CTAB-Promoted Prussian Blue-Modified Electrode and Its Cation Transport Characteristics for K$^+$, Na$^+$, Li$^+$, and NH$_4^+$ Ions

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A Prussian blue (PB) film was deposited on a glassy carbon (GC) electrode by cyclic voltammetry in the presence of the cationic surfactant cetyltrimethylammonium bromide (CTAB). The electrode thus formed showed 4-fold enhancements in redox current and charge values in pure KCl electrolyte as well as greater stability than an electrode prepared in the absence of CTAB. This improved performance of a PB + CTAB electrode versus a PB electrode was further demonstrated using SEM, XRD, and electrochemical impedance spectroscopy (EIS) measurements. A comparative study was undertaken on the cation transport characteristics of PB and PB + CTAB electrodes for Na$^+$, Li$^+$, and NH$_4^+$ ions. We obtained a CV pattern for a CTAB-promoted PB film, which showed ideal Nernstian behavior at all scan rates from 5 to 140 mV s^{-1}. Conditions for the formation and preservation of these ideal and stable PB films are discussed. Possible mechanisms for the beneficial effects of CTAB are proposed.

1. Introduction

Prussian blue (PB) (iron(III) hexacyanoferrate(II)) is the prototype transition metal hexacyanide; it was the first coordination compound reported in the scientific literature.[1] Moreover, PB has attracted the interest of electrochemists due to its applications, as a thin film on a bare electrode, for the electroanalysis of various substances (e.g., alkali ions,[2] potassium ion,[3−5] ammonium,[6] hydrogen peroxide,[7] thiol,[8] oxidase enzyme,[9] lactic acid,[10] ascorbic acid,[11] electroinactive cations,[12] sulfite,[13] sucrose,[14] acetylcholinesterase,[15] and persulfate anions[16]). Bare electrodes modified with PB films also find applications in electrocatalysis,[17,18] electrochromism,[19,20] and batteries.[21,22]

Improving PB film in terms of cation detecting limits and stability is one of the essential objectives in the research on its electroanalytical applications. We have successfully employed a particular strategy for improving the electrochemical performance of PB film, by using the cationic surfactant cetyltrimethylammonium bromide (CTAB) for the immobilization of PB on a bare electrode.[23] This CTAB-promoted PB-modified electrode can be used for electroanalysis and the other applications mentioned above.

This paper reports the enhanced performance of a PB + CTAB film versus a PB film, in terms of increased currents, redox activity, crystallinity, and stability. We undertook a comparative study of the behaviors of PB and PB + CTAB electrodes in the supporting electrolytes KCl, NaCl, LiCl, and NH$_4$Cl. The investigation was on the effects of pertaining cations on the redox behavior of the PB + CTAB film and also on the utility of this film electrode as a sensor for K$^+$ ions. The beneficial effects of CTAB in terms of electroanalytical ap-

plications are also valid for electrocatalytic applications. The beneficial role of CTAB in the modification of a bare electrode with PB film is emphasized. The improved PB-modified electrode is expected to find applications in other branches of electrochemistry. We demonstrate in this paper symmetric redox peaks for a PB + CTAB film, which showed ideal Nernstian behavior at all scan rates from 0.005 to 0.14 V s^{-1}. We believe this represents an ideal CV pattern for a PB-modified electrode, as explained in detail later in this report.

2. Experimental Section

All cyclic voltammetric (CV) experiments were carried out with a potentiostat coupled to a Wenking voltage scan generator (VSG 72) and an *x-y* recorder (Rikadenki RW 201). A three-electrode cell, composed of a platinum counter electrode, a normal calomel reference electrode (NCE), and a glassy carbon (GC) working electrode (area: 0.03 cm^2) was used for modifying a GC electrode. Prior to modification, the GC electrode was polished with emery papers of grades 1/0 to 4/0 successively. The modifying solution contained 0.1 M KCl, 0.02 M HCl, 0.5 mM FeCl$_3$, and 0.5 mM K$_3$Fe(CN)$_6$. CTAB was added to the modifying solution at its critical micelle concentration (cmc), that is, at 0.92 mM. It is important to mention here that the cmc value of CTAB (0.92 mM) mentioned is the value of its cmc in pure water. We are unsure of its exact value in the modifying solution, and thus, its cmc may change to some extent in the modifying solution. The modification of a bare GC electrode with a PB film was accomplished by cycling the electrode potential between −0.2 and 1 V at 0.1 V s^{-1} versus NCE for 15 min. A thick Prussian blue film was formed on the electrode, as could be clearly judged by the naked eye. The intensity of the blue color was greater for a film formed in the presence of CTAB. After potential cycling, the electrode was washed with distilled water and stored in 0.1 M KCl. CV responses of PB and PB + CTAB-modified electrodes were recorded in 0.1 M KCl/NaCl/LiCl and NH$_4$Cl at the scan rate of 0.1 V s^{-1} versus NCE after 15 min of cycling. A fresh

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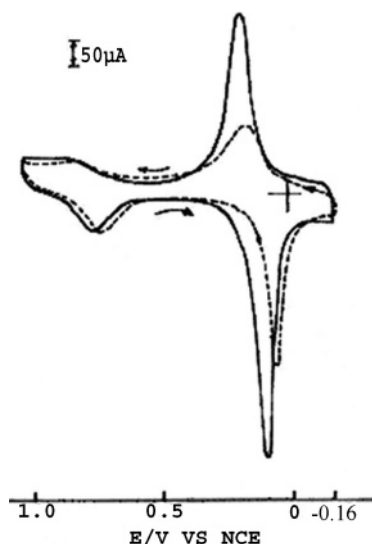§ Present address: Department of Chemistry, Korea University, Seoul, 136-713, Korea.

1150 *J. Phys. Chem. B, Vol. 112, No. 4, 2008*

Vittal et al.

