Spectroelectrochemistry of New Prussian Blue Films Prepared by a Cast Method

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(Received July 31, 1990)

New Prussian Blue (PB) films were prepared by being cast from colloidal PB dispersions in an organic solvent containing cationic surfactants. The electrochromic behaviors of the cast PB films are similar to those of electrodeposited PB films. However, the cyclic voltammetries of both the PB films were quite different from each other. To make the difference clear, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and X-ray photospectroscopy (XPS) were used in measurements of these films grown on Pt and indium tin oxide electrodes. The EDX results for fresh PB films indicated that cast films contain K^+ ions, suggesting a soluble-form PB, $KFe[Fe(CN)_6]$, while electrodeposited films do not, suggesting an insoluble-form PB, $Fe_4[Fe(CN)_6]_3$. The transient spectral observations indicated the participation of a unique electrochemically active iron(III) site in the reductive cycles of a cast film, although the participation of a plural electrochemically active iron(III) sites was proposed for an electrodeposited film. After a repeated cyclic scan a cast PB film maintained its unique active site, while an electrodeposited film had plural sites comprising both a soluble and an insoluble form of PB.

Prussian Blue (PB, iron(III) hexacyanoferrate(II), Fe(III/II)) is a well-known colorant used extensively in the formulation of paints, lacqures, and painting inks. Recently, Neff devised a chemical method to deposit thin films of this material onto platium and gold electrodes,[1] and were the first to investigate the electrochemistry of these films.[2,3] Neff's preparation method was modified by Itaya et al., who reported on the spectroscopies and electrochemical properties of these films prepared electrochemically on a number of substrates;[4,5] they then applied this knowledge to construct an electrochromic display.[6] For such a device to be practically useful, however, the preparation method must be modified to allow deposits on a large area and to also allow long-term stability. It is not very easy to manufacture a uniform PB film of large area by the above-mentioned methods. Though the casting of PB colloids in a nonaqueous solvent is considered to be effective to overcome this problem, such a cast film has not yet been developed.

We have found that PB colloids can be extracted from an aqueous solution by an organic solvent containing some cationic surfactants.[7,8] A PB composite film was prepared onto a transparent electrode by casting an extracted PB solution. This novel method is unique in that it enables the preparation of uniform PB films of large area. The cast PB film can be electrochemically reduced or oxidized, demonstrating a stable electrochromism, as observed in electrodeposited PB films. In this paper we describe the results of electrochemical, analytical, and spectroelectrochemical studies of a cast PB film and compare them with those of electrodeposited PB film in order to clarify the difference between the two PB films.

Experimental

Materials. Potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$, and iron(III) chloride, $FeCl_3 \cdot 6H_2O$ were the purest grade commercially available. Cationic surfactants, such as hexadecyltrimethylammonium chloride (HTAC), were purified by the standard procedures.

Preparation of Cast PB Films. The colloidal dispersions of PB were prepared by rapid mixing of aqueous solutions of both $K_4[Fe(CN)_6]$ and $FeCl_3 \cdot 6H_2O$ at an equimolar ratio. The colloidal solution, thus prepared at the concentration of 20 mmol dm^{-3} (or less), was continuously stirred before extraction in order to prevent any aggregation of the colloids; the colloidal PB was then extracted from the solution within 1 d. The extraction was carried out by using a chloroform solution containing two- or three-fold moles of a cationic surfactant.[8] The extracted chloroform solution of PB (hereafter denoted as PB-surfactant) was dried over anhydrous magnesium sulfate. To form a cast PB-surfactant film, the solution of PB-surfactant was cast onto an indium tin oxide electrode (ITO, 1 cm×1 cm, 10 Ω/□) for spectroelectrochemical studies, and onto a Pt electrode for elemental analysis by EDX.

It was found that, in general, a treatment that involved one H_2O-immersing and air-drying of the as-cast film substantially enhanced the adhesion of the cast film on the electrode. To obtain stable voltammograms, all of the cast films were finally immersed in pure H_2O and dried in a desiccator before performing a voltammetric scan.

Preparation of Electrodeposited PB Film. The electrodeposited PB films were prepared by using essentially the same method proposed by Itaya et al.[4,5] The PB was deposited galvanostatically (10 μA cm^{-2}) for 8 min onto the same ITO electrode (1 cm×1 cm, 10Ω/□) from an aqueous solution containing $K_3[Fe(CN)_6]$ (20 mmol dm^{-3}), $FeCl_3 \cdot 6H_2O$ (20 mmol dm^{-3}), KCl (0.01 mol dm^{-3}), and HCl (0.01 mol dm^{-3}).

