

Role of acidity on the electrochemistry of Prussian Blue at plain and Nafion film-coated electrodes

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Abstract. Prussian Blue (PB) coated on plain platinum (Pt) shows a redox wave at 0.44 V vs SCE in addition to the two usual redox waves at 0.82 and 0.12 V vs SCE when the electrodes were dipped in acidic KCl solution. PB incorporated into Nafion film-coated on Pt electrode exhibited the same behaviour even in the presence of neutral KCl solution. In acidic KCl, the additional redox wave observed for PB incorporated into Nafion film shifted positively to 0.39 V vs SCE and the peak separation was reduced to 30 mV. The observed additional redox wave for PB coated on plain Pt electrode and incorporated into Nafion film-coated Pt electrodes was assigned to the partial reduction of PB occurring due to the insertion of protons into the film. The effect of various cations on the electrochemistry of PB incorporated into Nafion film-coated electrode was also studied.

Keywords. Prussian Blue; Nafion film; modified electrodes.

1. Introduction

The multimetal complex ferricferrocyanide called Prussian Blue (PB) $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ has been known for many years (Holtzman 1945; Robin 1962). In the last decade, the electrochemical properties of PB have been studied extensively (Itaya *et al* 1986; Lundgren and Murray 1988; McCarger and Neff 1988). The major features of PB include its easy preparation (Ellis *et al* 1981) and its applications in the field of solid state batteries (Honda and Hayashi 1987; Kaneko and Okada 1988), electrochromic display devices (Mortimer 1991) and in electrocatalysis (Itaya *et al* 1984). PB exists in two forms, the 'insoluble' $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ and the soluble $\text{KFe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ forms. By employing *in situ* spectroelectrochemical (Mortimer and Rosseinsky 1984) and quartz crystal microbalance techniques (Feldman and Melroy 1987), it has been shown that the PB film was deposited as insoluble PB on the electrode even in the presence of K^+ ion in the depositing solution but on continuous cycling insoluble PB was converted into the soluble form. Later, it has been shown (Lundgren and Murray 1988) that the complete conversion into soluble form might not occur even after several cycles. Even though several reports (Itaya *et al* 1986; Lundgren and Murray 1988; McCarger and Neff 1988) have appeared on PB, the electrochemical behaviour associated with different redox states and the variable composition of PB have not been understood completely.

Nafion, a perfluorosulphonate ion-exchange membrane, acts as a super acid (Olah *et al* 1985) and provides an acidic environment for adsorbed molecules (Olah *et al* 1985; Weir and Scaiano 1987). Nafion membranes have been used to prepare solid state cells

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with PB (Kaneko and Okada 1988), to coat the surface of the PB film (Mortimer 1991; Kaneko *et al* 1992) and to polymerize PB within the film (Honda *et al* 1989). However, the electrochemistry of PB incorporated into Nafion film has not been studied directly in the past. Using the sensitizer *tris*(2,2'-bipyridine)ruthenium(II) and PB complexes, a photoredox system has been constructed (Kaneko *et al* 1984, 1986). To construct photoelectrochemical cells using Nafion-coated electrodes it is necessary to incorporate both the sensitizer molecule and PB into the Nafion film. In the present investigation, we have carried out electrochemical studies of PB incorporated into Nafion films; the acidic nature of the Nafion film influences the electrochemical properties of PB at the coated electrode. We report the results in this paper.

2. Experimental

2.1 Materials

Reagent grade chemicals were used as received. A 5% Nafion film (Aldrich) was diluted to 2% solution using methanol before use. Nafion-coated Pt (1 cm²) or glassy carbon electrode (GC, 0.07 cm²) was prepared by casting 8 μ l of 2% Nafion solution on a plain Pt or GC electrode and drying at room temperature. The Nafion-coated electrode was rinsed and kept in distilled water for 30 min before use yielding a film thickness of 1 μ m (Martin and Dollard 1984; Gobi and Ramaraj 1994).

2.2 Apparatus and procedure

Prussian Blue was deposited on the plain Pt by potential cycling or dipping equimolar mixture of 5 mM FeCl₃ and K₃[Fe(CN)₆] in 0.01 M KCl and 0.01 M HCl (Lundgren and Murray 1988). The PB incorporated Nafion-coated electrode was prepared by soaking the Nafion-coated Pt or GC electrode in the above solution for 30 min. The Nafion film became blue in colour indicating the absorption of PB into the Nafion film. Then the PB-coated Pt electrode (represented as Pt/PB) and PB incorporated into Nafion film-coated Pt and GC electrodes (represented as Pt/Nf/PB and GC/Nf/PB) were rinsed with triply distilled water and immersed in KCl or water for 12–24 hours to remove the uncomplexed ferric ions (Honda and Hayashi 1987).

Pt/PB, GC/PB, Pt/Nf/PB or GC/Nf/PB and a 1 cm² platinum plate were used as working and counter electrodes. Cyclic voltammograms were recorded on an EG and G Princeton Applied Research 273 A Potentiostat/Galvanostat equipped with RE0151 recorder. The amount of PB coated onto the electrode was determined by the coulometric method (Oyama and Anson 1980). The potentials were measured and reported with respect to a Saturated Calomel Electrode (SCE). All solutions were outgassed with nitrogen.