Figure 1. CV responses of PB (dashed line) and PB + CTAB (solid line)-modified GC electrodes in 0.1 M KCl at 0.1 V s^{-1}.
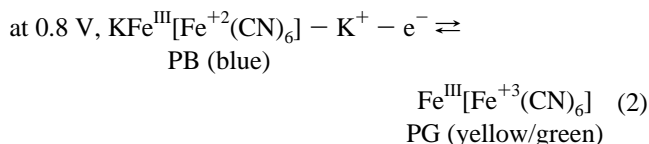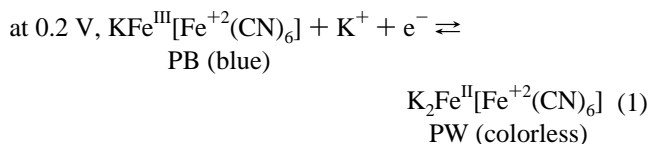
electrode was prepared for each of the supporting electrolytes mentioned, that is, KCl, NaCl, LiCl, and NH$_4$Cl.

All chemicals were of analytical grade and were used without further purification. Double distilled water was used to prepare solutions. A modification solution was prepared freshly in each case of the supporting electrolytes.

Scanning electron micrographs (SEMs) of coated platinum electrodes (Pt., area: 1 cm^2) were obtained using a JEOL JSM 35 CF microscope. XRD patterns of PB and PB + CTAB films on Pt surfaces were recorded using a JEOL (JDX-8030) X-ray powder diffractometer. Electrochemical impedance spectra (EIS) were recorded using a computer-controlled impedance unit (PAR Galvanostat/Potentiostat model No. 273 coupled to a PAR lock-in amplifier model No. 230) and a computer-controlled data acquisition system. To achieve this, a small ac potential was applied to an electrochemical system containing a PB or PB + CTAB-modified GC working electrode and a Pt counter electrode in 0.1 M KCl. The complex impedance was measured over a frequency range of $10^5 - 10^{-2}$ Hz at an amplitude of 5 mV.

3. Results

3.1. Cyclic Voltammetric Characterization of PB and PB + CTAB Films in 0.1 M KCl. The dotted line in Figure 1 represents the cyclic voltammetric response of a PB film in 0.1 M KCl, while the solid line represents the CV response of a PB + CTAB film. The two sets of redox peaks in the CVs can be represented by the following reactions:[24]

at 0.2 V, KFe^{III}[Fe^{+2}(CN)$_6$] + K$^+$ + e$^-$ $\rightleftharpoons$
PB (blue)

$$K_2Fe^{II}[Fe^{+2}(CN)_6] \quad (1)$$
PW (colorless)

at 0.8 V, KFe^{III}[Fe^{+2}(CN)$_6$] $-$ K$^+$ $-$ e$^-$ $\rightleftharpoons$
PB (blue)

$$Fe^{III}[Fe^{+3}(CN)_6] \quad (2)$$
PG (yellow/green)

The above reactions relate to the soluble form of PB (the potassium-containing form), because the PB film was formed in the presence of KCl after a long period (15 min) of cycling

TABLE 1: Cyclic Voltammetric Current Values of PB + CTAB-Modified Electrodes in 0.1 M KCl Solution at the Scan Rate of 0.1 V s^{-1} [a]

concentration of CTAB (mM)	$I_{pa} \times 10^{-6}$ (A)	$I_{pc} \times 10^{-6}$ (A)	I_{pa}/I_{pc}
0.01	37.5	107.5	0.35
0.1	42.5	107.5	0.40
0.5	60.0	105.0	0.57
0.92	87.5	155.0	0.57
2.00	20.0	20.0	1
2.5	no peaks	no peaks	

[a] Each modification was carried out separately at a different CTAB concentration. (GC area: 0.03 cm^2).

TABLE 2: Cyclic Voltammetric Current and Charge Values of a PB-Modified Electrode in 0.1 M KCl Solution at Different Scan Rates[a]

scan rate (V s^{-1})	$I_{pa} \times 10^{-6}$ (A)	$I_{pc} \times 10^{-6}$ (A)	I_{pa}/I_{pc}	Q_a (mC cm^{-2})	Q_c (mC cm^{-2})
0.005	3.50	11.0	0.32	1.43	1.37
0.020	7.50	21.0	0.36	1.43	1.42
0.040	12.00	28.0	0.43	1.58	1.57
0.100	22.00	44.0	0.50	1.03	1.04
0.160	29.50	54.5	0.54	0.88	0.87
0.200	34.00	60.00	0.57	0.91	0.90

[a] Values pertain to the Fe^{+2}/Fe^{+3} redox center of the PB molecule, i.e., at 0.2 V. (GC area: 0.03 cm^2).

TABLE 3: Cyclic Voltammetric Current and Charge Values of a PB + CTAB-Modified Electrode in 0.1 M KCl Solution at Different Scan Rates[a]

scan rate (V s^{-1})	$I_{pa} \times 10^{-6}$ (A)	$I_{pc} \times 10^{-6}$ (A)	I_{pa}/I_{pc}	Q_a (mC cm^{-2})	Q_c (mC cm^{-2})
0.005	6.5	33.0	0.50	4.20	4.10
0.020	40.5	61.5	0.66	4.20	4.12
0.040	66.0	97.5	0.68	4.56	4.54
0.100	120.0	186.0	0.65	4.87	4.85
0.160	162.0	258.0	0.63	4.13	4.06
0.200	186.0	297.0	0.63	4.27	4.26

[a] Values pertain to the Fe^{+2}/Fe^{+3} redox center of the PB molecule, i.e., at 0.2 V. (GC area: 0.03 cm^2)

the electrode potential in it. It is clear from eq 1 that a K$^+$ ion enters and exits the unit cell in the PB $\rightleftharpoons$ PW transition, that is, at the redox center Fe^{+2}/Fe^{+3}. Even a cursory glance at the figure reveals the remarkable improvement in current values of the PB + CTAB electrode.

All further discussions pertain to electrochemical reactions occurring at 0.2 V, that is, at the Fe^{+2}/Fe^{+3} redox center. The intercalation and corresponding deintercalation of a K$^+$ ion and other cations into the PB channels take place only at this center, as has been well established by previous reports.[24,25] Moreover, redox currents were enhanced by CTAB selectively at this center. The second center at 0.8 V involves the transport of electrolyte anions.[24] We chose the critical micelle concentration of CTAB for this research, unless otherwise specified, because the best results in terms of the currents obtained were achieved at this concentration (Table 1). The concentration at which micelles first become detectable is defined as the cmc of the surfactant, and it is also the concentration at which abrupt changes in physical properties occur. Apparently micelle formation at this concentration of CTAB enabled the best currents to be obtained from the PB + CTAB electrode (Table 1). It is important to mention here that a change in the concentration of CTAB did not cause any change in peak CV potentials.

