm.s^{-1} [7] for GC electrode subjected to potentiostatic polarization (pretreatment 1) in 0.5M H_2SO_4.

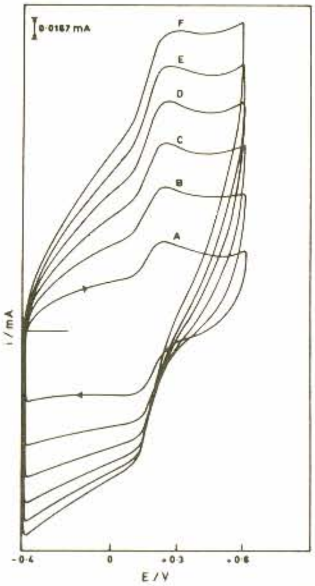

Fig. 1: Cyclic voltammetric response of emery polished GC in 1 mM ferro/ferricyanides in 0.5M KCl at different scan rates (mV.s^{-1}) (A) 50 (B) 100 (C) 150 (D) 200 (E) 250 (F) 300

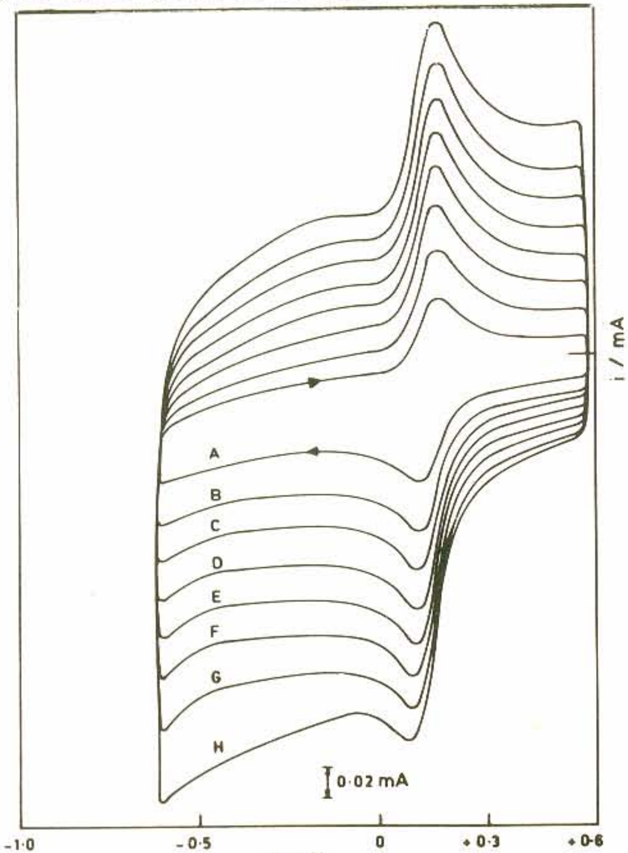

Fig. 2: Cyclic voltammetric response of electrochemically pretreated GC in 1 mM ferro/ferricyanide in 0.5M KCl at different scan rates (mV.s^{-1}) (A) 50 (B) 100 (C) 150 (D) 200 (E) 250 (F) 300 (G) 350 (H) 400

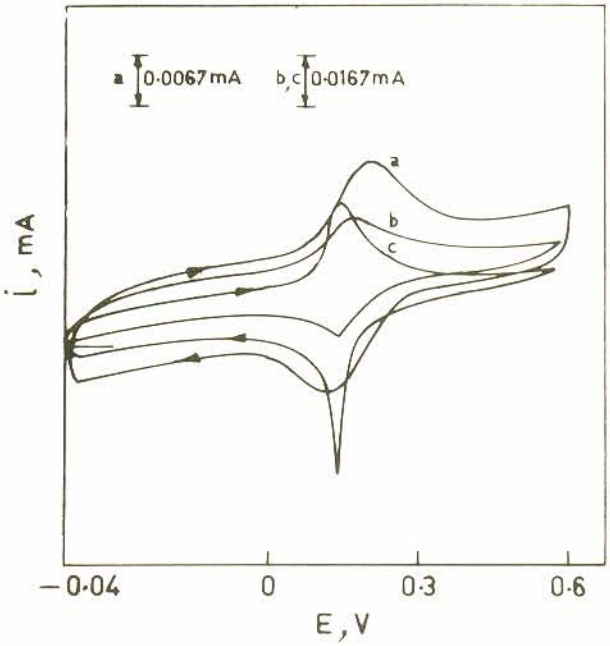

Fig. 3: Cyclic voltammetric response of GC (a) polished with emery strips, (b) electrochemically polarized in presence of the redox species (c) electrochemically cycled in presence of the redox species (sweep rate = 5mV.s^{-1})

GC electrode subjected to potentiostatic polarization at +1.5V for 30 mins. in 0.5M H_2SO_4 gives the cyclic voltammetric response represented in Fig. 2 in 0.001M ferro/ferricyanides in 0.5M KCl at different scan rates.

