SOLVENT AND CATIONIC EFFECTS AS PROBES FOR INVESTIGATING SURFACE PB FILMS

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The facile intercalation/deintercalation of supporting electrolyte cation being the key factor in deciding the utility of surface PB films for various applications, the present study focuses attention in understanding the influence of different cations in water and acetonitrile media on the PB surface films formed under two distinct experimental conditions. Cyclic voltammetry and impedance measurements in the said media are used as experimental tools for probing the above.

Keywords: Prussian blue, solvent and cationic effects and surface studies.

INTRODUCTION

Prussian blue films have been widely investigated for use in electrochromic devices [1,2] in solid state batteries [3,4], as ion-selective electrodes [5,6] and as signal enhancing devices [7,8] in addition to the applications to electrocatalysis [9]. The selectivity of PB films towards cation permeability and transport, and the stability of the PB layer in different cationic environment are all dependent on the composition of the PB films, which in turn is decided by the mode of film preparation [10-14]. Typically, the PB films are known to exist in two different forms viz., the soluble form and the insoluble form, designated by the species, with and without K' ions respectively. Evidence has been provided that the galvanostatically [9] and potentiostatically formed [15] films are insoluble in nature while potentiodynamically [16] formed films are of a mixture of soluble and insoluble forms. Various efforts to characterize such films are being explored and innovated [17-19] which are expected to throw light on one hand to assess the suitability of species of PB and its analogues for above targeted applications and on the other hand, in studying their electron transfer kinetic properties in these ostensibly stable and internally ordered (zeolitic fcc) electroactive species. In an attempt to characterize these films, it is considered to be of sufficient interest, to probe the feasibility of characterizing PB films through simple electrochemical methods themselves, making use of the cation and solvent influence on the surface redox reactions which these films exhibit. Towards this end, the present study is undertaken to prepare PB films of distinguishable nature in terms of their K' content, through manipulation of the preparative solution composition and to investigate their response to solvent and cation environmental influences. The above studies employing cyclic voltammetry and impedance spectral measurements, have demonstrated the feasibility of the proposed approach, whose details are described in what follows.

EXPERIMENTAL

Cyclic voltammetric experiments are carried out using BAS 100 A (Bioanalytical system, USA). A three electrode cell assembly with glassy carbon (area 0.07 cm²) working electrode, Pt auxiliary electrode and Ag/AgCl reference electrode is employed. Analar grade chemicals are used for solution preparation. No stock solutions are employed. The solutions are freshly prepared by the following sequential addition of reagents, viz., K₃Fe(CN)₆, FeCl₃ and HCl.

PB films are deposited with no addition of K' to the preparative solution (as KCl) on the glassy carbon by potentiodynamic cycling between -100 to 1000 mV vs Ag/AgCl in 2 mM solutions of K₃Fe(CN)₆ and FeCl₃ and are designated as film (B). Analar grade HCl is added to maintain the pH (2-3) of the solution during the above preparation. PB film (A) on the other hand, is prepared by the same procedure with an exception that the preparative solution contains 0.5 M KCl in it. The film A would
correspond to the conventional PB films whose properties vary with the properties of film B prepared and investigated for cation and solvent effects in this work are expected to provide the clues for the stated objective of the present work. Impedance measurements are done for PB films (A and B) in KCl solutions. The AC impedance system used is of PAR model 368 from USA. All the potentials are referred to Ag/AgCl unless otherwise stated.

The modified PB films (B) are subjected to cyclic voltammetric experiment in aqueous 0.1 M NaClO₄ and 0.1 M LiClO₄ solutions. For the studies in acetonitrile (ACN), the PB films (B) obtained in aqueous media are air dried, at room temperature and then exposed to acetonitrile. The cyclic voltammetric experiments are carried out in 0.1 M KClO₄, 0.1 M NaClO₄ and 0.1 M LiClO₄ supporting electrolytes in ACN.

RESULTS AND DISCUSSION

Formation of Films [A] and [B] - Cyclic voltammetry

Cyclic voltammograms recorded while the PB film (film A) is being formed are shown in Fig. 1a. The three redox peaks appearing at Eav = 120 mV, 228 mV and 745 mV are consistent with the expected process viz., PB $\xrightarrow{\text{solution reaction}}$ PW (surface reaction), Fe(CN)$_6^{3-}$ $\xrightarrow{\text{solution reaction}}$ Fe(CN)$_6^{3-}$ and PB $\xrightarrow{\text{surface reaction}}$ PY occurring as shown below [20].