Tables 2 and 3 compare the current and charge values of PB and PB + CTAB electrodes, respectively. The values shown in the tables pertain to the Fe^{+2}/Fe^{+3} center of PB and PB + CTAB

CTAB-Promoted Prussian Blue-Modified Electrode

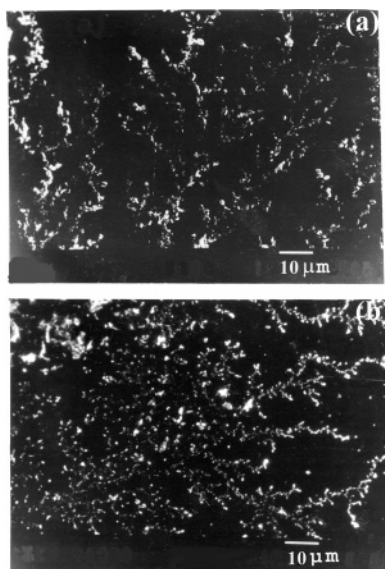*J. Phys. Chem. B, Vol. 112, No. 4, 2008* **1151**

Figure 2. Scanning electron micrographs of PB films, deposited on Pt electrodes: (a) without CTAB, and (b) with CTAB, at 1000 magnification.

films. The charges under the peaks were manually computed and calculated. From these two tables it is clear that the ratio of the anodic to cathodic charges for each film is unity, irrespective of whether the film was formed in the presence or absence of CTAB. These current and charge values show an increase by 4- to 5-fold at higher scan rates for PB + CTAB film, which is in tune with the CVs shown in Figure 1, and they reflect a remarkably faster surface electron transfer for the PB + CTAB film. The surface concentration ($\Gamma_{Fe^{3+}}$) of the electroactive species responsible for the PB $\rightleftharpoons$ PW transition, that is, that of the Fe^{3+} ion, was calculated using the following equation:[26]

$$\Gamma_{Fe^{3+}} = Q_t / nFA_{geo}$$

where Q_t is the charge, n is the number of electrons involved in the electrochemical reaction, F is the Faraday constant, and A is the electrode area. The surface concentrations of electroactive species for the PB and PB + CTAB electrodes at the scan rate of 0.1 V s^{-1} were calculated to be 3.55×10^{-7} and 16.82×10^{-7} mol cm^{-2}, respectively; charge values were taken from Tables 2 and 3, n was 1 in our case, and the electrode area was 0.03 cm^2. Charge values were obtained by integrating the anodic peak areas in CVs and applying a background correction. These surface concentration values clearly reflect greatly improved PB deposition due to the involvement of CTAB.

3.2. Characterization of PB and PB + CTAB Films by SEM, XRD, and EIS. Scanning electron micrographs of PB and PB + CTAB films are shown in Figure 2, parts a and b, respectively, both parts at 1000 magnification. Although the morphological characters of both films show primarily dendritic features, more dendrites are present in the PB + CTAB film. In addition, the PB + CTAB film is more homogeneous, that is, it shows a better microstructural arrangement. This observation concurs with the XRD results discussed below.

Figure 3 depicts the XRD patterns of PB and PB + CTAB films. Both films have a crystalline nature, as can be noted from the sharp PB peaks (indicated by open circles) in both cases. However, on comparing peak intensities in the two patterns, that is, the intensities associated with open circles in the two figures, it is evident that the degree of crystallinity is much
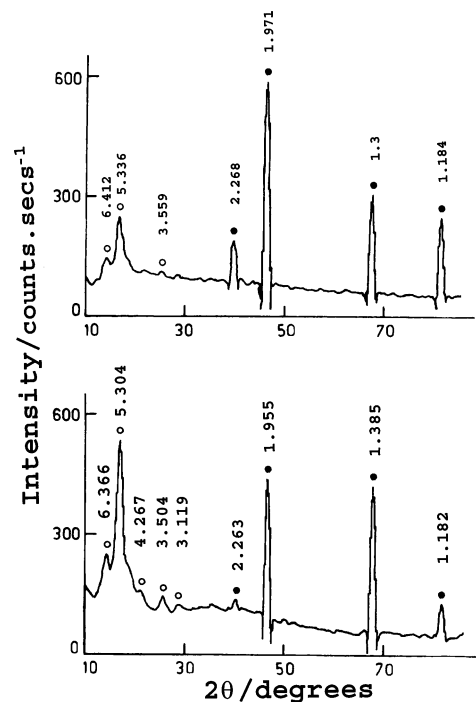

Figure 3. X-ray diffraction patterns of (a) PB film, and (b) PB + CTAB film on Pt electrodes (open circles indicate PB or PB + CTAB film, and closed circles indicate the Pt substrates).

higher for the PB + CTAB film. The relative intensity of the PB film is 246 (Figure 3a) at a 2θ of 13.5, while this reaches 533 (Figure 3b) for the PB + CTAB film. The peaks observed at 2θ values of from 39.7 to 83° are due to the platinum substrate. A careful observation of peak intensities (open circles) in both parts of the XRD figure also indicates that each ratio of peak intensities for the PB film is the same as the corresponding ratio of peak intensities for the PB + CTAB film. The Nyquist plots (Z' versus Z'') obtained for the PB and PB + CTAB films, recorded in 0.1 M KCl at the formal potential of PB $\rightleftharpoons$ PW redox reaction (0.2 V), are shown in Figure 4, parts a and b, respectively. On comparing Z_{re} and Z_{im} values of the PB film with corresponding values of the PB + CTAB film, it is noted that the total impedance of the cell with the PB electrode is twice as large as that of the cell with the PB + CTAB electrode. Other elements of impedance being the same for both cells, the differentiating element of resistance is the PB film; the film formed in the presence of CTAB assumes a lesser resistance to ion and electron transfer. In other words, K^+ ion transport for the PB + CTAB film is much more facile than that for the PB film. CVs and EIS curves indicate that CTAB facilitates a PB film probably with improved lattice channels, increased porosity, and reduced structural disorder, because the CVs and EIS of PB and PB + CTAB films involve permeability of K^+ ions and this permeability is related to lattice defects and structural disorder in the films. Our observation concerning the improved morphology of the PB + CTAB film is also consistent with the results of Senthil Kumar et al., who observed in their SEM images film imperfections in the form of holes and scratches in the PB film, but a uniform PB + CTAB film without holes and scratches.[27a] They also observed a far higher diffusion coefficient or permeability for K^+ ions for a PB + CTAB film, which also supports our observation concerning improved morphology of this film.