Voltammetric and Spectroelectrochemical Measurement. Voltammograms were obtained with a Toho Technical Research model PS-2000 potentiostat equipped with a model FG-02 function generator and a model 3320 digital coulometer. A small KCl-saturated Ag–AgCl electrode was used as a reference. The cell used for spectroelectrochemical measurements was almost the same as that designed by Hoang et al.[9] and was purged with pure nitrogen gas. In

order to measure the transient spectral change during the electrochemical process, rapid scanning multichannel photodiode array spectrometers (Otsuka Electronics Co., MCPD-100A and IMUC-7000S) were used with an ITO working electrode. The MCPD coupled with Toho's model FG-02 function generator was triggered and operated by an NEC model 9801-VX personal computer. The transient absorption spectra were recorded at a 12.5 s interval with slow scanning (2 mV s^{-1}) of the ITO potential, and at a 0.08 s interval with stepping of the ITO potential. All potential values cited in this paper refer to Ag/AgCl.

Surface Analyses. A Hitachi S-430 scanning electron microscope (SEM) and a KEVEX-7000 energy-dispersive X-ray analyzer (EDX) were used to examine the alteration in the surface morphology as well as the chemical composition of the films on the surface both before and after immersing into the electrolyte, as well as subsequent voltammetric scanning in an electrolyte of 0.1 mol dm^{-3} $KClO_4$ at pH 4.0.

Results and Discussion

Chemical Composition of the PB in the Extracted Solution and in the Cast Film. We have shown that PB colloids can be extracted by an organic solution containing cationic surfactants.[7,8] The fact that only cationic surfantants can extract the PB colloids from the aqueous solution suggests the formation of composite micelles between the cationic surfactant molecules and negatively charged PB colloids having $Fe^{III}[Fe^{II}(CN)_6]^-$ units.

In general, PBs prepared in various ways can be devided into two formulations (a "soluble" form, $KFe^{III}[Fe^{II}(CN)_6]$, and an "insoluble" form, $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot 6H_2O$) depending on the specific preparation conditions.[10] The PB, which was recrystallized[11] or electrodeposited,[4,5] was reported to have the composition of $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot 6H_2O$, the "insoluble" form. For PB prepared by mixing $K_4[Fe(CN)_6]$ and $FeCl_3$, Wilde et al. proposed that when an excess of $K_4[Fe(CN)_6]$ to $FeCl_3$ is used a "soluble" PB is formed, while an excess of $FeCl_3$ to $K_4[Fe(CN)_6]$ gives an "insoluble" PB.[12] In fact, the composition of PB as a colloidal form in an aqueous solution was reported by Kaneko et al. as $KFe^{III}[Fe^{II}(CN)_6]$, the "soluble" form.[13]

In order to clarify the relation between the preparation conditions and the extractability by surfactants, an extraction of PB was carried out by an organic solution containing such cationic surfactants as HTAC (hexadecyltrimethylammonium chloride) from various aqueous PB solutions which were prepared by altering the molar ratio between potassium hexacyanoferrate(II) and iron(III) chloride. It was then found that the extraction of PB is effective only when the ratio of $Fe^{II}/(Fe^{II}+Fe^{III})$ is larger than 0.5.[8] This fact strongly suggests that only the "soluble" form PB can be extracted by an organic solution containing cationic surfactants.

The extracted PB solution was cast onto an ITO electrode or a Pt electrode to form a cast PB-surfactant film. Among the cationic surfactants examined, cationic surfactants with a longer alkyl chain than C_{14} were effective to form a stable cast PB film.

The chemical composition of PB in the cast film was measured by energy-dispersive X-ray analysis (EDX), which showed that cast PB film is still composed of the "soluble" form PB.[8] Details are discussed later in the present paper.

