MODIFIED ELECTRODES WITH METAL HEXACYANOFERRATES

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Metal hexacyanoferrates have generated much interest in the recent past. They find application in electrocatalysis, ion-exchange, electrochemistry, photoelectrochemistry, etc. In this review, the preparation and characterization aspects of modified electrodes with hexacyanoferrates are presented. Analogues of hexacyanoferrates are also briefly discussed.

INTRODUCTION

Chemically modified electrodes offer interesting, novel and useful interfaces with electrolyte solutions. In contemporary electrochemistry, modified electrode is an electrode, the surface of which is manipulated by derivatizing it in such a way that the electrode thereafter exhibits the chemical, electrochemical, optical and other properties of the derivatised/imobilized molecules. Such modified electrodes with improved interfacial properties have potential applications in stereoselective electroanalysis, photovoltaic generators, electrodeposition, etc. Substrate electrodes such as platinum, carbon or semiconductors (e.g. SnO2) are permanently modified with substances containing easily oxidisable/reducible groups using procedures involving covalent linkage between the substrate and the modifying agent or by the irreversible adsorption of the adsorbate molecules. The large volume of literature on this topic has been reviewed by Murray [1].

In recent years, the electrochemistry of metal hexacyanoferrates has gained good attention in view of the stable surface modification with these compounds [2]. The present review is an account of these developments highlighting the preparation and characterisation aspects of such modified electrodes along with some important properties pertaining to ion transport, photoelectrochemical behaviour and electrochromism of such modified surfaces.

HISTORICAL DEVELOPMENT

Prussian Blue (PB) is an important pigment for paints, lacquers, and printing ink [3]. There are two proposed forms of PB, designated as “water insoluble PB” Fe₄[Fe(CN)₆]₃ and “water soluble PB” K₄Fe₄(CN)₆ [4,5]. It has been shown that the chemical reduction and oxidation of PB can lead to Prussian white (Everitts salt) and Prussian green (Berlin green), respectively [4-6]. The PB and its analogues have fcc crystal structure with a lattice constant of about 10 Å [7].

Thin films of PB can conveniently be deposited by chemical means or electrodeposited by galvanostatic [8] potentiostatic [9] or potential cycling [10] methods. The presence of two redox centres in the PB molecule gives rise to two distinct redox peaks in the cyclic voltamogram as shown in Fig 1. These two redox transitions correspond to PW → PB at 0.2 V and PB → BG at 0.8 V vs SCE, respectively, as depicted by equations 1-4. At 0.2V

\[ \text{K}_4 \text{Fe}_4[\text{Fe(CN)}_6]_3 - \text{K}^+ + e^- \rightarrow \text{KFeFe(CN)}_6 \ldots (1) \]

At 0.8V

\[ \text{KFeFe(CN)}_6 - \text{K}^+ + e^- \rightarrow \text{FeFe(CN)}_6 \ldots (3) \]

\[ \text{Fe}_4[\text{Fe(CN)}_6]_3 - 3e^- + 3\text{A}^- \rightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 \ldots (4) \]

Fig 1: Cyclic voltammetric response of PB modified electrode in 0.5M KCl.
Scan rate 50 mV/s⁻¹

ION EFFECTS

The fcc structure of PB and its analogues allows only alkali metal cations in their channelled structures. Therefore, the studies on the ability of different electrolyte cations to get into the cage structure have gained considerable attention. Such studies using electrodes modified by conventional procedures [5-7] are discussed in detail. The entry and exit of cations during oxidation/reduction necessitated by the electroneutrality considerations of the film have been studied by cyclic voltammetry by Ozeki et al [11]. A quantitative demonstration of the ion incorporation in the crystal structure referred to above was achieved through studying the weight change of the film during oxidation/reduction, using a quartz crystal microbalance [12]. The ion permeability seems to depend on the hydrated diameter of the cation judging from studies similar to the above extended over a large number of cations viz. K⁺, Na⁺, NH₄⁺, Rb⁺, Cs⁺, etc. Investigations using PB films prepared in our laboratory [13] revealed the unique reversible response characteristics in the presence of Na⁺ in CV suggesting the uptake...
and release of the sodium cation in the lattice of PB to be highly reversible (Fig. 2). Besides, the splitting of the CV peaks reveals the possible existence of two forms of sodium incorporated PB species. Similar observations are noted in the cobalt analogue of PB which will be discussed later.

Fig. 2: Cyclic voltammetric response of PB modified electrode in 0.5 M NaCl. Scan rate 50 mV s\(^{-1}\).