3.3. Cation Transport Characteristics of PB and PB + CTAB Films. It has been well-established that a PB film has a specific alkali metal cation transport characteristic due to its
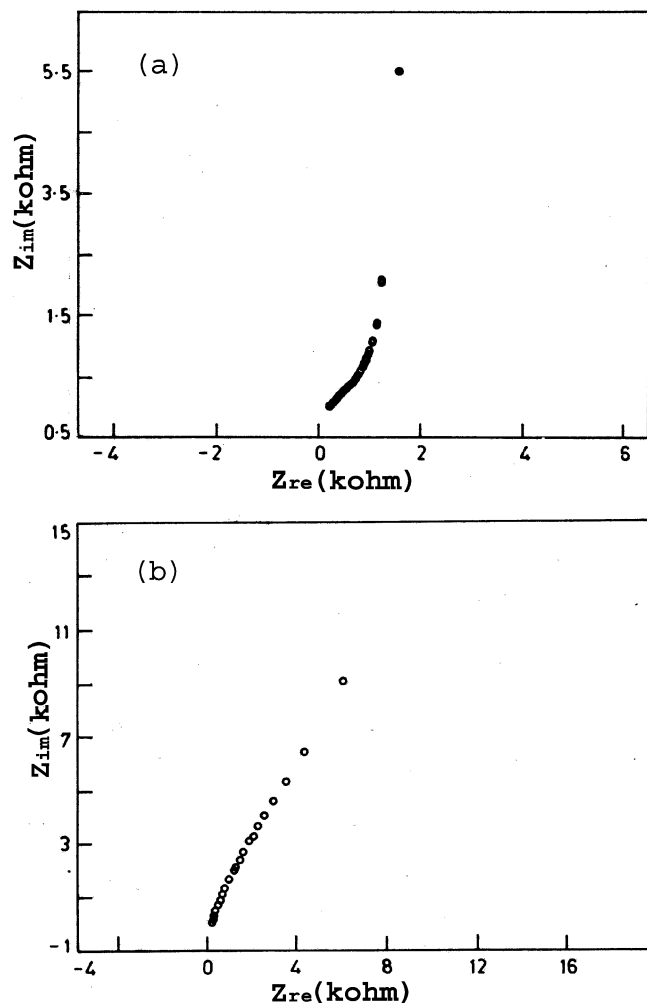
Figure 4. Nyquist plots of PB films on GC electrodes at the formal potential of 0.2 V vs NCE in 0.1 M KCl: (a) without CTAB, and (b) with CTAB.

ordered zeolite cagelike structure.[24,25] This characteristic forms the basis for a PB-modified electrode as a sensor for cations.[2−6] Though reports have been issued on the cation transport characteristics of conventional Prussian blue films,[24,25] these PB films were prepared in the absence of a surfactant. Itaya et al., one of the pioneering groups to invent the electrochemical deposition of a PB film, reported the irreversible damage to a PB film caused by Na$^+$ ions in solution.[24] Crumbliss et al., who made an extensive study of PB deposits, reported that a PB electrode, subjected to potential cycling in aqueous solution containing Li$^+$ ions, totally lost its original redox activity and produced no redox signal even when the electrode was potential cycled in aqueous KCl solution.[25] These authors have not depicted regained CV responses of their PB-modified electrodes in KCl after their subjection to potential cycling in different electrolytes. As will be discussed below, redox activity of a PB film was regained in 0.1 M KCl in the present study, after being exposed to the electrolyte NaCl or LiCl. Moreover, this regaining of CV response in 0.1 M KCl was much more pronounced for PB + CTAB films, compared to that for PB films.

For this part of the research, PB and PB + CTAB films were immobilized on glassy carbon electrodes and their cation transport properties were examined for Na$^+$, Li$^+$, and NH$_4^+$ ions. The regaining of PB film properties after exposure to the influence of each of these cations was also verified. It should be emphasized here that all CVs shown in this research report
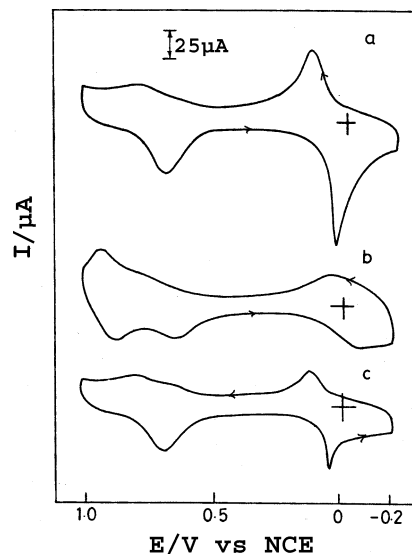

Figure 5. CV responses of a PB-modified GC electrode at 0.1 V s^{-1} in (a) 0.1 M KCl, (b) 0.1 M NaCl, and (c) 0.1 M KCl; the electrode was exposed to them in the given order.

are stable forms that were recorded after CVs had been stabilized by 15 min of cycling.

(a) Cyclic Voltammetric Studies in Sodium Chloride. Figure 5a shows the CV response of a PB-modified electrode in 0.1 M KCl at a scan rate of 100 mV s^{-1}. The sharp peaks at about 0.2 V indicate the facile transport of K$^+$ ions into and out of PB lattice channels and thus indicate that PB channel sizes are compatible with K$^+$ ions. When this electrode was washed and its response was observed in 0.1 M NaCl, the cyclic voltammogram assumed the shape shown in Figure 5b. The CV is characterized by a redox center at 0 V, an anodic peak at 0.95 V, and two cathodic peaks at 0.9 and 0.65 V. It is clear, by comparing Figure 5, parts a and b, that a considerable charge reduction occurs at the Fe^{+2}/Fe^{+3} redox center. The charge reduction that occurs in NaCl electrolyte is possibly due to the restrictions for the entry of hydrated Na$^+$ ions (hydrated radius = 1.83 Å) into the PB lattice (hydrated radius = 1.6 Å), with respect to the entry of hydrated K$^+$ ions (hydrated radius = 1.25 Å).[24,25] When this electrode was rewashed and its response re-observed in 0.1 M KCl, its original CV response was regained (Figure 5c), but with lower charges than those observed in KCl (Figure 5a).

