

INORGANIC CHARGE TRAPPING INTERFACE CONTAINING PRUSSIAN BLUE AND COPPER HEXACYANOFERRATE

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Ion exchange of Prussian Blue with transition metal ion leading to the formation of corresponding analogues is reported. Bilayers of Prussian Blue/CuHCF were constructed by a procedure involving the ion exchange of Fe^{2+} in Prussian Blue with Cu^{2+} leading to the formation of CuHCF overlayers. The bilayer thus formed shows interesting charge trapping characteristics due to restricted cation/electron movement through the film interface. UV-vis spectra and X-ray diffraction patterns give evidence for the bilayer formation and cyclic voltammetry is employed to show the effect of bilayers on electron/ion transfer.

Keywords: Ion exchange, Prussian Blue and X-ray diffraction.

INTRODUCTION

Work on polymeric bilayer electrodes has generated interest in recent literature, based on the expectation that polymer/polymer hetero junction may serve as a charge trapping interface, allowing for unidirectional charge transport [1-6].

Organic conducting polymers that can be reversibly switched between two redox states have been used as components of bilayer and multilayer electrodes. It is possible to design junctions between a conducting polymer and a redox polymer or between two conducting polymers. The sequence of outer film charge trapping and untrapping reactions has been demonstrated with several combinations of redox polymer films [1-3].

The factors governing the ultimate stability of a trapped outer polymer film redox state and the rate at which outer film redox states can be trapped and untrapped remain unclear [4]. The phenomena has been demonstrated so far only with regard to organic conducting polymers.

Formation of mixed metal hexacyano ferrate films of Ni-Fe and Mn-Fe was reported from this laboratory [7] wherein the interesting possibility of substitution of high spin iron centers of Prussian Blue with Ni^{2+} and Mn^{2+} ions in the low spin centers was indicated.

The chemistry and electrochemistry of films of mixed MHCF have come to focus more recently [8-10], in which the authors employ mechanically immobilized PB or mixture of PB analogue powders that were obtained by chemical precipitation in solution.

These investigations employing suitable carbon substrates on which the MHCF powders were introduced by physical contact, investigated their electrochemical behaviour on potential cycling with a view to correlate their observed responses with compositional and structural transformations in such films. It may be reiterated here that exploration of

- i) the feasibility of the entry of a second metal ion into the PB lattice [11] during electrochemical cycling leading to mixed MHCFs and

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ii) the possible route through which it takes place (in the event it enters the PB lattice), whether through channels or through lattice sites of the latter is of considerable interest both from the view point of basic studies as well as applications. In a recent publication from this school [10], formation of bilayered composites involving epitaxial growth of two MHCFs is inferred from the observations of absence of any deceleration effect on electron and ion transfer through them.

In the present communication we demonstrate that GC/Prussian Blue/Copper hexacyanoferrate can act as a charge trapping/untrapping interface under suitable experimental conditions and some preliminary voltammetric observations on this system are reported.

EXPERIMENTAL

An all glass three electrode cell assembly was used for the experiments Glassy carbon (BAS) served as working electrode (area = 0.07 cm²). A Pt foil 2 cm² served as counter electrode. All the potentials are referred to a Normal Calomel Electrode (NCE).

A Wenking Potentiostan POS 73 coupled with Rikadenki recorder Rw 201 were used to record the cyclic voltammograms.

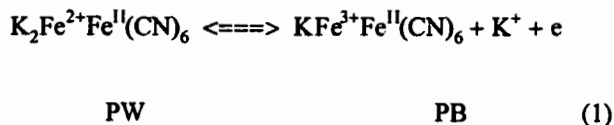
Electrochemical modification of Prussian Blue on GC was achieved by cycling the working electrode potential from 0 V to 1 V in a medium containing 0.5 M KCl + 0.1 M HCl + 0.5 mM K₃Fe(CN)₆ + 0.5 mM FeCl₃ at 0.1 Vs⁻¹ for 15 cycles. The modified electrodes were characterized in 1 M KCl solution.

The Prussian blue modified electrode was cycled in 0.01 M CuSO₄ in the potential range 0 V to 1 V at a sweep rate of 0.1 Vs⁻¹ for further modification of Prussian Blue. UV-VIS spectral measurements were performed using Hitachi U-3400 and XRD measurements using Jeol JDX 8030. ITO glasses (< 20 ohm/cm²) were employed for XRD measurements.