Electrochromic Behaviors of the Cast Films. The electrochromic behaviors of the cast PB-surfactant films were investigated by in-situ UV-vis spectroscopy, as mentioned briefly in a preliminary communication.[7] Figure 1(a) shows the absorption spectral changes of the PB-HTAC film measured under voltammetric scanning between −0.3 V and +1.4 V vs. Ag/AgCl with a scan rate of 50 mV s^{-1}. The color changes of the PB-HTAC film are not so large, compared with those of the electrodeposited PB film (Fig. 1(c)), for which the so-called Berlin Brown (BB, Fe(III/III), at +1.4 V vs. Ag/AgCl), and Prussian White (PW, Fe(II/II), at −0.3 V vs. Ag/AgCl) are well-known.[5] This small change in color may be due to the low ionic conductivity of the PB-HTAC film. To improve the conductivity of the PB-HTAC film,

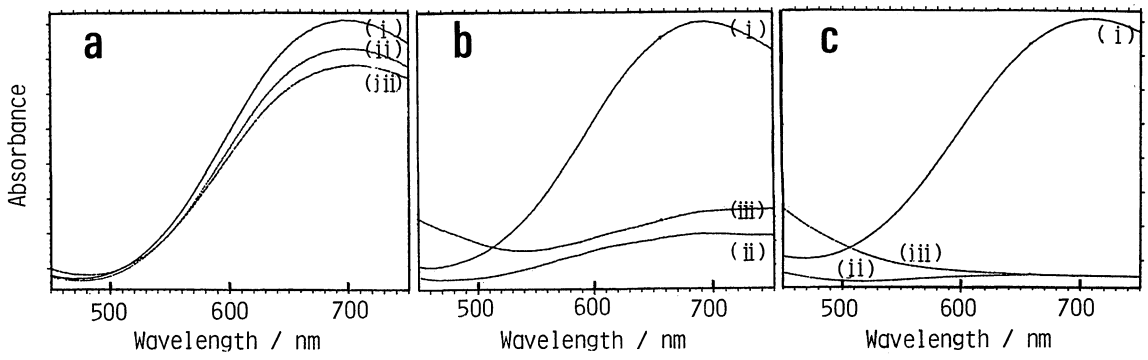

Fig. 1. Absorption spectral changes of the cast PB films, (a) PB-HTAC and (b) PB-HTAC-$LiClO_4$, and (c) the electrodeposited PB film measured under repeated voltammetric scanning. The curves show spectra at (i) +0.5 V, (ii) −0.3 V, and (iii) +1.4 V.

lithium perchlorate $LiClO_4$ in acetone was added to the extracted PB-HTAC solution in chloroform as a promoter for ionic conductivity.[14] The mixed solution was cast to form a PB-HTAC-$LiClO_4$ film. The UV-vis spectra of the PB-HTAC-$LiClO_4$ film at the oxidized and reduced states show a clear and rapid electrochromic behavior, as shown in Fig. 1(b). The oxidized and reduced films are yellow and colorless at +1.4 V and −0.3 V, respectively. The transient spectral changes of the PB-HTAC-$LiClO_4$ film are similar to those of an electrodeposited PB film dipped in an aqueous electrolyte (Fig. 1(c)).

Figure 2 illustrates the change of the absorbance at 700 nm (λ_{max} of PB) in the PB-HTAC, PB-HTAC-$LiClO_4$ and electrodeposited PB films, for which the potential is stepped between +0.5 V and +1.4 V. The electrochromic response of the PB-HTAC-$LiClO_4$ film (b) is remarkably more rapid than that of the PB-HTAC film (a), and close to that of the electrodeposited PB film (c). This would be due to the higher ionic conductivity of the PB-HTAC-$LiClO_4$ film than PB-HTAC. A similar behavior in the electrochromic response of these films was also observed in a reduction by potential stepping between +0.5 and −0.3 V.

The reproducibility of the electrochromic response is one of the most important factors for the practical utilization of the films. The electrodeposited PB film is known to be well reproducible in the reduction and