Figure 6, parts a−c, depict the corresponding responses of the PB + CTAB-modified electrode in 0.1 M KCl (a), 0.1 M NaCl (b), and again in 0.1 M KCl (c). Enhanced anodic and cathodic charges at the Fe^{+2}/Fe^{+3} center can be seen in Figure 6a relative to those in Figure 5a, due to the influence of CTAB. It is interesting to note that shape of the CV in Figure 6b is very similar to that in Figure 5b, indicating that the surfactant did not influence the basic behavior of the PB film in NaCl. This implies that the original PB structure is retained and that the change in the shapes of the CVs in Figures 5b and 6b relative to those in the Figures 5a and 6a, respectively, is due to the insertion of hydrated Na$^+$ ions. Just as shown by Figure 5c, Figure 6c also shows the regaining of CV response by PB in KCl, but this is partial in both Figures 5c and 6c, relative to their respective original CVs in KCl, that is, CVs before exposure to NaCl. Itaya et al. have reported irreversible damage to the PB film subjected to 0.1 M NaCl.[24] Ozeki et al. have reported that the PB film was stripped off the electrode (gold) after several cyclic scans.[28] However, we did not find this, as we found that PB film response was regained in 0.1 M KCl by
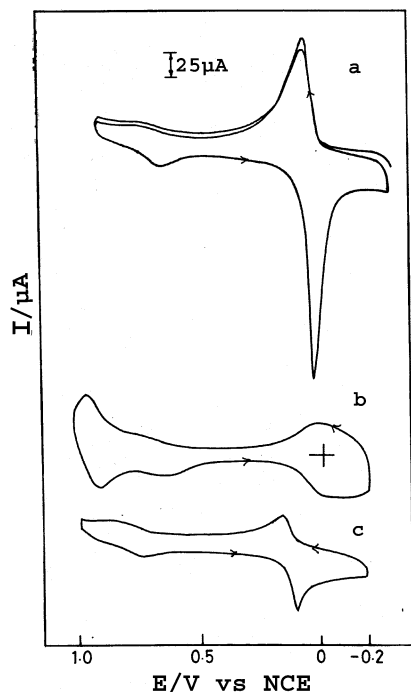
CTAB-Promoted Prussian Blue-Modified Electrode

J. Phys. Chem. B, Vol. 112, No. 4, 2008 **1153**

Figure 6. CV responses of a PB + CTAB-modified GC electrode at 0.1 V s^{-1} in (a) 0.1 M KCl, (b) 0.1 M NaCl, and (c) 0.1 M KCl; the electrode was exposed to them in the given order.
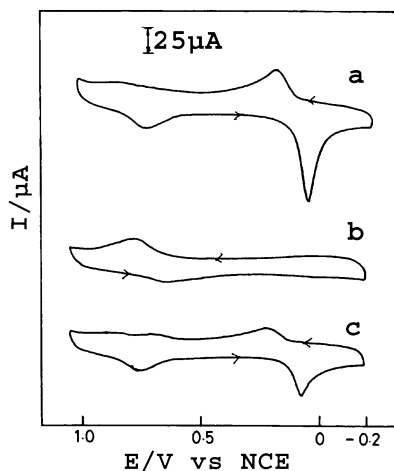
Figure 7. CV responses of a PB-modified GC electrode at 0.1 V s^{-1} in (a) 0.1 M KCl, (b) 0.1 M LiCl, and (c) 0.1 M KCl; the electrode was exposed to them in the given order.

Figure 8. CV responses of a PB + CTAB-modified GC electrode at 0.1 V s^{-1} in (a) 0.1 M KCl, (b) 0.1 M LiCl, and (c) 0.1 M KCl; the electrode was exposed to them in the given order.

PB and PB + CTAB films, even after about 15 min of cycling (about 48 cycles). A small redox response is apparent as a hump at around 0 V in Figures 5b and 6b. This may be attributed to the presence of residual K$^+$ ions on the surface of the PB film.

(b) Cyclic Voltammetric Studies in Lithium Chloride. Figure 7a shows the CV response of the PB electrode in 0.1 M KCl at a sweep rate of 0.1 V s^{-1}, and Figure 7b shows its corresponding response in 0.1 M LiCl. Interestingly, the first redox center of Fe^{+2}/Fe^{+3} transition at 0.2 V disappears without any trace in Figure 7b. This phenomenon is also attributed to the restrictions for the entry of Li$^+$ ions into the PB channel, due to the larger hydrated radius of Li$^+$ ion (2.37 Å) than that of K$^+$ ion. Finally, when the electrode had been washed and subjected to potential cycling in KCl electrolyte, the original CV response was regained, though with smaller peak currents and charges (Figure 7c).
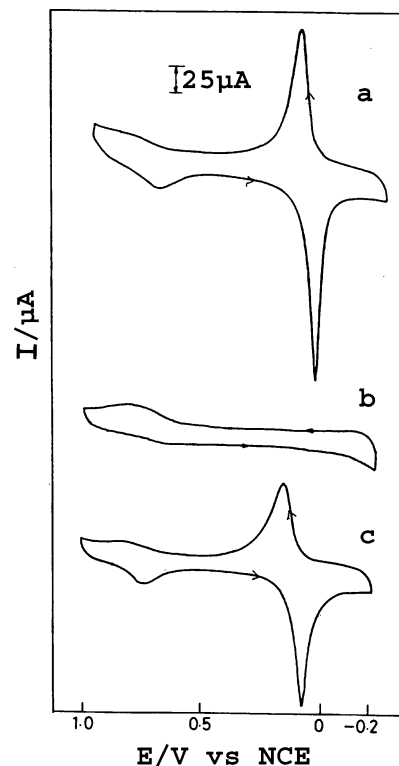
Figure 8 depicts the CV responses of the PB + CTAB electrode, sequentially recorded in 0.1 M KCl (a), 0.1 M LiCl (b), and then in 0.1 M KCl (c). Excluding the enhanced currents and charges in Figure 8, parts a and c, versus those in Figure 7, parts a and c, respectively, no other influence of CTAB was evident. It should be noted that CTAB did not influence the transport characteristics of Li$^+$ ions into PB channels. Crumbliss et al., a pioneering group in the area of PB-modified electrodes, reported that a PB electrode subjected to potential cycling in aqueous solution containing Li$^+$ ions lost its original redox activity totally, and that no redox signal was observed even when the electrode was potential cycled in aqueous KCl solution.[25] In the case of a PB + CTAB film we obtained excellent CV-response regain in KCl. That is to say, the original CV response in KCl was regained for the PB + CTAB electrode after exposure to lithium chloride, and that regain of response was better than that observed for the PB electrode (cf. Figure 7c).