RESULTS AND DISCUSSION

Fig. 1 shows the typical cyclic voltammogram of Prussian Blue modified electrode prepared according to the procedure described in the experimental section. The two redox processes seen at 0.19 V and 0.85 V are assigned to the transitions PW \rightleftharpoons PB and PB \rightleftharpoons PY transition respectively. The corresponding reactions are represented as follows.

At 0.19 V



At 0.85 V

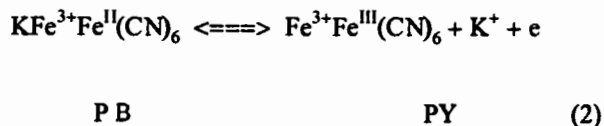


Fig. 2 shows the voltammetric behaviour of the first and subsequent cycles of the same electrode in 0.5 M KCl after treating the electrode in 0.01 M CuSO₄ for 10-12 cycles at 0.1 Vs⁻¹. This treatment causes the disappearance of the redox peak due to high spin iron redox reaction at 0.19 V (Fig. 2). On the other hand, new redox processes could be seen at 0.45 V and 0.65 V. The

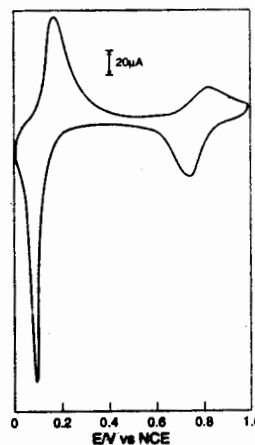


Fig. 1: CV response of Prussian Blue modified electrode in 1 M KCl sweep rate 0.02 Vs⁻¹

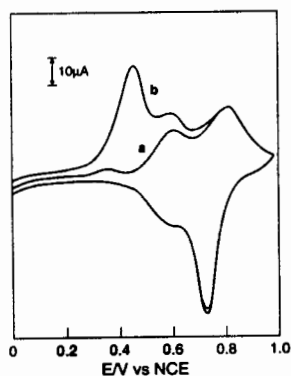


Fig. 2: First cycle (a) and subsequent cycle (b) response of Prussian Blue modified electrode precycled in 0.01 M CuSO₄ for 10 cycles at 0.100 Vs⁻¹ in 0.5 M KCl

former one is totally irreversible and the latter is well reversible among the two processes.

Fig. 2 shows the CV response in the subsequent cycles of the above modified electrode. The new redox process developed at 0.65 V and the redox reactions corresponding to redox reactions of low spin iron of PB at 0.85 V remain stable over a number of cycles while the peak at 0.45 V observed in the first scan was not seen in the subsequent scans.

The new redox couple seen at 0.65 V can be identified as resulting from the formation of copper hexacyanoferrate (CuHCF) by comparing the redox potential with that of CuHCF modified electrode [12-13]. The formation of CuHCF proceeds through ion exchange according to eqn.



The above process is confirmed by an experiment by cycling the electrode for more than 10 cycles at a sweep rate of 100 mVs⁻¹ in CuSO₄ solution which resulted in the complete conversion of PB to CuHCF as seen from Fig. 3.

This result is further confirmed by UV-vis spectrum of Prussian Blue film and the film cycled for 10 minutes in Cu²⁺ solution as seen from the Fig. 4. XRD results also indicate a clear shift in

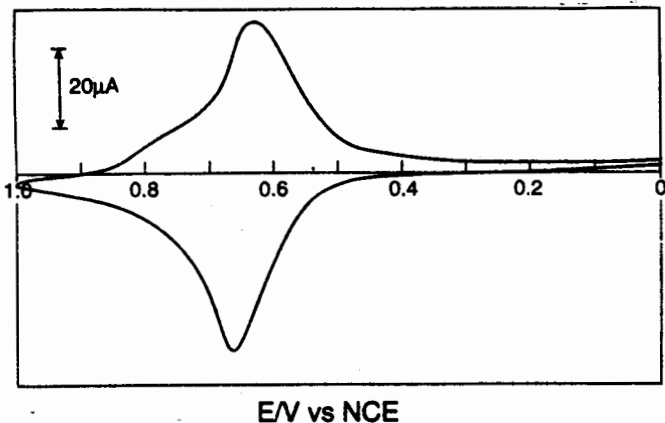
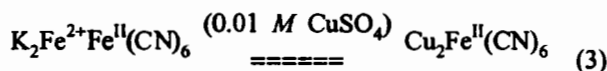