\[
\begin{align*}
K[Fe^{II}Fe^{II}(CN)_6] & \xrightarrow{\text{surface reaction}} K[Fe^{III}Fe^{III}(CN)_6] + K^+ + e^{-} \quad (1) \\
K[Fe^{III}Fe^{II}(CN)_6] & \xrightarrow{\text{surface reaction}} Fe^{III}[Fe^{II}(CN)_6] + K^+ + e^{-} \quad (2) \\
Fe(CN)_6^{4-} & \xrightarrow{\text{solution reaction}} Fe(CN)_6^{3-} \quad (3)
\end{align*}
\]

Corresponding cyclic voltammograms for the film [B] during its preparation are shown in Fig. 1b. The similarity of the CV response of films ‘A’ and ‘B’ in terms of the number of peaks, not withstanding the contrasting behaviour of increasing peak currents in case of film A with number of potential cycles as against decreasing currents in case of film B, is striking and points out the difference in the nature of species undergoing redox reactions. Careful examination of Ep data reveals the following: The PW $\xrightarrow{\text{solution reaction}}$ PB peak potential in case of film B occurring at 10 mV is seen shifted cathodically by 110 mV as compared to the same in case of film A. Remembering that the preparative solution for film B contained only protons and is devoid of excess potassium cations in its supporting electrolyte of HCl (c.f. in the case of film A, it was prepared in presence of added KCl, 0.05 M to the reaction mixture and potential cycled) the observed negative shift of 110 mV could arise as a result of the above compositional change. More specifically, one would infer the charge neutralization (for forming the reduced form of PB viz., PW) through uptake of K$^+$ from solution (eq 1 above) to be drastically reduced in case of film B due to the limited presence of K$^+$ ions (mM) solely arising out of dissociation of the reactant $K_x[Fe^{III}Fe^{II}(CN)_6]$ (unlike 0.5 M KCl available through the dissociation of supporting electrolyte KCl in case of film A). However participation of protons concurrently, in the charge neutralization process along with the limited K$^+$ in case of film B is quite feasible [21,22] and in fact should be inferred to explain the Ep shift in CV in above, giving a prussian blue with a formula $K_{1-x}H_x[Fe^{III}Fe^{II}(CN)_6]$, where X < 1 and the equation for PB $\xrightarrow{\text{solution reaction}}$ PW reaction as

\[
K_{1-x}H_x[Fe^{III}Fe^{II}(CN)_6] + H^+ + e^{-} \xrightarrow{\text{solution reaction}} K_{1-x}H_x[Fe^{II}Fe^{II}(CN)_6]
\]
where $Y = 1+X$. It may be realized that PW in Eq. 4 is partially protonated form of PW given in Eq.1 earlier, viz., $K_2^{\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}\text{(CN)}_6}$. Large evidence exists in literature in support of the PB species in which protons concurrently enter with other cations as counter ions for charge neutralization and provide evidence for the above observation in the case of film B.

The position of second surface reaction (PB $\overset{\rightarrow}{\longrightarrow}$ PY) is seen to be practically unaltered in the films A and B (occurring around 745 mV) implying that the nature of cation viz., excess $K^+$ or $H^+$ in solution has no influence on the nature of the redox species undergoing the transformations. In view of the above experimental observations with the implication noted above, it is considered not necessary any further to discuss the role of cation $K^+$ or $H^+$ on PB $\overset{\rightarrow}{\longrightarrow}$ PY, under our film formation conditions.

**Film B in water and ACN with 0.1 M NaClO$_4$ supporting electrolyte**

To probe further into the properties of the partially protonated PB species, its CV response was examined in the solvents, water and acetonitrile, with a view to gain further insight into its electrochemistry. Figs. 2 (a and b) present the cyclic voltammograms obtained for the film B in water and acetonitrile with 0.1 M NaClO$_4$. It may be noticed that the film B exhibits three sets of peaks marked as I, II and III in CV in contrast to only two sets of peaks in the case of film A. The CV response is seem to be altered as compared to that in the absence of NaClO$_4$ (c.f. protonated PB does not give three voltammetric peaks as discussed earlier).

To understand the above characteristic response, it can be visualized that Na$^+$ ions enter PB film with a resulting composition $K_{1-x}Na_x[Fe^{\text{II}}Fe^{\text{III}}Fe^{\text{II}}\text{(CN)}_6]$ in which protons would be replaced by sodium ions. The observed response of PB film towards Na$^+$ ions both in water and acetonitrile asserts the above. One can therefore write the redox reaction for PB $\overset{\rightarrow}{\longrightarrow}$ PW reaction in NaClO$_4$ as

$$K_{1-x}Na_x[Fe^{\text{II}}Fe^{\text{III}}Fe^{\text{II}}\text{(CN)}_6] + Na^+ + e \overset{\rightarrow}{\longrightarrow}$$

$$K_{1-x}Na_y(Fe^{\text{II}}Fe^{\text{III}}Fe^{\text{II}}\text{(CN)}_6)$$

(5)

**PB** | **PW**
---|---

The broad redox peaks at $\approx -50$ mV in water and $\approx 135$ mV in ACN are due to above cited PB $\overset{\rightarrow}{\longrightarrow}$ PW reaction. The negative shift in peak potential in water can be assigned to higher hydration of Na$^+$ ions [23]. The lower solvation energy of the cations leading to shift in potentials is reported [24]. The electrochemical response in Figs. 2 (a and b) clearly demonstrates the similarity in the cyclic voltammetric characteristics of film B in both the solvents. This altered response as compared to the response of conventionally prepared PB film (c.f. film A confirms the Na$^+$ ion entry into the film B, under both solvated and hydrated conditions.