3. Results and discussion

3.1 Electrochemistry of PB at plain Pt electrode

A typical cyclic voltammogram recorded for Pt/PB in 0.05 M KCl is shown in figure 1 (A). It shows clearly two distinct redox waves at 0.12 and 0.82 V. The redox wave observed at 0.12 V corresponds to the redox reaction between Fe^{III}/Fe^{II} (PB) and Fe^{II}/Fe^{II} (called Prussian White, PW) and the redox wave at 0.82 V corresponds to the redox reaction between Fe^{III}/Fe^{II} (PB) and Fe^{III}/Fe^{III} (called Berlin Green, BG) (Itaya *et al* 1986).

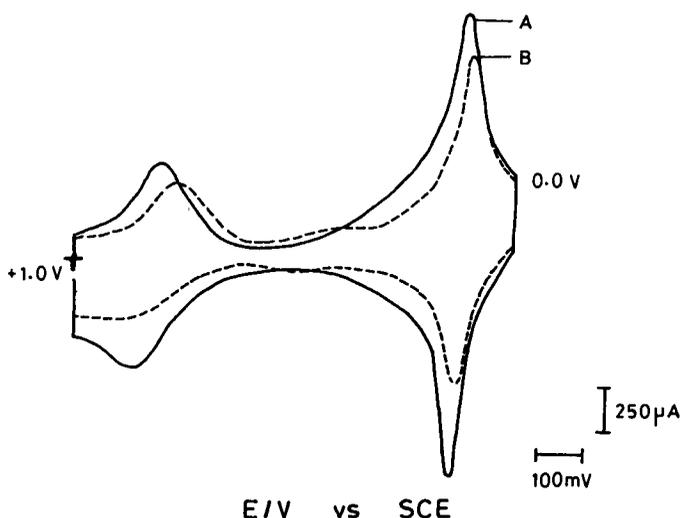


Figure 1. Cyclic voltammograms of Pt/PB in 0.05 M KCl (A) and in a mixture containing 0.05 M KCl and 0.005 M HCl (B); Scan rate = 50 mv/s.

The cyclic voltammogram recorded for Pt/PB in a mixture containing 0.05 M KCl and 0.005 M HCl (acidic KCl) solution is shown in figure 1(B). It shows an additional redox wave at 0.44 V in addition to the two usual redox waves observed at 0.12 and 0.82 V. Plichon and Besbes (1992) have observed a shoulder-like irreversible reduction wave around 0.40 V vs SCE for PB coated onto SnO₂ electrode in acidic KCl supporting electrolyte solution. However, in the present investigation, we observed a redox wave at 0.44 V, which disappeared on continuous cycling or upon addition of higher concentration of KCl (> 0.1 M) to the acidic KCl supporting electrolyte solution. For the same electrode, the amount of charge consumed for the reduction of PB in acidic KCl was higher than that for 0.05 M KCl solution. The addition of higher concentration of HCl (> 0.01 M HCl) into the supporting electrolyte solution resulted in the loss of ferric ions from the PB film. The ferric ion present in solution was detected by spectrophotometric methods (Lundgren and Murray 1988). The addition of 0.005 M HCl to 0.05 M KCl solution shifted the potential anodically and the oxidation of PB to BG became more pronounced. The intensity of the reduction at 0.12 V also decreased. This is due to the partial oxidation of PB to BG at pH 2 or 3 which becomes fully oxidized only at neutral condition or at higher KCl concentration (Feldman and Melroy 1987). However, the appearance of the new redox wave at 0.44 V has to be noted. It has been already reported that K⁺ ions are inserted into the PB film during the redox reactions at neutral condition (Mortimer and Rosseinsky 1984). Later, it has been found that K⁺ ions are exchanged by H⁺ ions in the PB film when dipped in acidic KCl supporting electrolyte solution (Lundgren and Murray 1988; Plichon and Besbes 1990). This has been established by different workers by using mass loss data (Feldman and Melroy 1987; Lundgren and Murray 1988), mirage detection experiment (Plichon and Besbes 1990) and FTIR spectroscopy (Christensen *et al* 1990). These reports have clearly established that the H⁺ ion was diffusing into the PB film when dipped in acidic KCl solution. The diffusion coefficient of H⁺ ion ($3.4 \times 10^{-5} \text{ cm}^2/\text{s}$) is higher than that of K⁺ ion ($1.2 \times 10^{-5} \text{ cm}^2/\text{s}$) and hence the H⁺ ion easily exchanges the K⁺ ion in the

PB film (CRC Handbook 1968). Also in the case of Li^+ exchanged PB film, the H^+ ion enters into the PB film (Plichon and Besbes 1992).