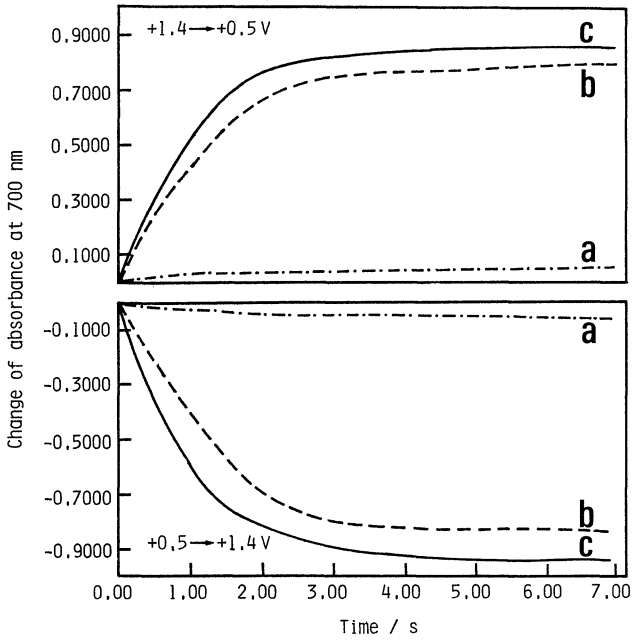

Fig. 2. Absorbance changes at 700 nm with time for (a) PB-HTAC, (b) PB-HTAC-$LiClO_4$, and (c) electrodeposited PB films when the potentials are stepped from +0.5 V to 1.4 V (lower parts) and from +1.4 V to +0.5 V (upper parts) in 0.1 mol dm^{-3} $KClO_4$.

reoxidation of PB. With respect to a cast PB film, on the negative potential step, the electrochromic response of a cast PB-HTAC-$LiClO_4$ film is as stable as that of the electrodeposited PB film during repeated potential steps. On the positive potential step, furthermore, the electrochromic response of the cast PB-HTAC-$LiClO_4$ film is more stable than that of the electrodeposited PB film. This behavior may be due to a higher stability of the oxidized form of PB in a cast film than in an electrodeposited film. More detailed discussions regarding this behavior is given later in terms of a cyclic voltammogram and spectroelectrochemistry.

Voltammetry of PB-HTAC-$LiClO_4$ Films. Cyclic voltammograms (CV) of the cast PB-HTAC-$LiClO_4$ films were taken in a 0.1 mol dm^{-3} $KClO_4$ electrolyte at a scanning rate of 20 mV s^{-1}. An example is shown in Fig. 3(a), as well as the CV of the electrodeposited PB film in Fig. 3(b).

In the region of a negative potential scan (between +0.5 V and −0.3 V), which causes a reduction of PB to PW, the CV curves of both the cast and the electrodeposited PB film are similar to each other regarding fundamental features. However, a precise comparison of both CV curves makes the differences clear. To make the difference more clear, the CVs of both films were measured at a slow scanning rate of 2 mV s^{-1} as well. The results are shown in Figs. 4(a) and (b), which are quite different each other.

The CV curve of the cast film is both sharper and simpler than that of the electrodeposited film, which has a complex curve comprising a sharp peak centered at 0.18 V and broad shoulders at ca. 0.0 V and 0.3 V. In successive scans, the CV peak feature of the cast film remains without any large change, even though the peak current at 0.18 V increases slightly. In contrast, on an electrodeposited film, the broader shoulder observed in the first reductive scan gradually diminishes during repeated scans and becomes sharp; this is rather similar to the simple wave observed for a cast film. This sharp spike was earlier noted by Ellis et al.[2] for a PB-modified gold electrode. Itaya et al.[5] assumed that uncoordinated $[Fe(CN)_6]^{4-/3-}$ and $Fe^{2+/3+}$ ions seem to be reason for the current spike. However, we have found that the sharp spike could not be observed on an electrodeposited PB film voltammetrically scanned in an aqueous KCl solution.[15] On the other hand, such sharp spikes were frequently observed on polymer-modified electrodes,[16,17] for which a structural change was proposed as a possible reason for the spikes, since the structures of polymers are strongly affected by the redox reaction. In the present case, repeated scans caused a structural change of the electrodeposited PB to a new one which has a similar structure to that of cast PB, even though some part of the virgin form of the electrodeposited PB remained. The structural change of the electrodeposited PB is discussed again later on the basis of spectroelectrochemical measure-