The peaks are well defined both in the forward as well as in the reverse scan.

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The peak separation ΔE_p which is a measure of rate of electron transfer is exactly 60 mV in the scan rate range of 50 mV.s^{-1} to 400 mV.s^{-1} revealing that the system shows good reversible behaviour on a GC electrode pretreated by potentiostatic polarization. E_{av} is 0.14V vs NCE. The peak current ratio is nearly unity over the range of scan rates employed characterizing an uncomplicated reversible single electron transfer.

The value of $i_p/Ac\nu^{1/2}$ for oxidation and reduction was calculated and found to be constant at all the scan rates studied. This confirms that the reaction is under diffusion control. The diffusion coefficient value for reduction of ferricyanide is 0.45×10^{-5} cm^2.s^{-1} for oxidation of ferrocyanide and 0.69×10^{-5} cm^2.s^{-1}.

The diffusion coefficient is assigned a value of D = 0.763 × 10 cm^2.s^{-1} in 1M aqueous potassium chloride supporting electrolyte at 298K [11] as measured chronopotentiometrically via the electrode reaction:

$$Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-} \quad \ldots (2)$$

The value of diffusion coefficient for ferrocyanide obtained in the present case agrees with the reported values.

GC electrode subjected to electrochemical pretreatment in KCl containing the redox species

GC electrode subjected to potentiostatic polarization at +1.5 V for 30 min. in 0.5M KCl containing ferro/ferricyanide gives the cyclic voltammetric response as represented in Fig. 3, curve b. It is seen from the figure that the peak is sharp during sweep in the negative direction and broad during sweep in the positive direction. This sharpening of peak in the cathodic direction is due to product adsorption on the electrode surface [18].

An important point to be noted at this juncture is that GC polished with emery strips alone does not give rise to such behaviour (Fig. 3, curve a) both due to the immediate availability of material for reaction at the surface (i.e. mass transfer is not needed) and the limited amount of reactant present. The large surface coverage by strongly adsorbed electroactive species has been responsible for the adsorption type peaks observed in the present case.

As seen from Fig. 3 (curve b), the ΔEp value is $\sim$ 20 at 5 mV.s^{-1}. The reduction in ΔEp value supports the view that the electron transfer reaction occurs through adsorbed state as discussed earlier. E_{av} value varies with scan rate to a lesser extent compared to that of emery polished GC electrode. The ratio of peak currents is less than unity suggesting that there is complication due to adsorption.

The cyclic voltammogram obtained in 1 mM ferro/ferricyanide in 0.5M KCl background electrolyte with GC electrode subjected to pretreatment (ii) in the same medium reveals interesting characteristics Fig. 3, (curve c). The peaks are sharp and narrow both in the anodic as well as in the cathodic scan. In the case of potentiostatically polarised GC it has been observed that the peaks are sharp only in the anodic direction. The observations with potential cycled electrode indicates that potential cycling between a positive and a negative potential helps in stabilizing the redox groups on the GC surface.

The electrode which has been subjected to potentiostatic polarization in all probability consists of redox groups rich in oxidized form. This surface may influence oxidation of ferrocyanide and the experimental evidence supports this view. On the other hand, a surface subjected to potential cycling will be homogeneous with respect to redox groups as a result of the negative potential limit.

The ΔEp value is 0 to 10 mV in the scan rate range of 5 to 45 mV.s^{-1} and 40 to 50 mV in the range 50 to 400 mV.s^{-1} This type of behaviour is characteristic of a surface bound redox reaction, wherein the electron transfer reaction occurs through an adsorbed state. Such observations on electrochemically pretreated GC electrode are hitherto unreported.

The following of background current as a result of potential cycling is also evident from the cyclic voltammograms. E_{av} value is $\sim$ 0.167 V which compares well with the values obtained in the case of emery polished and potentiostatically polarised electrode.

CONCLUSION

From cyclic voltammetric studies with emery polished and electrochemically pretreated GC electrode in ferro/ferricyanide in neutral KCl medium, the following conclusions have been drawn regarding the electrode behaviour. (1) Ferro/ferricyanide system exhibits quasireversible behaviour on emery polished glassy carbon in KCl medium. (2) It has been possible to get perfectly reversible behaviour with a peak separation of 60 mV over a wide range of scan rates from 5 to 400 mV.s^{-1} using a potentiostatically polarized glassy carbon electrode. (3) If the polarization or potential cycling is carried out in solution containing the redox species in solution, special type of adsorption peaks are obtained which have been found to lead to permanent electrochemical modification of the electrode surface.

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