3.2 Incorporation of PB into Nafion film

The polymerization of PB in Nafion membrane has been reported by Honda *et al* (1989). However, the site of adsorption of PB and its electrochemical behaviour in the Nafion membrane was not discussed. The swollen Nafion film contains hydrophobic fluorocarbon phase, hydrophilic sulphonate ionic clusters and the interfacial region formed between these two (Yeager and Steck 1981; Kyu and Eisenberg 1982). The interfacial region is known to accommodate neutral molecules which upon oxidation migrate to ionic cluster region (Rubinstein 1985). The insoluble form of PB present in solution forms colloidal particles (Itaya and Uchida 1986; Feldman and Melroy 1987). When the Nafion coated Pt (Pt/Nf) or GC (GC/Nf) electrode is dipped in a solution containing the insoluble PB particle $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$, the PB is absorbed into the Nafion film. Since the PB particle is insoluble and neutral it will occupy the interfacial region of the Nafion film. It has been already reported that the molecules adsorbed into the hydrophobic region of the Nafion film were electrochemically inactive (Rubinstein

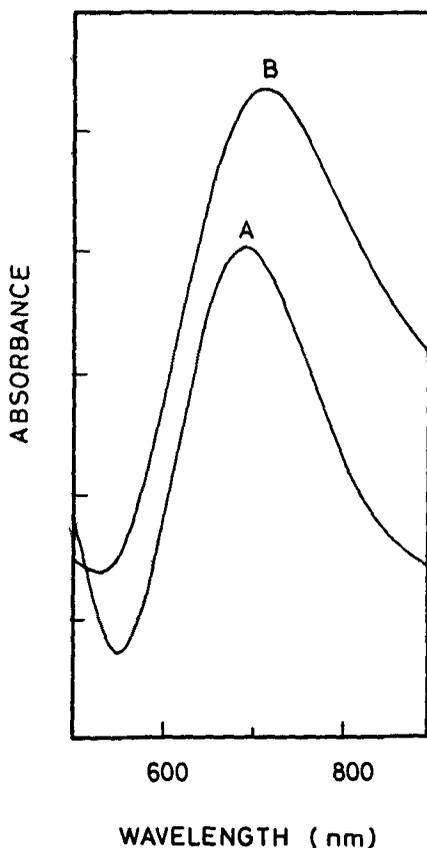


Figure 2. Absorption spectra of PB incorporated into Nafion film-coated onto a transparent glass plate (A) and PB coated on quartz glass plate (B).

1985). The neutral and small charged molecules occupy the interfacial and ionic cluster regions; whereas the high charged molecules occupy the ionic cluster regions (Harth *et al* 1989). The Pt/Nf electrode turned blue in colour after absorption of PB. The absorption spectrum recorded for PB incorporated into Nafion film coated onto transparent quartz glass plate is shown in figure 2A. The observed absorption maximum around 685 nm was assigned to PB (Honda *et al* 1989) and clearly shows the presence of PB within the Nafion film. The absorption spectrum recorded for PB coated onto quartz glass plate (figure 2B), showed an absorption maximum around 700 nm. The absorption spectrum recorded for PB and Nf/PB films coated onto quartz glass plate did not show significant change when dipped in acidic KCl solution and this indicates the fact that the insertion of H^+ ion into the PB films did not bring about any change.

3.3 Electrochemistry of PB incorporated into Nafion coated Pt electrode

The cyclic voltammogram recorded for Pt/Nf/PB in 0.05 M KCl is shown in figure 3A. It shows a redox wave at 0.34 V in addition to the two usual redox waves which are characteristic for PB (Itaya *et al* 1986). It is also evident that only partial oxidation of PB has occurred during the scan. A similar behaviour has also been observed for GC/Nf/PB. Upon continuous cycling, the redox wave observed at 0.34 V decreased very much and the oxidation of PB became very clear (figure 3B). This result shows that in the first scan the PB incorporated into Nafion film experiences the acidic environment imposed by the Nafion film and in the subsequent continuous cycling more K^+ ions from solution are exchanged into the Nf/PB film. This K^+ ion insertion into the Nafion film improves the oxidation wave for PB at 0.82 V. It has been reported that the complete oxidation of PB at 0.90 V occurred only when the K^+ ions were inserted into the PB film (Feldman and Melroy 1987). The cyclic voltammogram

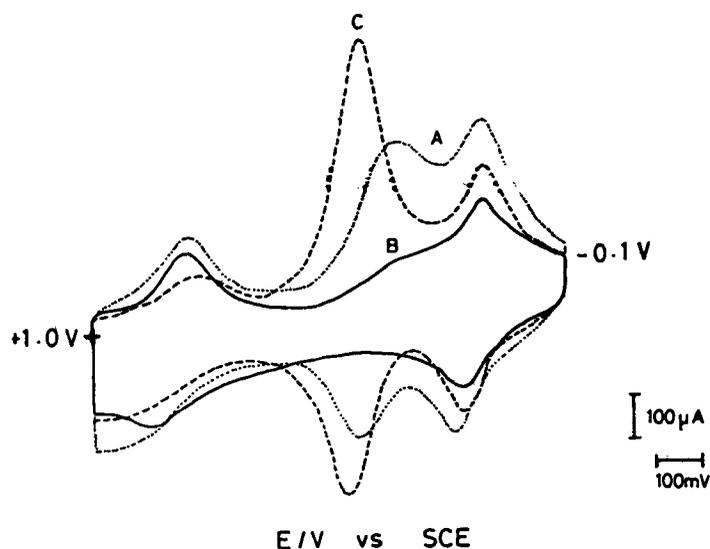


Figure 3. Cyclic voltammograms of Pt/Nf/PB in 0.05 M KCl (A); after continuous cycling (B) and in a mixture containing 0.05 M KCl and 0.005 M HCl (C). Scan rate = 50 mV/s.