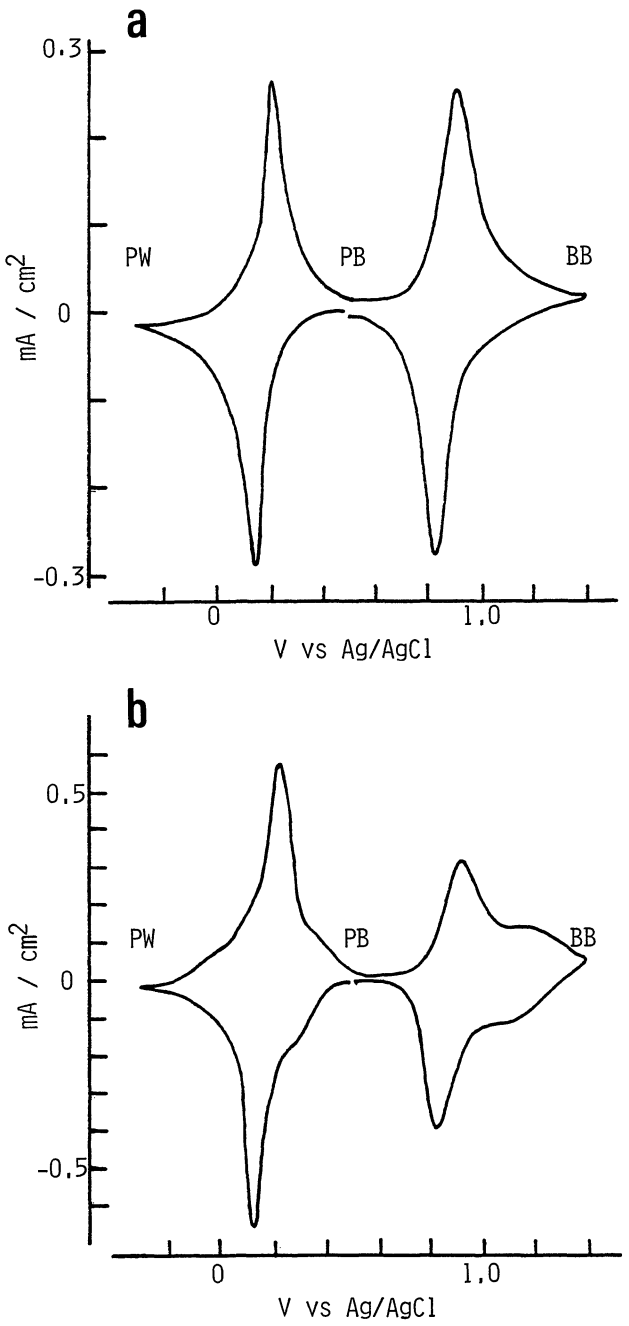

Fig. 3. Cyclic voltammograms of (a) PB-HTAC-$LiClO_4$ and (b) electrodeposited PB films on ITO electrodes in 0.1 mol dm^{-3} $KClO_4$. Scan speed= 20 mV s^{-1}. Only the stable voltammograms are presented.

