

Simple electrochemical immobilization of the ferro/ferricyanide redox couple on carbon electrodes

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A simple novel and stable modification procedure for the incorporation of ferro/ferricyanide on to carbon surfaces is reported. By analysis of the voltammetric behaviour of the modified electrode in pure supporting electrolyte it is established that the incorporated species correspond to Prussian blue.

1. Introduction

Modified electrodes are currently the subject of intensive investigation due to their potential for such applications as improved and/or (stereo selective) electrosynthesis, photovoltaic generators, electroanalyses etc. among others. Substrate electrodes such as platinum carbon or semiconductors such as SnO_2 are permanently modified with substances containing easily oxidizable/reducible groups using procedures involving either covalent linkage between the substrate and the modifying agent or irreversible adsorption of the adsorbate molecule. The primary objective of all the modification research is to immobilize redox groups that can be reversibly cycled over prolonged periods of polarization such that they act as good electron transfer mediators to bring about electrocatalysis. In the case of carbon electrodes modification through incorporation of quinone/hydroquinone redox species either chemically or electrochemically or covalently linking with polymer films have been attempted and their catalytic activity, for example, for oxygen evolution, oxidation of organics such as ascorbic acid, NADH etc. has been demonstrated [1-8].

Attempts are also in vogue to incorporate reversible redox groups such as the ferrocene-ferricinium system. Polymer films such as poly-4 vinyl pyridine/acrylamide/vinyl pyridine gels have also been used as immobilizing agents in the above studies. A large body of literature has accumulated on this topic and is the subject matter of a review by Murray [9].

In this communication we report for the first time a simple direct and permanent modification of glassy carbon electrode by the most common and easily oxidizable/reducible redox couple - ferro/ferricyanide.

2. Experimental details

Potassium ferrocyanide and potassium ferricyanide obtained from E. Merck, Darmstadt, were used as received. 'Analar' potassium chloride was used for preparing the background electrolyte.

Cyclic voltammetric experiments were performed

with a conventional three-electrode potentiostat, a Wenking Potentiostat Generator POS73, and an X-Y recorder (Rikadenki RW 201, Japan). All potentials were measured against a Normal Calomel reference electrode (NCE).

Prior to modification the glassy carbon (GC) electrode was polished with polishing papers 1/0 to 4/0 successively.

3. Results and discussion

Glassy carbon polished with emery strips gives the expected response in 1 mM ferrocyanide in 0.5 M KCl with characteristic reversible behaviour of the anodic and cathodic peaks and ($E_{pa} - E_{pc}$) tending to 60 mV at low sweep rates ($\approx 5 \text{ mV s}^{-1}$). When the GC electrode is subjected to limited cycling between -0.4 V and $+0.8 \text{ V}$ at a scan rate of 1 V s^{-1} containing 1 mM ferrocyanide, no change in voltammetric behaviour was observed. However, when the anodic potential limit was extended up to $+1.5 \text{ V}$ and cycled between -0.4 and $+1.5 \text{ V}$ for 30 min at 1 V s^{-1} in 1 mM ferro cyanide or, preferably, in an equimolar mixture of ferro/ferricyanide in 0.5 M KCl, the response represented in Fig. 1 was obtained whilst the ferro/ferricyanide species were present in solution with E_{pa} at 0.16 V and E_{pc} also at 0.16 V.

The following features are conspicuous in the voltammograms brought about by the cycling pretreatment. (1) Reduction in the peak separation between E_{pa} and E_{pc} (ΔE_p) approaches zero volts at a scan rate of 0.005 V s^{-1} suggesting that adsorption of redox species is involved in the electron transfer reaction. (2) Sharp and narrow peaks (Fig. 1) for oxidation, as well as reduction, again characterize adsorption behaviour. (3) Enhancement of the peak current value for oxidation and reduction by roughly 2.5 times when compared to the current values obtained with an emery polished GC electrode (electrodes without pretreatment). Even though catalytic activity (for example towards ferrocyanide oxidation) was observed with a GC electrode electrochemically pretreated in 0.5 M H_2SO_4 , medium, adsorption type peaks (with $\Delta E_p \rightarrow 0$) were not observed as in the