(c) Cyclic Voltammetric Studies in Ammonium Chloride. The CV response of a PB electrode in 0.1 M KCl at a sweep rate of 0.1 V s^{-1} is shown in Figure 9a. Its corresponding response in 0.1 M NH$_4$Cl is shown in Figure 9b. A reduction in peak currents at the Fe^{+2}/Fe^{+3} center is observed in NH$_4$Cl versus those obtained in Figure 9a. This reduction of peak currents due to the exposure to NH$_4$Cl is not as large as those observed in the cases of exposures to NaCl or LiCl (cf. Figure 9b vs Figures 5b and 7b); moreover, these peaks at the Fe^{+2}/Fe^{+3} center are sharper than those in the case of NaCl (cf. Figure 5b). The original response of the PB electrode was readily obtained when the NH$_4$Cl-exposed electrode was again potential cycled in KCl medium (Figure 9c). This observation indicates that NH$_4^+$ ions cannot block PB channels permanently, because the electrode recovers its original response in KCl medium, though with slightly reduced peak currents (up to 20%). It should be noted that the hydrated ionic radii of NH$_4^+$ and K$^+$ are identical, that is, 1.25 Å. The corresponding CV responses of
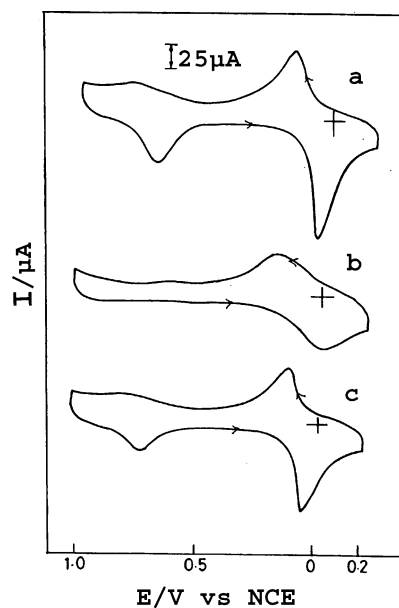
Figure 9. CV responses of a PB-modified GC electrode at 0.1 V s^{-1} in (a) 0.1 M KCl, (b) 0.1 M NH$_4$Cl, and (c) 0.1 M KCl; the electrode was exposed to them in the given order.

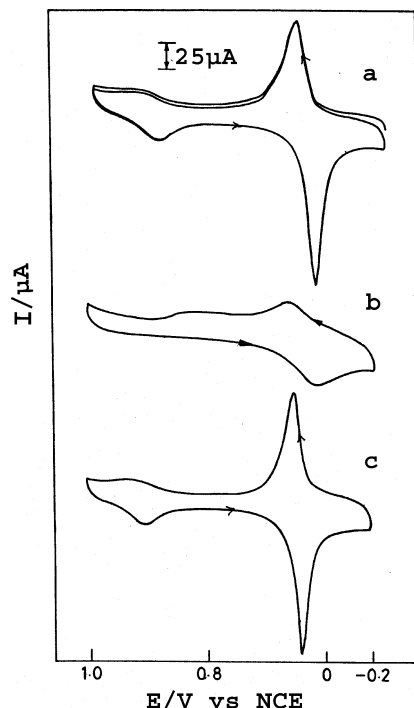**Figure 10.** CV responses of a PB + CTAB-modified GC electrode at 0.1 V s^{-1} in (a) 0.1 M KCl, (b) 0.1 M NH$_4$Cl, and (c) 0.1 M KCl; the electrode was exposed to them in the given order.

the PB + CTAB electrode in KCl, NH$_4$Cl, and then KCl are shown in Figure 10, parts a, b, and c, respectively. The higher currents observed in KCl electrolyte in Figure 10, parts a and c, versus those in Figure 9, parts a and c, respectively, were expected, due to the influence of CTAB. Careful observation reveals that the anodic-to-cathodic peak current ratio approaches unity in the case of the regained PB film. Unlike that observed in the case of NaCl or LiCl, the CV shape is completely regained in KCl after exposure to NH$_4$Cl (cf. Figures 6c, 8c, and 10c). This may be explained considering that the hydrated ionic radii of NH$_4^+$ and K$^+$ are identical, that is, 1.25 Å, and thus their permeability into the lattice channels of PB should be the same.
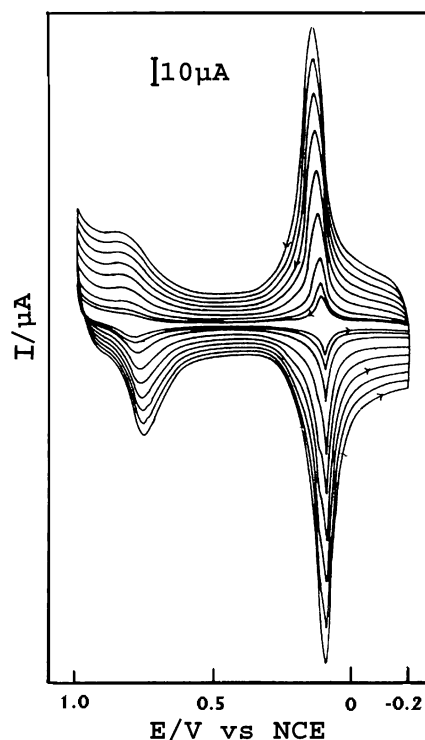

Figure 11. CV responses of a PB + CTAB-modified GC electrode in 0.5 M KCl + 0.01 M HCl at the scan rates of 0.005, 0.01, 0.02, 0.04, 0.08, 0.1, 0.12, and 0.14 V s^{-1}; the modification was carried out in 0.1 M KCl + 0.01 M HCl.