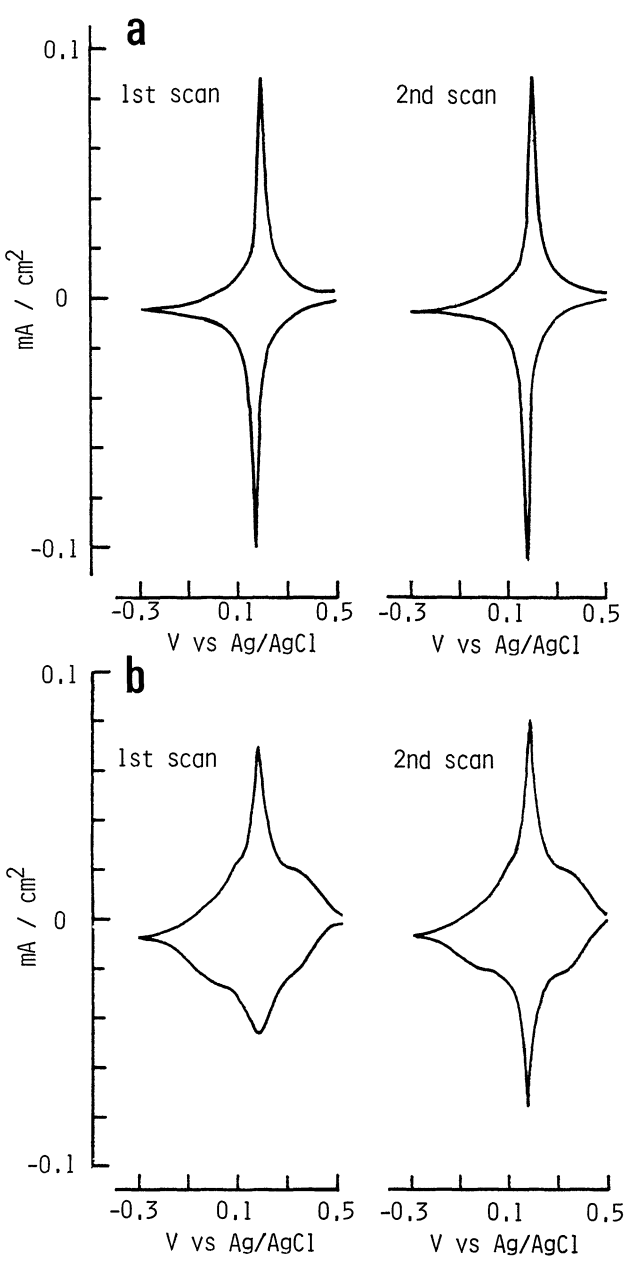

Fig. 4. Cyclic voltammograms of (a) PB-HTAC-$LiClO_4$ and (b) electrodeposited PB films on ITO electrodes in 0.1 mol dm^{-3} $KClO_4$. Scan speed= 2 mV s^{-1}. The first and second reductions are presented, respectively.

ments.

On the other hand, the oxidation of PB in a positive potential scan has been reported to correspond to a partial of full oxidation of the hexacyanoferrate(II) sites to Berlin Green (BG) or Berlin Brown, depending on the positive extent of the potential scan.[4,5] A positive potential scan (between +0.5 V and +1.4 V) causes an oxidation of PB to BB. If the voltammetric scanning started directly from Fe(III/II) to Fe(III/III) for a cyclic electrochemical oxidation of PB, a small loss of the peak current occurred for the cast film in successive scans, while a considerable decay of the peak current was observed for the electrodeposited PB film. It is possible that a cast film can be oxidized to a fully oxidized form with considerable stability, as proposed above. However, a cast film is highly stable if it is pretreated by a reductive cycle from Fe(III/II) to Fe(II/II) before the oxidative scan, as was reported for electrodeposited films.[5]

In an oxidative scan of a pretreated PB film, the CV

curve of a cast PB film is much sharper and simpler than that of an electrodeposited film, as well as in the reductive curve. A symmetrical single redox peak was observed for a cast film in a positive potential scan, while two separate waves were observed for an electrodeposited PB film at electrode potentials higher than +1.0 V in addition to the main redox peak at +0.92 V, as previously reported.[4,5] This indicates that the oxidation of a cast film is also much simpler than that of an electrodeposited film.

These voltammetric differences suggest that electrochromism occur under different reactions in both cast and electrodeposited films. The electric charge used for the oxidation wave is about 70% of that for the reduction wave in an electrodeposited PB film. The ratio was reported to give fairly accurate proof for the formula of the electrodeposited PB, proposing the redox reactions according to the Eqs. 1 and 2:[4,5]

$$Fe^{III}_4[Fe^{II}(CN)_6]_3 + 4K^+ + 4e^- = K_4Fe^{II}_4[Fe^{II}(CN)_6]_3 \quad (1)$$

and

$$Fe^{III}_4[Fe^{II}(CN)_6]_3 + 3X^- - 3e^- = Fe^{III}_4[Fe^{III}(CN)_6]X_3. \quad (2)$$

On the basis of the above considerations, the ratio of the charges for the cast film was measured. The ratio shown in Fig. 3(a) is about 1.05, rather than 0.7 for an electrodeposited film. This result gives the first fairly consistent proof that the formula of cast PB is the "soluble" form, $KFe[Fe(CN)_6]$, which had been proposed due to the result of extractability, as mentioned above. On the basis of the results of coulometry and the EDX (vide infra), the possible electrochemical reactions of the "soluble" PB in the cast film can be proposed as follows:

$$KFe[Fe(CN)_6] + K^+ + e^- = K_2Fe[Fe(CN)_6] \quad (3)$$

and

$$KFe[Fe(CN)_6] - K^+ - e^- = Fe[Fe(CN)_6]. \quad (4)$$

SEM and Analytical Studies. SEM photographs of cast PB–HTAC–$LiClO_4$ films and electrodeposited PB films are shown in Figs. 5 and 6, respectively. Included in these Figures for a comparison are SEM photographs of the electrodes (a) before and (b) after treatment by immersing or voltammetric scanning in aqueous $KClO_4$. No morphological change was observed for the electrodeposited PB film after immersing or voltammetric scanning. On the contrary, the integrity of the cast PB–HTAC–$LiClO_4$ film, which has been kept after immersing in pure H_2O, became breached in places after immersing in aqueous $KClO_4$, and the porous substructure became visible. The typical rough, porous surface was retained and no decomposition of the film was observed during repeated voltammetric scanning. A similar morphological change was also observed for cast PB–HTAC films during the same treatments. These results suggest that though a morphological change is rarely brought