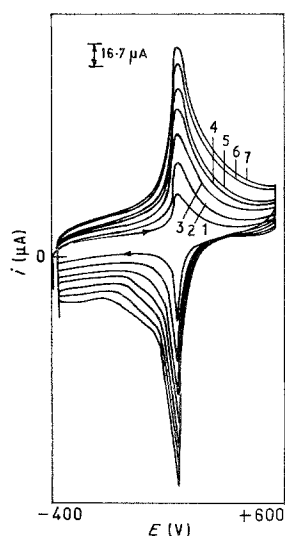


Fig. 1. Voltammetric response of a glassy carbon electrode subjected to modification pretreatment in 1 mM ferro/ferricyanide. Scan rates from (1) 0.005 V s^{-1} to (7) 0.035 V s^{-1} in steps of 0.005 V s^{-1} . $E_{pa} = 0.16 \text{ V}$, $E_{pc} = 0.16 \text{ V}$ at 0.005 V s^{-1} .

present case. Further, it is significant to note that the GC electrode, after thorough washing with water, gave the response represented in Fig. 2 in pure 0.5 M KCl with no ferro/ferricyanide in solution, thereby indicating the incorporation of surface redox groups on the GC surface. Catalysis of such surface incorporated redox groups towards the model ferro/ferricyanide system showed far greater current response (several fold - typically ten times) as compared to unmodified electrodes.

The redox behaviour exhibited by the electrode in Fig. 2, which is characteristic of a surface reaction even in solutions devoid of the redox species (ferro/ferricyanide), is new. No reports exist in the literature suggesting the incorporation of the above redox species even though a voluminous literature exists on this GC system. The linear plot of i_p against scan rate (Fig. 3)

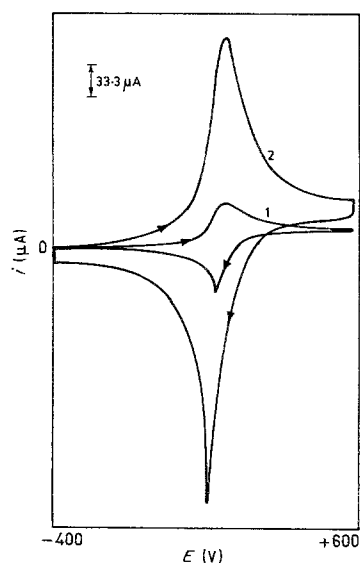


Fig. 2. Voltammetric response of a modified glassy carbon electrode in 0.5 M KCl. Scan rates: (1) 0.005 V s^{-1} , (2) 0.05 V s^{-1} . $E_{pa} = 0.16 \text{ V}$, $E_{pc} = 0.16 \text{ V}$ at 0.005 V s^{-1} .

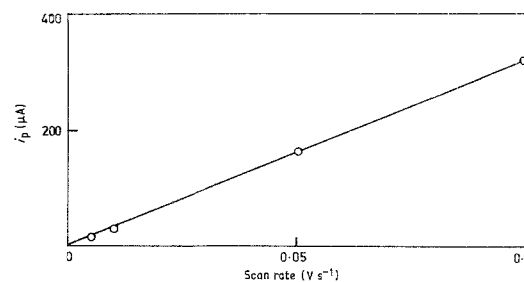


Fig. 3. Typical linear plot of peak current against scan rate for a modified electrode in 0.5 M KCl medium.

further confirms a surface reaction by the bound redox groups.

The response of the modified electrode, after a few polishings with emery strips, is represented in Fig. 4 at different scan rates, again in pure supporting electrolyte, viz 0.5 M KCl. It is interesting to note that polishing reduces the peak current values but is insufficient to completely remove the incorporated redox species from the surface. This confirms that modification was not only permanent but occurred in depth on the GC surface.

Typical values of surface coverage by the adsorbed cyanide molecules from the recorded voltammograms by integration of the current peaks, corresponded to $2.4 \times 10^{-9} \text{ mol cm}^{-2}$. Incidentally it is reported [9] that the quantities of electroactive centres in the modified films range from about 10^{-10} to about $5 \times 10^{-6} \text{ mol cm}^{-2}$, that is from 1 to 20 000 monolayers.

Although the nature and mode of incorporation of redox groups is not immediately clear, all the experimental results presented above confirm the permanent modification of the GC. Ferro/ferricyanide in KCl is one of the most widely studied systems although no previous reports indicate its permanent incorporation on carbon. However, modification is not found to take place in experiments in which cycling within