recorded for Pt/Nf/PB in acidic KCl is shown in figure 3C and it shows a well resolved redox wave at 0.39 V in addition to the redox wave at 0.12 V. This observation shows that the additional redox wave appeared mainly due to the presence of H^+ ions within the Nf/PB film. The presence of H^+ ions in the supporting electrolyte solution enhances the redox process at 0.39 V. The continuous cyclic voltammogram recorded for Nf/PB in the presence of acidic KCl does not result in the elimination of the redox wave at 0.39 V. An average of $7.1 \times 10^{-3} H^+$ ions exist in a $-SO_3^-$ cluster or 140 ionic clusters contain one H^+ ion even in the case of Na^+ exchanged Nafion film (Rubinstein 1985). In the present investigation, we concluded that the presence of acidic environment in the Nafion film is responsible for the appearance of the additional redox wave at 0.34 V when Pt/Nf/PB dipped only in 0.05 M KCl solution.

When 0.005 M HCl was added to 0.05 M KCl solution, the additional redox wave observed at 0.34 V for Pt/Nf/PB was shifted to 0.39 V and also the peak separation was reduced from 90 mV to 30 mV (figure 3c). The total charge measured for the reduction of PB at Pt/Nf/PB in acidic KCl is higher than that of the charge measured in 0.05 M KCl solution. The electrochemical data observed for Pt/PB and Pt/Nf/PB in aqueous KCl and acidic KCl solutions are summarised in table 1.

3.4 Effect of concentration of H^+ and K^+ ions on the electrochemistry of PB incorporated into Nafion film

The cyclic voltammograms recorded for Pt/Nf/PB in a mixture containing 0.05 M KCl and 0.005 M HCl solution and also at increased concentration of KCl are shown in figure 4. In figure 4, a gradual decrease in the peak current at 0.39 V with a simultaneous increase in the peak current at 0.12 V was observed. When the concentration of KCl in the supporting electrolyte solution is increased, a higher amount of K^+ ion enters into the Nafion film and interacts with PB upon redox cycling. Due to K^+ ion insertion, the intensity of the redox wave responsible for H^+ ion insertion decreases at 0.39 V and the peak separation also increases. On the other hand the increase of HCl concentration in the supporting electrolyte solution leads to the appearance of more predominant redox wave at 0.39 V with a corresponding decrease in the peak current at 0.12 V (figure 5).

3.5 Electrochemical behaviour of Fe^{3+} and $Fe(CN)_6^{3-}$ ions at Nafion coated electrode in comparison with PB

The cyclic voltammograms recorded for Fe^{3+} ion in a mixture containing 0.05 M KCl and 0.005 M HCl using Pt/Nf and Pt electrodes are shown in figure 6. It shows a redox

Table 1. Electrochemical data of Pt/PB and Pt/Nf/PB in 0.05 M KCl and a mixture containing 0.05 M KCl and 0.005 M HCl.

Electrode system	[KCl] (M)	[HCl] (M)	$^1E_{1/2}$ (V)	ΔE_p (mv)	$^2E_{1/2}$ (V)	ΔE_p (mv)	$^3E_{1/2}$
Pt/PB	0.05	—	0.12	35	—	—	0.82
	0.05	0.005	0.11	35	0.44	90	0.81
Pt/Nf/PB	0.05	—	0.14	70	0.34	90	0.82
	0.05	0.005	0.11	50	0.39	30	0.79

$^1E_{1/2}$ = Fe(III) Fe(II)/Fe(II) Fe(II); $^2E_{1/2}$ = additional redox wave (Fe(II) Fe(II)/Fe(II) Fe(II)); $^3E_{1/2}$ = Fe(III) Fe(II)/Fe(III) Fe(III); ΔE_p = peak separation.