Fig. 3: CV response of Prussian Blue modified electrode after 10 minutes cycling in 0.01 M CuSO₄ in 0.5 M KCl

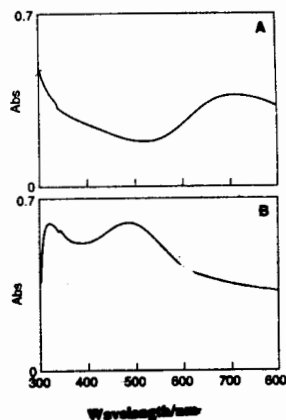


Fig. 4: UV-VIS spectra of (a) ITOs coated with Prussian blue and (b) Prussian Blue cycled in 0.01 M CuSO₄ for 10 minutes

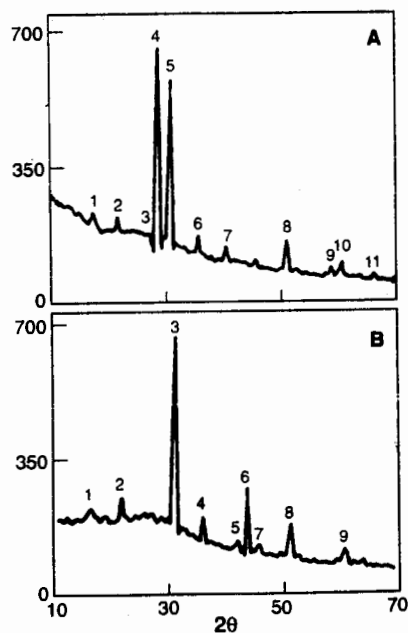


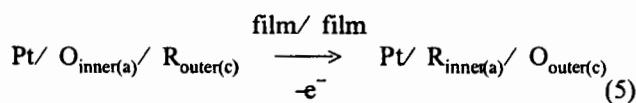
Fig. 5: The XRD patterns of (a) Prussian Blue modified film on ITO and (b) the film after 12 cycles in 0.01 M CuSO₄ solution

the 'd' values which offer evidence for the incorporation of Cu^{2+} into the PB lattice as seen from the XRD patterns of (a) Prussian Blue film and (b) Prussian Blue film cycled for 12 cycles in CuSO_4 (Fig. 5).

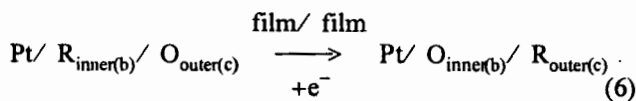
In the case of electrodes modified with mixed hexacyanoferrates the redox process corresponding to all the MHCFs could be seen in the case of PB-MHCF composites ($M = \text{Ni}, \text{Mn}$ etc.) [7]. The voltammetric features obtained in the present study are entirely different from the ones reported for mixed analogues. The voltammetric pattern resembles a bilayer electrode of PB and CuHCF (Fig. 2). When the PB modified electrode is cycled in CuSO_4 solution, the outer layer of PB is converted to CuHCF by ion exchange and it proceeds inwardly till all the high spin Fe^{2+} is replaced by Cu^{2+} . When the exchange is partial, only few layers are converted to CuHCF and the inner layers remain intact as PB resulting in a bilayer electrode.

The scheme suggested by Pickup *et al.* [14] for charge trapping/untrapping is given below and it is adopted to explain the bilayer formation in the present case.

Charge trapping

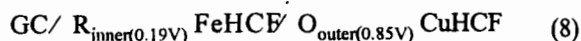
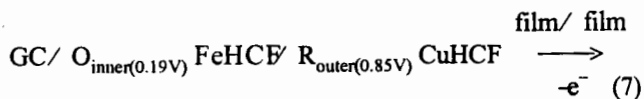


Charge untrapping

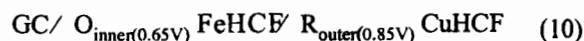
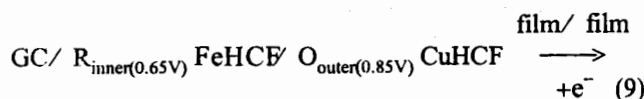


Following this scheme in the present case, the three potential levels correspond to a ~ 0.19 V, b ~ 0.65 V and c ~ 0.85 V and charge trapping and untrapping processes can be represented as follows.