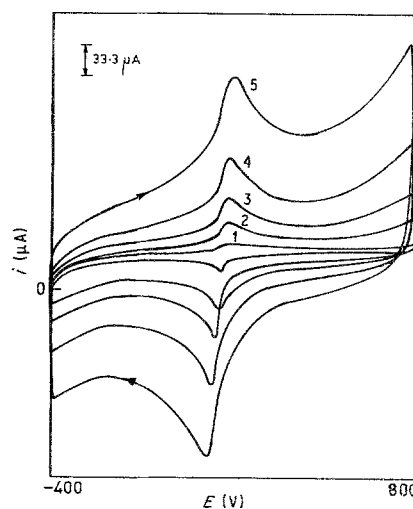


Fig. 4. Voltammetric response of insufficiently polished GC electrode (after modification) in 0.5 M KCl. Scan rates: (1) 0.005 V s^{-1} , (2) 0.01 V s^{-1} , (3) 0.05 V s^{-1} , (4) 0.1 V s^{-1} , (5) 0.2 V s^{-1} . $E_{pa} = 0.15 \text{ V}$, $E_{pc} = 0.15 \text{ V}$ at 0.005 V s^{-1} .

limited anodic potential values (up to +0.8 V or even 1 V) is carried out as described earlier. It is understood that the modification is necessarily associated with the oxidation of the GC surface and the localized acidity provided by the phenolic and/or carboxylic groups generated at +1.5 V, which was employed by us for pretreatment in order to obtain modification. Furthermore, results of experiments carried out in different media containing the ferrous/ferric system confirmed that modification is only obtained in the ferro-ferricyanide system [10]. The above observations, together with the fact that the Prussian blue/Prussian white system containing ferricyanide has a redox potential in close proximity to that of the modified couple, lead us to suspect that the incorporation of the redox species may be associated with the formation of some Prussian blue on the surface. However, the reported [11] solution composition and experimental (electrolytic) conditions for Prussian blue formation are entirely different from the present conditions with respect to solution composition as well as hydrogen ion concentration [12]. Under the present conditions, at the potential of oxidation of the carbon surface wherein hydroxyl and carboxyl groups are generated, the localized pH change [14] could cause some dissociation of ferrocyanide to liberate free Fe(II) ions which would be oxidized to Fe(III) ions at the potential of +1.5 V (maintained in our experiments) and may combine with ferrocyanide forming Prussian blue

(Ferric-Ferrocyanide). Even though the mode of incorporation of redox species is different in the present case from the usual covalent linking procedure [9] the adsorption noticed appears to be strong, leading to permanent surface modification.

Finally, the inference made above on the involvement of Prussian blue in the modification gained support from the observation of a second redox couple Prussian blue/Berlin green on the surface, as manifested by a reversible peak at ≈ 0.9 V (Fig. 5) [13] when the potential scan was extended to 1.0 V during cycling using our modified electrode in the 0.5 M KCl medium. It can thus be inferred that the present work opens up a new route for electrochemical modification of carbon electrodes with Prussian blue, an observation of considerable practical interest considering the use of Prussian blue, in a number of device applications incorporating electronic display and batteries [13–16]. Work is now in progress using the present procedure to modify GC electrodes by substituting Fe(III) in Prussian blue with Ni, Cu, Co, Mo, Cr etc. and to study the catalytic properties of such modified electrodes. Platinum electrodes were also found to be modified similarly and so are being investigated.

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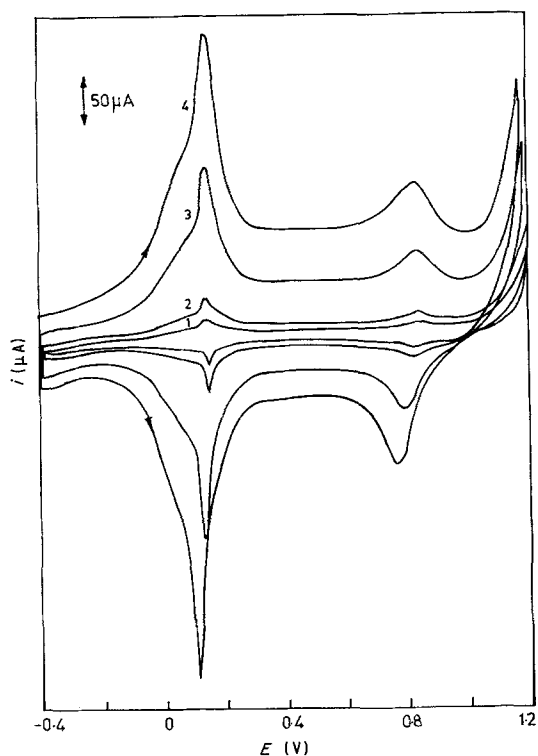


Fig. 5. Cyclic voltammetric response of modified GC electrode in 0.5 M KCl when the scan is extended to 1.2 V. Scan rates: (1) 0.005 V s⁻¹, (2) 0.01 V s⁻¹, (3) 0.05 V s⁻¹, (4) 0.1 V s⁻¹.