The shift in the Nernst potential amounting to 60 mV/decade concentration change exhibited by many PB or its analogues make them suitable candidates as ion selective electrodes. For device applications, appreciable sensitivity to a given cation in the presence of other alkali and alkaline earth cations is required. However, systematic studies on ion selectivity using PB and different analogues may be rewarding.

**ELECTROCATALYSIS**

The presence of two well defined reversible redox centres facilitates the electrocatalytic uptake of PB to mediate the electron transfer. Moreover, the two iron centres in PB, different in their channel environment (as a result of coordination to the adjacent carbon or nitrogen atom in the crystal lattice), can be profitably exploited for site selective electrocatalytic applications. Accordingly, it has been demonstrated [14] that ascorbic acid can undergo catalytic oxidation through mediated electron transfer at the first redox centre at 0.2 V involving ferrous/ferric moieties and the hydrazine sulphate at 0.75V involving ferro-ferricyanide moieties at the second redox centre, respectively. The surface bound outer sphere ferrous/ferric redox centre was also catalytic to the oxidation of the ferrocyanide in solutions [13]. The oxidation of ascorbic acid at the PB-modified glassy carbon electrode was also demonstrated by Dong et al [15]. Parallel efforts were made in our laboratory [15a] and by Dong [15] to modify Pt/carbon fibre microelectrodes with PB and study the catalysis of ascorbic acid oxidation using such modified microelectrodes. Such studies have wide applications in the in vivo analysis of biological systems. Our studies indicate that the thickness of PB on the electrode surface has profound effect on the electron transfer mediation abilities of PB. When the thickness is increased, catalytic currents for the ascorbic acid oxidation diminished; for thickness more than 3 µM, the films were not catalytic indicating that the charge transfer becomes slower at higher thicknesses.

**POWER SOURCES**

Since the PB is a mixed valent iron complex which can be both reduced and oxidised reversibly, it can store both negative and positive charges. Thus it could serve as an active material in both the anode and the cathode of secondary batteries. A secondary battery using PB at both the electrodes and with KCl in nafion as electrolyte was fabricated by Kaneko et al [16]. A photochargeable secondary battery with CdS/PB/ITO has been reported by the same research group [17]. The PB electrodes can be efficiently coupled with other reversible electrodes to get enhanced power density and are of current interest to several researchers.

**ELECTROCHROMISM**

The ability of PB to change its optical absorption characteristics with applied voltage in a stable and reversible manner (over \(10^6\) cycles) has opened up the possibility of its use in electrochromic devices [18]. Electrochromic cells with single film PB and with WO\(_3\)/PB, polyaniline/PB and PB/poly(methyl viologen) complementary cell have successfully been demonstrated [19-22].

The supporting electrolyte cations move in the PB lattice as hydrated ions. Ability of nonaqueous medium to affect the solvation sheath of the cation has been successfully used in the development of fast switching electrochromic devices [23]. An approach to prepare electroless deposits of amorphous PB also allows bigger cations such as Li\(^+\), Ba\(^2+\), etc. to enter the PB lattice [24]. Analogue of PB are not exceptions in exhibiting electrochromism and may even lead to the novel e.g. materials as found in the case of NiHCF in alkali [25].

**PHOTOELECTROCHEMICAL STUDIES**

In photocatalytic studies with conventional semiconductor devices [26-28] transitional metal cyanides or cyanide complexes are added as sensizers. The enhancement in photocurrent, the stability of the material against photocorrosion etc. are attributed to the formation of charge transfer complexes of the type, PB and its analogues. The photoresponse of PB when present in a bilayer composition along with ruthenium bipyridyl has been reported [29]. However, photocatalytic studies on pure PB has not been studied except for a recent publication by Kaneko et al [30] who describe the photoresponse of a PB-coated graphite. Photoelectrochemical studies on the PB film prepared by us [31] showed n-type behaviour in contrast to p-type behaviour observed by Kaneko et al. The spectacular enhancement in n-type photoresponse we observed in the presence of I\(_2\)/I\(^-\) (Fig. 3) redox system [29] is attributed to (1) the composition of the film being more in favour of reduced form of PB (i.e. PW as computed from the absorption spectral data (Fig 4) and (2) the possible chemical interaction between PB and I\(^-\) (i.e. PB + I\(^-\) \(\rightarrow\) PW to retain the PW state on the surface and hence its n-type character). Apart from PB, some analogues of PB such as InHCF have shown photoresponse characteristics. Further studies in this direction are in progress in this laboratory.

