

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 focusses 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 (zeolytic 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 cm^2) 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., $K_3Fe(CN)_6$, $FeCl_3$ 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 $K_3Fe(CN)_6$ and $FeCl_3$ 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 vis a vis 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.

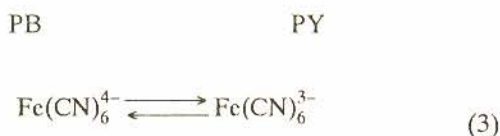
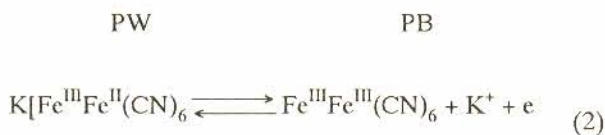
Impedance measurements are done for PB films (A and B) in KCl solutions. The AC impedance system used is of PAR model 368 from USA. All the potentials are referred to Ag/AgCl unless otherwise stated.

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 E_{av} = 120 mV, 228 mV and 745 mV are consistent with the expected process viz., PB \rightleftharpoons PW (surface reaction), Fe(CN)₆⁴⁻/₃₋ (solution reaction) and PB \rightleftharpoons PY (surface reaction) occurring as shown below [20].



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 E_p data, reveals the following: The PW \rightleftharpoons 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 K₃Fe(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 E_p 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 \rightleftharpoons PW reaction as

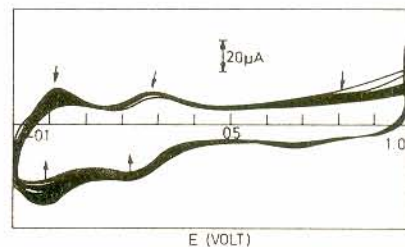
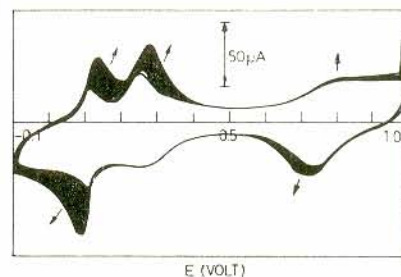
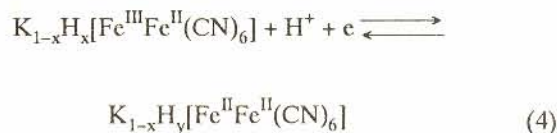


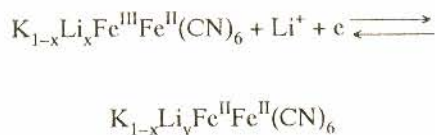
Fig. 1(a): CV for PB film A during formation; $\nu = 100 \text{ mVs}^{-1}$
 (b) CV for PB film B during formation; $\nu = 100 \text{ mVs}^{-1}$

PB \rightleftharpoons 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 metalocyanate films exhibit electrolyte cation dependent formal potentials and voltammetric shapes [26].

The appearance of single peak for PB \rightleftharpoons PW reaction as against the two surface waves for PB \rightleftharpoons PY 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 PW \rightleftharpoons PB oxidation reaction is indicated by a sharp peak at 18 mV and a surface wave at -175 mV while the PB \rightleftharpoons PW reduction reaction is marked by a hump at -185 mV, respectively. Similarly, in ACN, the PW \rightleftharpoons PB oxidation reaction is represented by a sharp peak at \approx 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 \rightleftharpoons PW redox reaction which may be represented as



PB

PW

(3) The sharp peaks may be attributed to PB \rightleftharpoons 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 \approx 810 mV and \approx 604 mV in the oxidation and reduction scans respectively. Similarly, in ACN, the same peaks appeared at \approx 835 mV and \approx 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 \rightleftharpoons PW redox region. Fig. 4a shows the CV response obtained. Only one set of peaks at E_{av} 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 E_{av} -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.

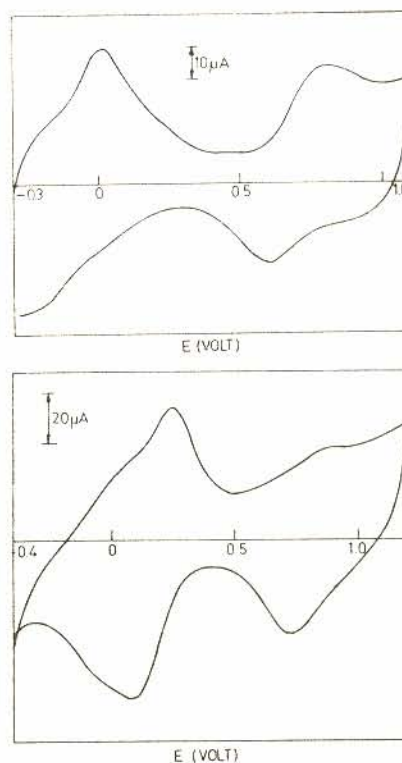


Fig. 3(a): CV for modified PB film B in 0.1 M LiClO₄ + H₂O solutions; $\nu = 100 \text{ mVs}^{-1}$
 (b): CV for modified PB film B in 0.1 M LiClO₄ + ACN solutions; $\nu = 100 \text{ mVs}^{-1}$