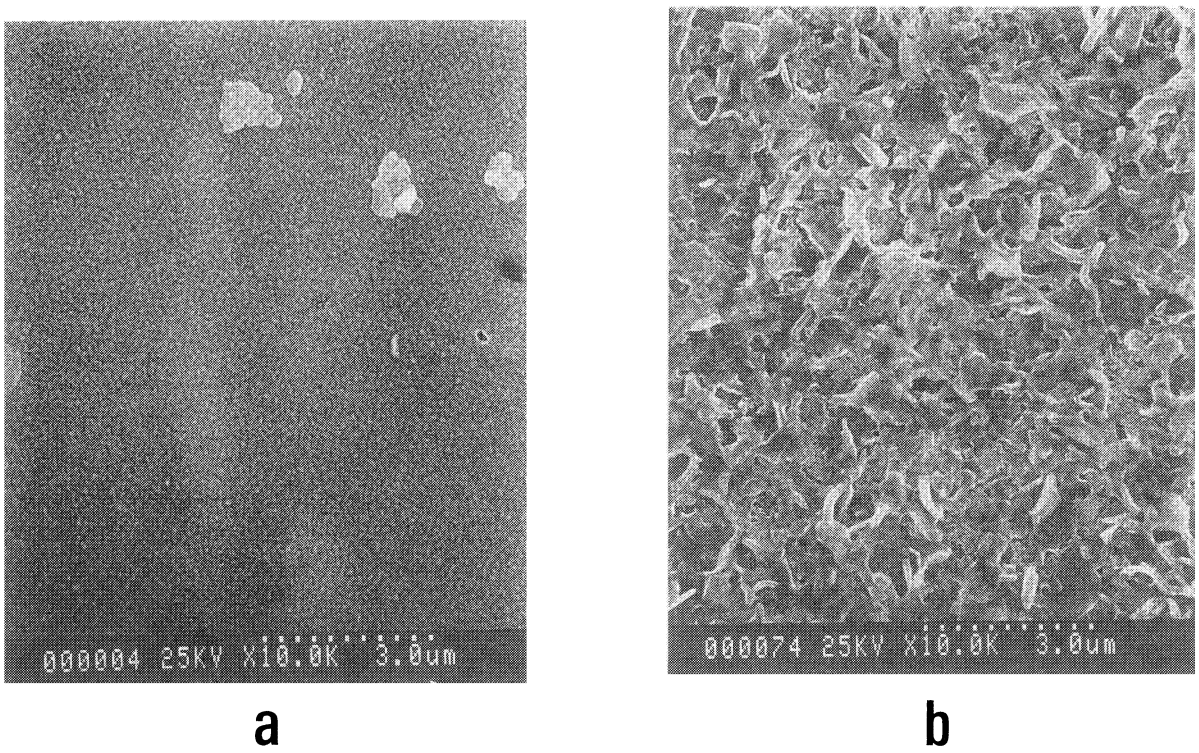

Fig. 5. Scanning electron micrographs of the cast PB–HTAC–$LiClO_4$ film (a) before and (b) after the treatment of immersing or voltammetric scanning in 0.1 mol dm^{-3} $KClO_4$. Mag.$\times 10^4$.