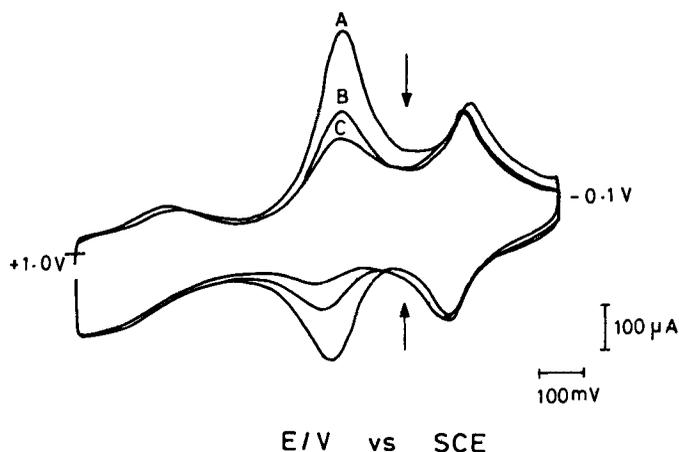


Figure 4. Cyclic voltammograms of Pt/Nf/PB in a mixture of 0.05 M KCl and 0.005 M HCl (A), 0.075 M KCl and 0.005 M HCl (B) and 0.1 M KCl and 0.005 M HCl (C). Scan rate = 50 mV/s.

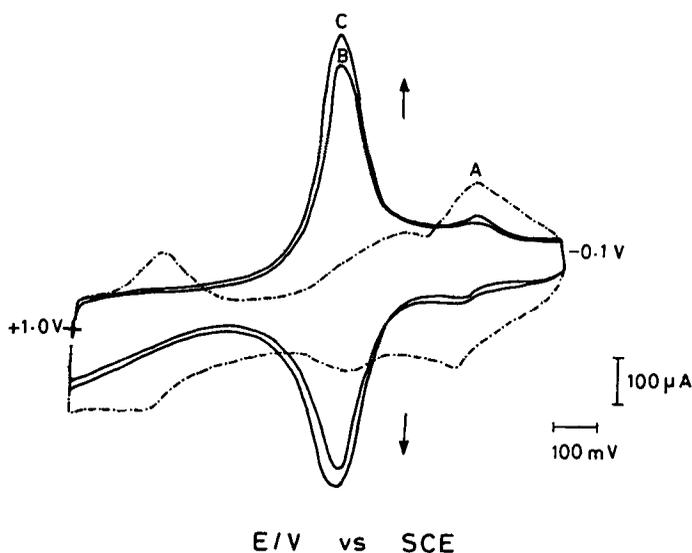


Figure 5. Cyclic voltammograms of Pt/Nf/PB in 0.05 M KCl (A), 0.05 M KCl and 0.001 M HCl (B) and 0.05 M KCl and 0.005 M HCl (C). Scan rate = 50 mV/s.

wave at 0.46 V with a peak separation of 60 mV at both Pt/Nf and Pt electrodes and the observed redox wave was assigned to $\text{Fe}^{3+/2+}$ couple (figure 6A and 6B). Further addition of HCl into the supporting electrolyte solution did not bring about any change in the cyclic voltammograms. On the other hand, the redox wave observed at 0.34 V for Pt/Nf/PB in 0.05 M KCl (figure 3A) was shifted from 0.34 V to 0.39 V in acidic KCl solution and the peak separation was reduced from 90 mV to 30 mV (figure 3C). In the case of PB coated on Pt electrode, the plot of peak current vs scan rate showed linearity for the reduction of PB (Fe(III)Fe(II)) to PW (Fe(II)Fe(II)) (Ellis *et al* 1981). In the present case, the cyclic voltammograms recorded for Pt/Nf/PB in an acidic KCl