Charge trapping



Charge untrapping



Cyclic voltammetric behaviour of the bilayer electrode presented in the Fig. 2 can be explained by the above scheme and the mechanism is discussed in the following.

In the case of PB and its analogues, the electron transfer is accompanied by intake or expulsion of counter cations as seen from eqns (1,2). When the potential of the electrode treated in solution containing Cu^{2+} is scanned from 0 V to 1 V in 0.5 M KCl, no peak could be seen at 0.19 V

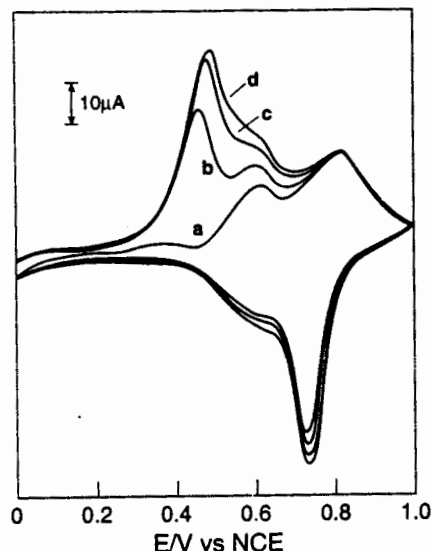


Fig. 6: First and subsequent cycle response of Prussian Blue modified electrode precycled in 0.01 M CuSO_4 for 10 cycles at 0.1 Vs^{-1} in 0.5 M KCl with different hold up times in minutes (a) 1 (b) 3 (c) 5 (d) 6

where the oxidation of Fe^{2+} of PB should have occurred. During this electron transfer, the concomitant expulsion of K^+ has to take place through the overlayer of CuHCF. Oxidation of CuHCF starts only at 0.40 V.

At this potential, the expulsion of K^+ from the inner PB layer and CuHCF outer layer takes place along with the oxidation of Fe^{2+} to Fe^{3+} which is shifted to 0.45 V in presence of the newly formed CuHCF overlayer.

No reduction peak corresponding to that of inner PB layer Fe^{3+} to Fe^{2+} is seen during the reverse scan. In other words, charge in the inner layer is trapped in its oxidised state in the event of formation of a CuHCF overlayer. This charge trapping is invariably associated with restricted flow of counter cations as seen from the shift in the anodic peak potentials as well as the absence of cathodic counter part during the scan reversal.

Again the appearance and persistence of peak at 0.45 V corresponding to the oxidation of Fe^{2+} greatly depends on the hold up time at 0 V (0 to 6 min was allowed) wherein slow diffusion of K^+ from solution could take place. This phenomenon is illustrated in Fig. 6, in which untrapping of the oxidized state is clearly seen from the enhanced peak current in the subsequent cycles.

When the PB coated electrode is cycled in 0.5 M KCl containing 2 mM CuSO_4 and the starting potential is shifted to -200 mV the following interesting observations are made.

- i) there is enormous increase in current (> 3 fold) in the redox centre associated with PB \rightleftharpoons PW transformations
- ii) the new redox peak appearing at 0.65 V greatly influences the redox reactions at 0.19 V and 0.85 V.
- iii) the stabilized response is marked with three redox reactions at 0.19 V, 0.65 V and 0.85 V all being reversible and
- iv) the disappearance of PB \rightleftharpoons PW redox transition and complete conversion to CuHCF is not noticed in this case, when cycled in 0.5 M KCl.

Since the starting potential of -200 mV is favourable for the existence of $\text{Cu}^+/\text{Cu}^{2+}$ ions in equilibrium, in the KCl medium the involvement of Cu^+ ions in the redox transitions of PW \rightleftharpoons PB has to be invoked, being responsible for enhanced currents and needs to be further substantiated by *in-situ* XRD measurements.

CONCLUSION

The Prussian Blue films on solid electrodes undergo lattice substitution of the high spin iron with transition metal ions like Cu^{2+} to yield the bilayers of PB/CuHCF. The charge trapping properties of these bilayers are interesting and offer scope for controlling directional electron transfer by a judicious choice of a combination of transition metal cations.

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