4. Discussion

4.1. Ideal CVs for PB Film Formed Electrochemically in the Presence of CTAB. One may consider the symmetry of cyclic voltammograms over the potential axis in KCl medium in Figure 1, which does not reflect an ideal modification of an electrode with a PB film. It has been mentioned several times above that PB films lost their charges to some extent after being subjected to potential cycling in pure supporting electrolytes; this loss of charges indicates inadequate stability of the films, because the stability of a film formed by cyclic voltammetry can be judged from its stable voltammetric response in a pure electrolyte; that is to say, there should be no decrease in the currents and charges after a considerable period of cycling the potential of the film electrode in a pure supporting electrolyte. Bearing these points in view, we performed a series of experiments, modifying the electrode with PB in the presence of CTAB, in which we varied the KCl concentrations at both the modification and response stages, without making changes in any other conditions, and obtained symmetric CV peaks over the potential axis, as shown in Figure 11. The pertaining PB film was formed in the presence of CTAB using 0.01 M KCl, and the response was obtained in 0.5 M KCl. The anodic-to-cathodic peak current and peak charge ratios approach unity at all scan rates from 0.005 to 0.2 V s^{-1}, and the peak separation is less than 0.06 V at all scan rates, indicating an ideal Nernstian behavior of PB + CTAB film (CVs with scan rates of 0.16 to 0.2 V s^{-1} are not shown for clarity). The CV peaks of CTAB-promoted PB film at these scan rates represent a CV pattern for a PB-modified electrode, because of the symmetry of the cathodic and anodic peaks on the potential axis, representing ideal reversible surface waves with a peak potential difference of less than 0.06 V and an anodic-to-cathodic peak current/charge ratio of unity at all scan rates from 0.005 to 0.2 V s^{-1}. This type of modified electrode is well-suited for electroanalytic and electrocatalytic applications.

CTAB-Promoted Prussian Blue-Modified Electrode

J. Phys. Chem. B, Vol. 112, No. 4, 2008 **1155**

4.2. Stability of PB Films Formed in the Presence of CTAB. PB + CTAB films were found to be thicker and more stable than those prepared in the absence of CTAB. Stability of a sensor in terms of current is one of the most important aspects for fabricating an amperometric sensor. We conducted a series of stability tests on PB films by varying KCl concentrations over 4 orders of magnitude (0.001 to 1 M) at the film formation stage and at its response stage in pure KCl. It was observed that a PB film prepared with 0.5 mM $FeCl_3$ + 0.5 mM $K_3Fe (CN)_6$ + 0.92 mM CTAB in 0.1 M KCl + 0.01 M HCl electrolyte, using other conditions as described in the experimental section, withstood 10^4 cycles without losing any current or charge, when potential-cycled in a 0.5 M KCl + 0.01 M HCl electrolyte. Whereas under the same conditions, a PB film made without CTAB lost about 30% charge. Senthil Kumar et al.[27b] tested the stability of the films prepared under the same conditions that we used before them[23] and observed far higher stability for PB + CTAB films than that for PB films. However they tested the stability in 0.02 M HCl + 0.1 M KCl, unlike us, and lost 20% of film activity after 1500 cycles (at this stage PB film showed a loss of 85%). The presence of OH^- ions during PB film formation is probably responsible for film decay, because OH^- ions that react with PB can form ferric hydroxide, as follows:

$$KFe^{III}[Fe^{+2}(CN)_6] + 3OH^- \rightarrow Fe(OH)_3 + Fe^{+2}(CN)_6 + K^+$$
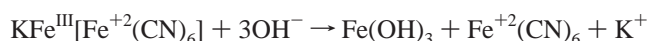
CTAB is a quaternary ammonium compound, and thus can act as a strong acid and nullify the effect of OH^- ions, and thereby stabilize the PB film. This stability test is by no means sufficient for a prototype sensor. Nevertheless, the results obtained reveal that employing CTAB for the electrochemical preparation of a PB film provides an excellent means of enhancing film stability. Gomathi et al. reported a procedure for storing used electrodes in KCl medium, according to which electrodes can be maintained in a stable state (without any deterioration in peak currents) for a considerable period of time.[29]

4.3. Cyclic Voltammetric Studies in Different Supporting Electrolytes. From the results obtained in different supporting electrolytes, it is evident that the peak currents at the redox center of Fe^{+2}/Fe^{+3} of PB are considerably reduced in the presence of Na^+, Li^+, and NH_4^+ ions, showing a blocking effect of these ions in the channels of the PB lattice. It is clear that K^+ ions are the most preferred cations for the entry into the channels of Prussian blue film. These considerations also hold good for a PB + CTAB film. CTAB does not interfere with the basic charge-transfer mechanism of a PB film. CTAB plays only a catalytic role in terms of affecting the charge transfer. The regaining of the basic CV shapes of PB and PB + CTAB films in pure KCl after they had been subjected to intercalation by Li^+, Na^+, and NH_4^+ cations reveals that the basis lattice structure of PB remains the same and is not permanently distorted by these cations. This is very important for a PB-modified electrode for the application as a sensor. In the discussions in section 3.3 (a, b, and c) it was mentioned that not only K^+ ions but also Na^+, Li^+, and NH_4^+ ions enter and exit at the same Fe^{+2}/Fe^{+3} redox center of the PB molecule, which also suggests that CTAB does not influence the basic lattice structure of the PB molecule. Ozeki[28] et al. reported that the PB film was stripped off when it was subjected to potential cycling in 0.1 M LiCl or 0.1 M NaCl, presumably because these large hydrated ions damaged the PB lattice. This obviously did not happen in our case. The persistent enhanced currents of PB + CTAB films at all stages of this investigation may have been

due to larger lattice channel sizes of the films, caused by CTAB during film formation. Larger lattice channel sizes facilitate more rapid ion transport and thereby higher currents. The very fact that PB + CTAB films did not give sharp current responses in the presence of Na^+ and Li^+ indicates that these increased channel sizes were still insufficient to enable the entries of these ions, that is, the lattice channel sizes of the PB film have probably increased only marginally and this allowed facile intercalation with K^+ only.