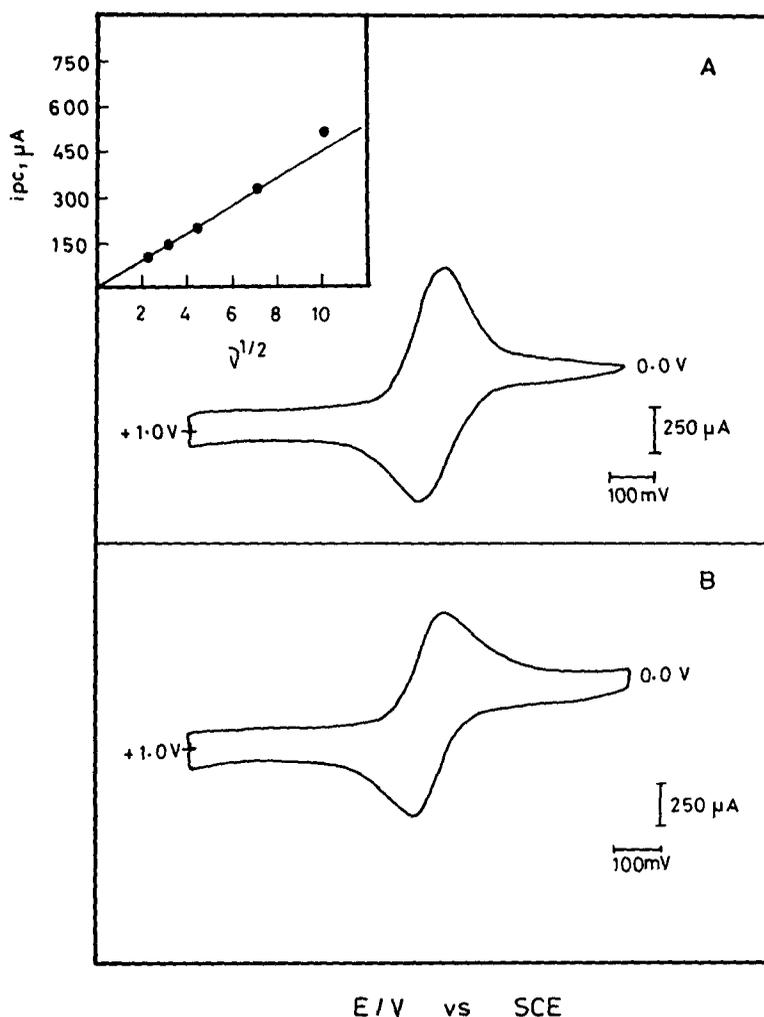


Figure 6. Cyclic voltammograms of Fe^{3+} ion in a mixture of 0.05 M KCl and 0.005 M HCl at Pt/Nf electrode (A) and Pt electrode (B); Scan rate = 50 mV/s. Inset: Plot of peak current vs scan rate.

at different scan rates for the redox wave observed at 0.39 V are shown in figure 7. The plot of peak current vs scan rate shows linearity (figure 7, inset). However, in the case of Pt/Nf/ Fe^{3+} (solution), the plot of peak current vs square root of scan rate shows linearity (figure 6A, inset). These results show that the additional redox wave observed at 0.39 V for Pt/Nf/PB is not due to the presence of free Fe^{3+} ions within the Nafion film.

Lundgren and Murray (1988) reported that a shoulder wave appeared around 0.33 V vs SSCE in the first reductive scan for PB film coated electrode in 0.5 M KCl solution. McCarger and Neff (1988) argued that the wave observed at 0.33 V vs SSCE for PB was responsible for the coprecipitated ferricyanide. Later, Plichon and Besbes (1992) observed a shoulder in the positive potential region for PB coated electrode in the presence of acidic KCl solution and ruled out the possibility of the involvement of the coprecipitated ferricyanide in the redox process by carrying out mirage effect experiment

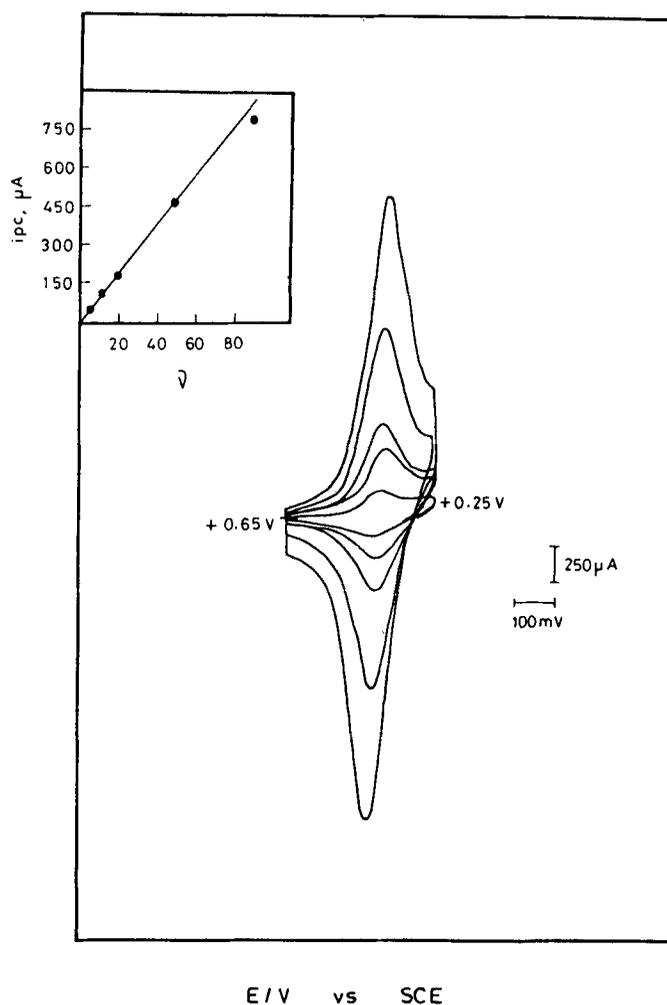


Figure 7. Cyclic voltammograms of Pt/Ni/PB in a mixture of 0.05 M KCl and 0.005 M HCl. Scan rate = 5, 10, 20, 50 and 100 mV/s; Inset: Plot of peak current vs scan rate.

and also discussed the H^+ ion insertion into the PB film (Plichon and Besbes 1990). To exclude the possibility of the involvement of $Fe(CN)_6^{3-}$ ions in the redox process at 0.39 V, the cyclic voltammograms were recorded for $Fe(CN)_6^{3+}$ using both Pt/Ni and Pt electrodes and are shown in figure 8. At both the electrodes the redox wave for $Fe(CN)_6^{3+/4-}$ couple was observed at 0.23 V with a peak separation 190 mV for Pt and 350 mV for Pt/Ni. This observation clearly rules out the possibility of the presence of free ferricyanide ion within the Nafion film.