The observed redox waves at $\approx 740$ mV and $\approx 755$ mV in H$_2$O and ACN may be assigned to PB $\overset{\rightarrow}{\longrightarrow}$ PY reaction involving $K^+$ as counter cation as represented by Eq.(2). The surface waves at 900 mV and 1130 mV in H$_2$O and ACN may be attributed to PB $\overset{\rightarrow}{\longrightarrow}$ PY reaction with Na$^+$ as counter cation. The equation for this redox reaction may be written as

$$K_{1-x}Na_x[Fe^{\text{III}}Fe^{\text{II}}Fe^{\text{II}}\text{(CN)}_6]$$

$$K_{1-x}Fe^{\text{III}}[Fe^{\text{III}}Fe^{\text{II}}\text{(CN)}_6] + Na^+ + e$$

(6)

The assumption would look reasonable, if one looks into the peak potentials of individual ions, at both the iron centres. In an earlier work [25], the $K^+$ free PB film prepared from Na$_3$Fe(CN)$_6$ and FeCl$_3$ solutions i.e. Na$_3[Fe^{\text{III}}Fe^{\text{II}}Fe^{\text{II}}\text{(CN)}_6]$ when cycled in 0.1 M NaNO$_3$, exhibited two sharp redox peaks at 0 mV and 1050 mV while the $K[Fe^{\text{III}}Fe^{\text{II}}Fe^{\text{II}}\text{(CN)}_6]$ film gave peaks at 210 mV and 890 mV for PB $\overset{\rightarrow}{\longrightarrow}$ PW and

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Fig. 2(a): CV for modified PB film B in 0.1 M NaClO$_4 + H_2O$ solutions; $v = 100$ mVs$^{-1}$

Fig. 2(b): CV for modified PB film B in 0.1 M NaClO$_4 + ACN$ solutions; $v = 100$ mVs$^{-1}$
PY reactions respectively. As the film differed only in the nature of cations, the resulting potential difference was due to the cations. It is known that metalloccyanate films exhibit electrolyte cation dependent formal potentials and voltammetric shapes [26].

The appearance of single peak for PB → PW reaction as against the two surface waves for PB ↔ PW reaction may be seen to arise as a result of the non-equivalent nature of both iron centres as well as to the nature of interaction of these cations at both centres [20]. The absence of sharp and well defined peaks with film B suggest the influence of composition of film B cycled in Na⁺ ions.

**Film B in water and ACN with 0.1 M LiClO₄ supporting electrolyte**

The cyclic voltammetric response obtained for PB film B in water and ACN with 0.1 M LiClO₄ supporting electrolyte are shown in Figs. 3(a and b). In water, the PB → PW oxidation reaction is indicated by a sharp peak at 18 mV and a surface wave at -175 mV while the PB ↔ PW reduction reaction is marked by a hump at -185 mV, respectively. Similarly, in ACN, the PB ↔ PW oxidation reaction is represented by a sharp peak at -244 mV and a surface wave at 0.0 mV, whereas the corresponding reduction reaction is shown by a peak around 100 mV and a hump at -65 mV respectively. The highlights of these observations on film (B) may be summarised as follows: (1) The cyclic voltammetric characteristics of film B, in response of Li⁺ ion are similar in water and ACN, except for the potential profile, which is due to the solvent effect. (2) There are indications that Li⁺ ion enters into the film as counter cation (as in the case of Na⁺ noted earlier) and sign at different potentials than that of K⁺ ions. The surface waves observed in ACN and water may be assigned to PB → PW redox reaction which may be represented as

\[ K_{1-x}Li_xFe^{II}Fe^{II}(CN)_6 + Li^+ + e^{-} \rightarrow K_{1-x}Li_xFe^{II}Fe^{II}(CN)_6 \]