It is well-known that a PB film with a particular CV response during the film formation in KCl retains the same response in pure KCl. This is why PB + CTAB films always retain their improved responses in pure KCl and other pure electrolytes. Unit cell volume, lattice defects, and water molecule framework of the lattice are important parameters that determine ion exchange property. CTAB apparently improves these parameters of the PB films. The lattice channel size of PB is about 3.2 Å.[25,30] It is not feasible at this moment to determine precisely the lattice channel size of a PB + CTAB film.

Senthil Kumar et al.[27a] proposed a good mechanism for the better deposition of a PB film in the presence of CTAB; however, the issue has not been resolved as to why CTAB selectively affects the Fe^{+2}/Fe^{+3} center and not the $Fe(CN)_6^{-4}/Fe(CN)_6^{-3}$ center (note that enhancements of current and charge are restricted to the former center). Before proceeding further, it is worth noting that the chemical composition of PB and PB + CTAB films remained the same after the influence of CTAB in the latter case, as is indicated by a characteristic CV response for the PB film in both cases and by their XRD spectra. The surface property of the PB + CTAB-modified electrode is also unchanged, as can be observed from the same background currents of the CVs in Figure 1. It has been well established[24,25] that the intercalation and deintercalation of potassium and other cations in PB channels take place only at the PB $\rightleftarrows$ PW center. The enhanced currents in the case of a PB + CTAB film can be well related to the ease of K^+ ion diffusion through the film.[7,31-33] There have been several reports on the bilayer/micellar adsorption of CTAB on electrode surfaces at cmc.[34,35] The adsorption of CTAB is envisaged to occur via the attachment of polar head groups to the hydrophilic ionic groups on GC, to provide hemimicelles of the surfactant with hydrophobic tails in union.[34-36] During hemimicelle formation, it can be visualized that the head groups also expose themselves to the aqueous solution, because of interactions between the hydrocarbon chains. In the present case, CTAB can adsorb onto the electrode surface through Br^- attachment to the Fe^{+2}/Fe^{+3} center of PB. Further, we demonstrated experimentally in our previous report[23] that bromine is evolved at the $Fe(CN)_6^{-4}/Fe(CN)_6^3$ center during PB film formation. Br^- ions can adsorb on the GC surface along with CTAB. The electrostatic attraction between Br^- ions at the electrode and K^+ ions in the electrolyte can favor more facile transport of K^+ ions into the lattice channels of the PB film. This facile transport of K^+ ions enables higher currents and charges only at the Fe^{+2}/Fe^{+3} center.

Referring to Table 1, it can be seen that the current values increase, pass through a maximum, and then decrease as CTAB concentrations are increased—the maximum value being at the cmc of CTAB. As mentioned already, several reports have been issued on the bilayer/micellar adsorption of CTAB onto electrode surfaces at the cmc.[34,35] CTAB exhibits different types of adsorptive behavior at carbon electrodes at different CTAB concentrations,[34,35,37,38] that is, as monomers, monolayers, bilayers, hemimicelles, and micelles. As has been discussed, CTAB affects current enhancement at the redox center at 0.2

V. The degree of this enhancement obviously depends on the adsorptive behavior of CTAB, which in turn depends on the CTAB concentration. Apparently the adsorptive behavior of CTAB at its cmc favors the best current and charge parameters. At higher concentrations of CTAB above its cmc a blocking effect of CTAB on the diffusion of K^+ ions is expected, which would obviously reduce the currents to a level of zero faradic current, as was observed in the case of 2.5 mM of CTAB (Table 1). It should be mentioned in this context, to better understand the blocking effect, that the micellar size of CTAB is about 3 nm, the hydrated radius of K^+ ion is 1.25 Å,[24,25] and the lattice channel size of PB is about 3.2 Å.[25,30]

The selective influence of CTAB in terms of enhancing currents and consequently charges at the Fe^{+2}/Fe^{+3} center (at 0.2 V) and not at the $Fe (CN)_6{}^{-4}/Fe (CN)_6{}^{-3}$ center (at 0.8 V) is a paradox, in view of the fact that CTAB is cationic and the Fe^{+2}/Fe^{+3} redox center involves cations. We are aware of no other theoretical attempts to resolve this issue, and experimental evidence is yet to be accomplished. Moreover, the proposed mechanism is only one of a few possibilities. A study of the microenvironmental behavior of CTAB at the electrode interface is required to understand the different degrees of enhancement of currents at different concentrations of CTAB, which is beyond the scope of this report.

5. Conclusions

Prussian blue films were formed on bare glassy carbon electrodes by cyclic voltammetry in the presence and absence of CTAB to obtain the corresponding modified electrodes. The cyclic voltammetric response of PB + CTAB-modified electrode revealed a 4- to 5-fold enhancement in the anodic and cathodic peak currents, relative to those of an ordinary PB-modified electrode. SEM, XRD, and EIS measurements further revealed remarkable improvement in a PB + CTAB film versus a PB film in terms of crystallinity, and they indicated that lattice defects were reduced and that lattice channel sizes had increased.

Symmetric CV peaks were obtained for a CTAB-promoted PB film in 0.5 M KCl + 0.01 M HCl electrolyte, under optimal film-preparing conditions. Moreover, these symmetric CV peaks show ideal Nernstian behavior at all the scan rates from 0.005 to 0.2 V s^{-1}, representing a CV pattern for a PB-modified electrode. Conditions required for high stability of the PB films formed in the presence of CTAB are also discussed.

Additional cyclic voltammetric experiments with different supporting electrolytes revealed that PB + CTAB films give enhanced current responses in the supporting electrolytes of KCl, NaCl, LiCl, and NH$_4$Cl, with reference to PB films prepared in the absence of CTAB. Moreover, it was observed that K^+ ions show best facile transport characteristics through the PB film, followed by NH$_4^+$, Na$^+$, and Li$^+$ (in order). In contrast to previous reports, we found that a PB film regains its original property after being subjected to potential cycling in NaCl or LiCl electrolyte. In addition, it is demonstrated that CTAB plays only a catalytic role in terms of promoting charge transfer. Mechanisms for the catalytic role of CTAB in the formation of a stable PB film and for its role in the selective enhancement of currents and charges at the Fe^{+2}/Fe^{+3} center of a PB molecule are discussed.

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