**ANALOGUES OF PRUSSIAN BLUE**

Nickel hexacyanoferrate

In an effort to arrest the surface instability of oxidatively unstable metals like nickel, ferro/ferricyanide solutions have been employed.
Stable surface derivatisation has been noticed due to the formation of nickel hexacyanoferrate redox species [32]. Subsequently, the ion transport and electron transfer mediation properties of such films were studied [33]. The appearance of only one set of redox peaks is attributed to the oxidation/reduction of ferrocyanide/ferricyanide system in the NiHCF. Interestingly, two redox centres were observed for the nickel analogue deposited on carbon substrates in our studies (Fig. 5) [34] and by Kulesza et al. [35]. The two redox centres are attributed to the oxidation/reduction reaction of inner sphere ferro/ferricyanide couple in the NiHCF with two different energetics, designated as potassium incorporated and potassium non-incorporated forms of NiHCF. In various supporting electrolytes the cyclic voltammetric response was characterised by the extent of peak splitting/shifting with respect to the alkali metal cation present. The interesting behaviour of the NiHCF in NaCl medium can be described as follows. The voltammetric response of the NiHCF in NaCl showed a transformation from an initial less symmetric response to a more symmetrical response (Fig. 6) when aged in NaCl for 24 hrs. This change in the surface peaks can be attributed to the slow structural transformation of NiHCF in NaCl.

Another interesting observation on NiHCF modified electrode is that when the modified electrode was treated in alkali, it got further derivatised to Ni(OH)₂ (Fig. 7) on the substrate surface which incidentally is also electrochromic in nature. The coulombic conversion efficiency of NiHCF film to Ni(OH)₂ was found to be 95-100%. The electrochromic switching time was 50 ms and the stability was extremely good. On the contrary, NiHCF film prepared on a nickel substrate is solubilised in alkali [25] which suggests that the composition of NiHCF prepared on Ni and glassy carbon may be different.

The mediated electron transfer mechanism has been demonstrated to be operative in the case of nickel surface derivatised with ferricyanide for the oxidation of ascorbic acid and hydrazine [36]. Thin films of NiHCF on glassy carbon has been used as stable and durable electrocatalyst for the reduction of Fe(III) in 11PL/C with electrochemical detection [37].

**Cobalt hexacyanoferrate**

The cobalt analogue of PB, exhibiting two excellent reversible redox centres very closely resembles PB in its CV response, was reported recently [38]. Both outer sphere cobaltous/cobaltic centre and the inner sphere ferro/ferricyanide redox centre are seen at 0.38 and 0.8V respectively, in 0.5M NaCl (Fig. 8). The excellent reversibility of CoHCF response in NaCl was similar to the behaviour of PB in KCl medium. The unique selectivity of CoHCF film for K⁺ ion in the presence of 50 times excess of Na⁺ ions (Fig. 9) makes these modified electrodes a suitable candidate for sensors for K⁺.

**Other analogues**

Electrochemical preparation of various analogues such as InHCF, MoHCF, TiHCF, CuHCF, PdHCF and CrHCF were reported by various research groups. All the above analogues are characterised by a single redox centre at their characteristic potentials [39-44]. The electrochemical modification of carbon electrodes with
Mixed metal hexacyanoferrates

The feasibility of preparing interfaces modified with mixed metal hexacyanoferrates was also studied [46]. Electrodes modified by PB-NiHCF and PB-Mn₂HCF composites were prepared and electrochemically characterised. Figure 9 illustrates typical CV response of the PB-MnHCF modified electrode in KCl. Most of the metal hexacyanoferrates have fcc structure which allows the modification of the electrode with mixed hexacyanoferrates structurally compatible [47]. The multiredox centres in the mixed hexacyanoferrates make these systems as models for investigating the mechanism of propagation of electrons through redox chains, a topic of considerable significance both in inorganic and in biological systems.

ZnHCF has also been reported [45].

CONCLUSIONS

Recent literature on the basic and applied aspects of PB and its analogues suggests their importance as materials for device applications in the near future. Even though structural similarity
exists between PB and its analogues [47], other differences in properties such as ion permeability, photo response, electrochromic properties, etc do exist. Study of the various analogues in a unified way will help in the understanding of electronic structure-property relationships.

![Cyclic voltammetric response of PB-MnHCF in 0.5M HCl](image)

**Fig. 10:** Cyclic voltammetric response of PB-MnHCF in 0.5M HCl

**REFERENCES**