3.6 Effect of different cations on the electrochemistry of PB incorporated into Nafion film

The electrochemistry of PB at different cations has been already reported (Itaya *et al* 1982; Lundgren and Murray 1988). It has been reported that the electrochemistry of PB

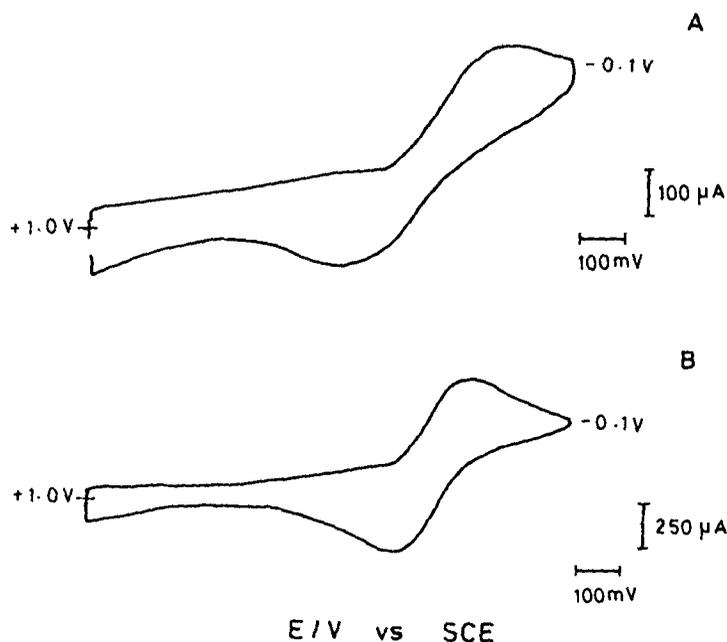


Figure 8. Cyclic voltammograms of $\text{Fe}(\text{CN})_6^{3-}$ ion in a mixture of 0.05 M KCl and 0.005 M HCl at Pt/Nf electrode (A) and Pt electrode (B); Scan rate = 50 mV/s.

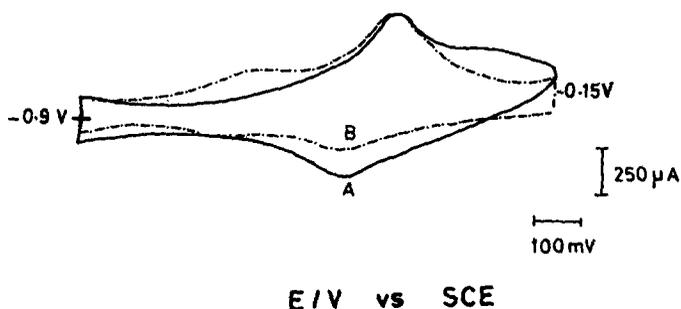


Figure 9. Cyclic voltammograms of Pt/PB in 0.05 M NH_4Cl (A) and in a mixture of 0.05 M NH_4Cl and 0.005 M HCl (B); Scan rate = 50 mV/s.

coated on plain electrode was not stable in the presence of NaCl as supporting electrolyte (Itaya *et al* 1982). However, in the presence of LiCl, the reduction of PB was observed only after cyclically reducing the PB in KCl solution (Lundgren and Murray 1988). The cyclic voltammograms recorded for Pt/PB on 0.05 M NH_4Cl was remarkably stable (figure 9a) and the redox waves were comparatively less symmetric. The cyclic voltammogram shown in figure 9A for Pt/PB in 0.05 M NH_4Cl is very similar to the reported one (Itaya *et al* 1982). In the case of CsCl a less stable nature was reported (Itaya *et al* 1982). The addition of 0.005 M HCl to 0.05 M NH_4Cl supporting electrolyte solution resulted in an additional redox wave at 0.44 V for Pt/PB as in the case of KCl solution and is shown in figure 9B. These results show that the H^+ ion is exchanged