(3) The sharp peaks may be attributed to PB ↔ PW redox reaction involving K⁺ ion flux, as appearance of sharp peaks for K⁺ ion in PB film, is a well distinguished and established feature. (4) The appearance of humps for Li⁺ ion flux strongly suggests the well known non-compatible size of Li⁺ ions with the PB lattice, due to its greater hydration/solvation. However, on continuous cycling, the peak and hump disappear to give a single broad peak as in case of Na⁺ ion. (5) In water, the redox peaks at low spin iron centre appeared quasireversibly at ≈ 810 mV and ≈ 604 mV in the oxidation and reduction scans respectively. Similarly, in ACN, the same peaks appeared at ≈ 855 mV and ≈ 734 mV in the forward and backward scans. The reaction responsible for the above may be identified as due to K⁺ counter cation similar to Eq.(2), also noted in the case of NaClO₄ earlier. The quasireversibility may be due to the partial incorporation of Li⁺ ions into the PB lattice which prevents easier ionic mobility of K⁺ ions within PB lattice. In order to study the efficiency of inter conversion between K⁺ and Li⁺ ions in aqueous solutions, the film (B) initially cycled in LiClO₄ is subsequently cycled in KClO₄ between -400 mV to 400 mV at the PB ↔ PW redox region. Fig. 4a shows the CV response obtained. Only one set of peaks at Eₘ ≈ 0.0 V appeared corresponding to the flux of K⁺ ions. The reverse procedure produced a CV response as in Fig. 4b. Single redox couple at Eₘ ≈ -70 mV appeared in LiClO₄, suggesting the reversible character of insertion/extraction of Li⁺ ions. However, the PB film is unstable in LiClO₄ after 10-15 cycles.

Fig. 3(a): CV for modified PB film B in 0.1 M LiClO₄ + H₂O solutions; \( v = 100 \text{ mV/s} \)

(b): CV for modified PB film B in 0.1 M LiClO₄ + ACN solutions; \( v = 100 \text{ mV/s} \)
CV response of PB films A and B in water with 0.1 M KClO₄ supporting electrolyte

PB film with partial protonation K₁₋ₓHₓ[Feᴵᴵ⁻Feᴵᴵ⁺(CN)₆] or cation substitution viz., K₁₋ₓMₓ[Feᴵ⁻Feᴵ⁺(CN)₆] (M = Na⁺/Li⁺) is further sought to be verified by the following strategy of subjecting both films A and B to cycling in 0.1 M KClO₄ and looking for identity of end results. Figs. 5a and b present the cyclic voltammograms obtained. The similarity in their characteristics may be recognized. The PB ←→ PW redox reaction seems to occur at Eₐₑ MOREORLESS 15 mV and 35 mV for films A and B respectively. Similarly, the peak potentials for PB ←→ PY reaction are at Eₐ₂ 700 mV and 720 mV, for films A and B respectively. The non-distinguishable features exhibited by film B, from that of film A, in presence of K⁺ ions could be due to perm selective nature of PB film towards K⁺ ions and its high degree of compatibility within the PB lattice. A hypothetical reasonable explanation may be given as follows:

It is well known that Prussian Blue is a zeolitic polymeric molecule with fixed negative charges and takes up alkali metal cations for charge neutralization. A large part of the negative charge density (σₐ) is compensated by cations within the ion exchange framework (σₑ). The extent of this compensation and hence the magnitude of (σₑ) depend on the type and concentration of cation and on the pH of the solution. In PB film, which has not been prioriy cycled in K⁺ ions to get the soluble form, when subjected to cycling in Na⁺ ions, the film with the intake of Na⁺ ions, showed distinctly different features. Similar is the case with Li⁺ ions. The electrochemical non equivalent sites recognised by Na⁺ and Li⁺ ions are not marked in case of K⁺ ions, since in this case, the exchangeable cations in the ion exchange frame work (PB) and the electrolyte cation in the diffuse double layer remain to be the same. Further impedance studies on these films substantiate these ideas which are presented below:

Impedance Measurements

The Nyquest plots (Z' vs - Z") obtained for films A and B recorded in 0.1 M KCl electrolyte at the formal potential of PB ←→ PW redox reaction are given in Figs. 6a and b. Based on the model suggested for thin film coated electrodes [27-29] the impedance data are analysed. The impedance diagrams at high frequencies reveal a depressed semicircle characteristic of charge transfer reaction (PB ←→ PW). The intercept of the extended semicircle on the real axis gives the charge transfer resistance (Rₑ) and solution resistance (Rₛ). However, beyond 100 Hz, in the low frequency region, the linear response noted indicates that the
mass transfer is the predominant mode of reaction control. These features are common to both the cases in Figs. 6a and b. The $R_{ct}$ for film A is $0.708 \times 10^{-2}$ Ω while for film B, it is $0.396 \times 10^{-2}$ Ω. The agreement in $R_{ct}$ values for these films A and B giving the same order indicates that they are similar in nature and these results are also in tune with the CV data discussed above.

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REFERENCES