CV response of PB films A and B in water with 0.1 M KClO₄ supporting electrolyte

PB film with partial protonation $K_{1-X}H_X[Fe^{III}Fe^{II}(CN)_6]$ or cation substitution viz., $K_{1-X}M_X[Fe^{III}Fe^{II}(CN)_6]$ ($M = Na^+/Li^+$) 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 \rightleftharpoons PW redox reaction is seen to occur at E_{av} MOREORLESS 15 mV and 35 mV for films A and B respectively. Similarly, the peak potentials for PB \rightleftharpoons PY reaction are at E_{av} 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 (σ_-) is compensated by cations within the ion exchange frame work (σ_+). The extent of this compensation and hence the magnitude of (σ_+) depend on the type and concentration of cation and on the pH of the solution. In PB film, which has not been priorly 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 Nyquist plots (Z' vs $-Z''$) obtained for films A and B recorded in 0.1 M KCl electrolyte at the formal potential of PB \rightleftharpoons 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 \rightleftharpoons PW). The intercept of the extended semicircle on the real axis gives the charge transfer resistance (R_{ct}) and solution resistance (R_Q). However, beyond 100 Hz, in the low frequency region, the linear response noted indicates that the

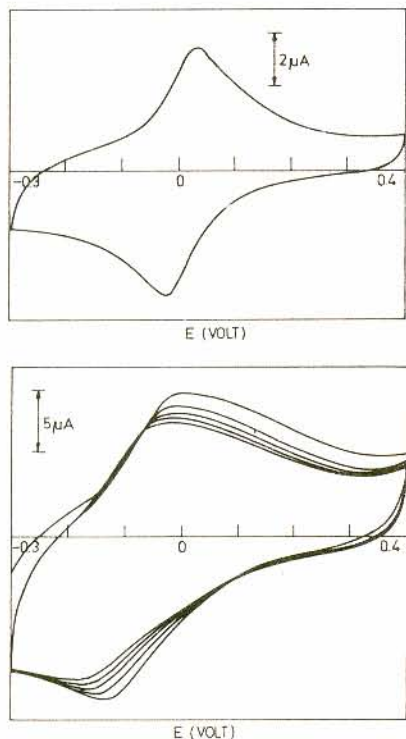


Fig. 4(a): CV for modified PB film B in 0.1 M KClO₄ + H₂O solutions (the film being initially cycled in 0.1 M LiClO₄ + H₂O solutions); $v = 100 \text{ mVs}^{-1}$
 (b): CV for PB film B in 0.1 M LiClO₄ + H₂O solutions (after removing from 0.1 M KClO₄ + H₂O solutions); $v = 100 \text{ mVs}^{-1}$

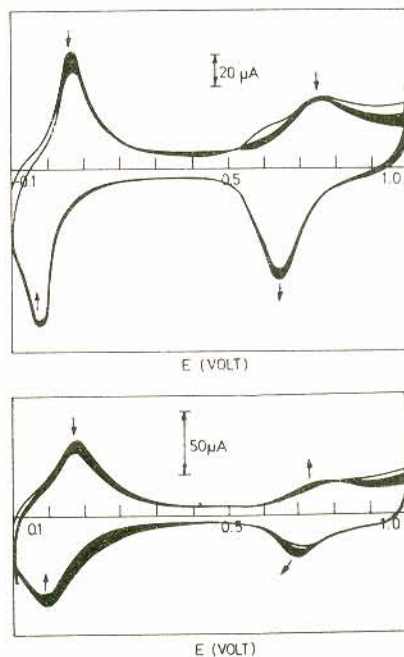


Fig. 5(a): CV for modified film A in 0.1 M KClO₄ + H₂O solutions
 (b) CV for modified PB film B in 0.1 M KClO₄ + H₂O solutions

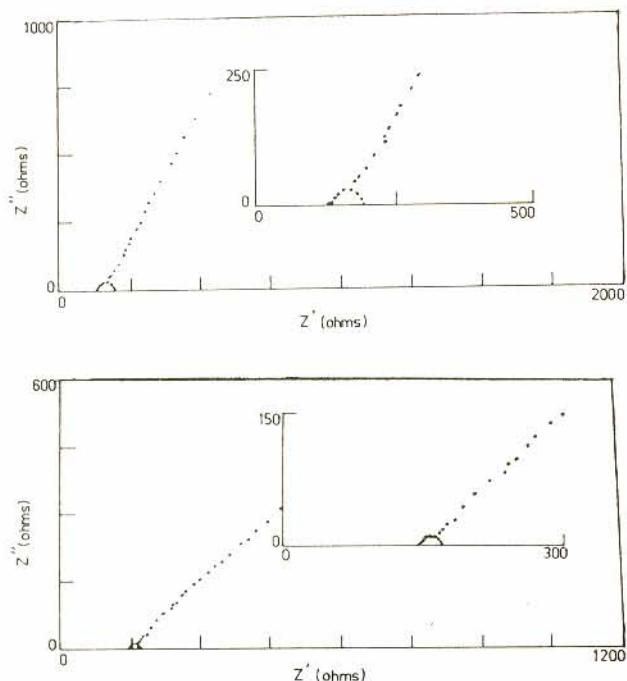


Fig. 6: Electrochemical impedance response of (a) PB film A in 0.1 M KCl solutions; (b) PB film B in 0.1 M KCl solutions

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 $0.708 \times 10^{-2} \Omega$ while for film B, it is $0.396 \times 10^{-2} \Omega$. 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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