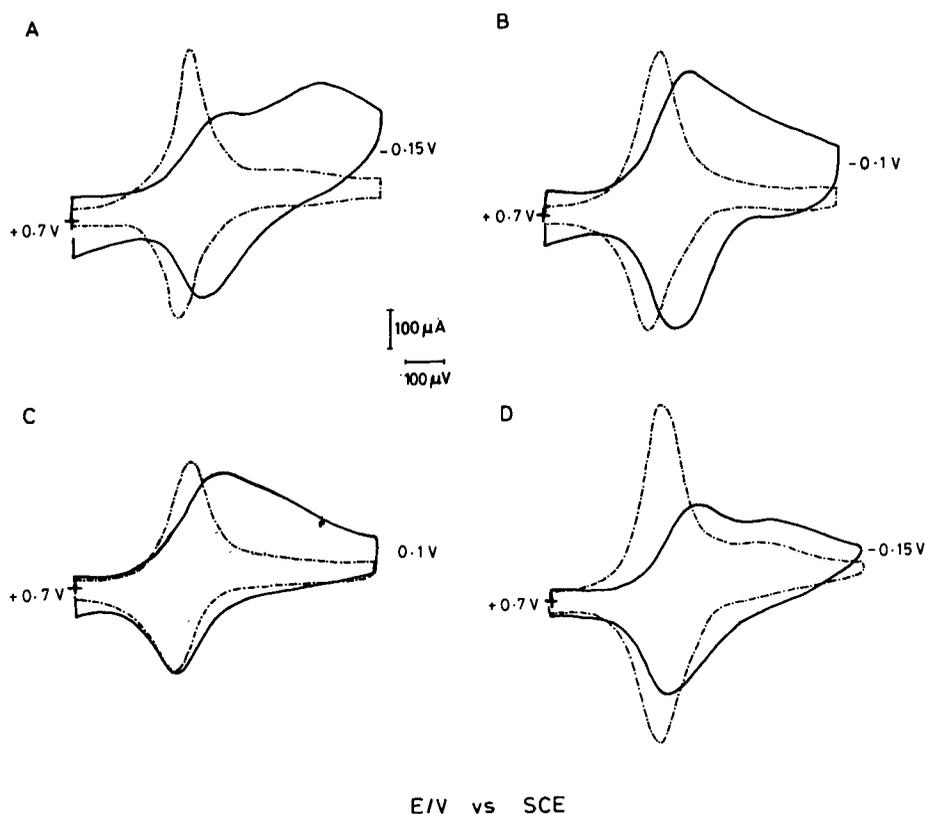


Figure 10. Cyclic voltammograms of Pt/Nf/PB in different supporting electrolytes. (A): 0.05 M LiCl (-----) and a mixture containing 0.05 M LiCl and 0.005 M HCl (———); (B): 0.05 M NaCl (-----) and a mixture containing 0.05 M NaCl and 0.005 M HCl (———); (C): 0.05 M CsCl (-----) and a mixture containing 0.05 M CsCl and 0.005 M HCl (———); (D): 0.05 M NH_4Cl (-----) and a mixture containing 0.05 M NH_4Cl and 0.005 M HCl (———), Scan rate = 50 mV/s.

with NH_4^+ ion in the PB film.

In the case of Pt/Nf/PB, the cyclic voltammograms recorded in 0.05 M of different supporting electrolytes like LiCl, NaCl and NH_4Cl are shown in figures 10A–D(——). In all the cases except CsCl and NaCl, additional redox waves at 0.34 V along with the usual redox waves at 0.12 V were observed as in the case of KCl supporting electrolyte solution. In the NaCl and CsCl supporting electrolytes, only the redox wave at 0.34 V was observed and the redox wave at 0.12 V was absent (figures 10B and 10C). The observed redox wave at 0.34 V can be explained on the basis of the acidic environment imposed by the Nafion film on PB which is not affected by the presence of different cations. The electrochemical data obtained for Pt/Nf/PB in different cations are summarised in table 2. The cyclic voltammograms recorded for Pt/Nf/PB in a mixture containing 0.005 M HCl and 0.05 M of different supporting electrolytes are shown in figures 10A–D(-----). In all the cases, the additional redox wave was shifted positively and the peak separation was reduced to 30 mV.

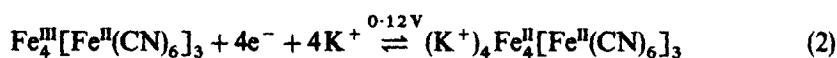
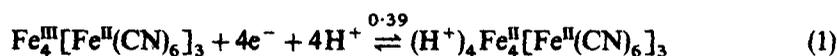
Table 2. The electrochemical data of Pt/Nf/PB in different cations at 0.05 M concentrations and containing 0.005 M HCl.

[Supporting electrolyte]	[HCl] (M)	$^1E_{pc}$ (V)	$^2E_{pc}$ (V)	ΔE_p (mv)
LiCl	—	0.07	0.30	50
LiCl	0.005	0.10	0.35	60
NaCl	—	—	0.30	50
NaCl	0.005	—	0.39	40
NH ₄ Cl	—	0.10	0.30	80
NH ₄ Cl	0.005	0.10	0.40	10
CsCl	—	—	0.32	120
CsCl	0.005	—	0.40	45

$^1E_{pc}$ and $^2E_{pc}$ = as in table 1 and represents the reduction potentials.

4. Conclusion

The PB incorporated into Nafion film coated Pt and GC electrodes were prepared and the electrochemical properties were studied in aqueous and acidic KCl solution and also in other supporting electrolytes. The H⁺ ion insertion was responsible for the redox wave observed at 0.39 V and K⁺ ion was responsible for the redox wave observed at 0.12 V for PB in an acidic KCl. The redox processes observed at 0.39 and 0.12 V for the Pt/Nf/PB are suggested as given in (1) and (2):



The effect of H⁺ ion on the electrochemistry of PB was clearly established by using Nafion film coated electrode.

Acknowledgements

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