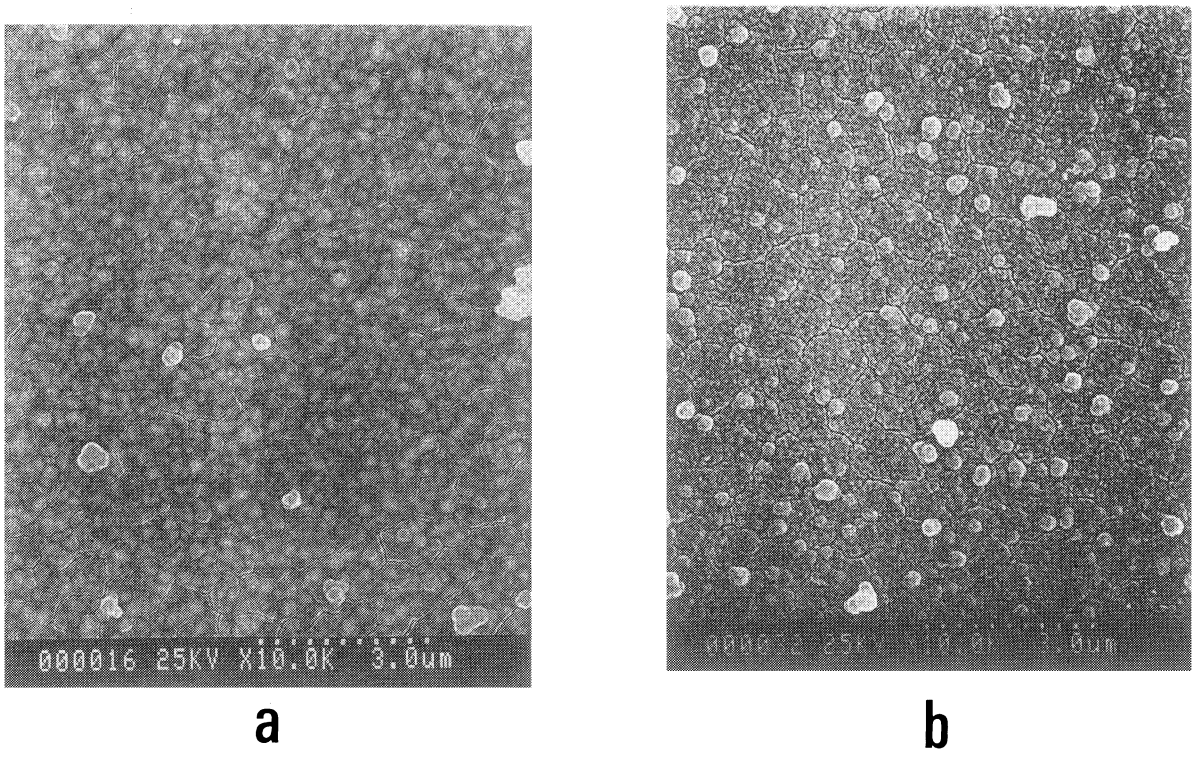

Fig. 6. Scanning electron micrographs of the electrodeposited PB film (a) before and (b) after the treatment of immersing or voltammetric scanning in 0.1 mol dm^{-3} $KClO_4$. Mag.$\times 10^4$.

about by an electrochemical reaction, it is probably due to a rearrangement of the surface structures of a film composed of PB and surfactants. In other words an "improvement" of the conductivity of the cast film by the addition of $LiClO_4$ is a probable reason for accelerating the electrochromic and voltammetric response, as mentioned above.

Since the uncertainty in composition of PB has hampered any interpretation of electrochemical studies concerning PB films, studies on the chemical composition are considered to give key knowledge on such films. In particular, the K^+ content of the films should reflect which form (soluble or insoluble) of mixed-valence complex is present. A series of the cast PB–HTAC–$LiClO_4$ films were analyzed by EDX and XPS in order to explore this problem; the EDX results were compared with those of electroposited PB films, as shown in Figs. 7 and 8.

The EDX (and some XPS) measurements reveal the presence of the K^+ ions on the cast PB–HTAC–$LiClO_4$ films, although K^+ is absent on the electrodeposited PB film in the as-deposited state, as previously reported.[18] The EDX data support the idea that a cast PB film comprises the "soluble" form, $KFe[(CN)_6]$, as proposed above.

The changes in the chemical composition of these films with a subsequent treatment were traced by EDX measurements. The K^+ ions appear in the electrodeposited PB film (Fig. 8(b)) as a result of simply immersing an as-deposited film in 0.1 mol dm^{-3} $KClO_4$ (at open circuit), while the K^+ content of the cast PB–HTAC–$LiClO_4$ film (Fig. 7(b)) is kept constant after immersion. On the contrary, the Cl^- content of a cast PB–HTAC–$LiClO_4$ film (Fig. 7(b)) increases in quantity, while the Cl^- peak of an electrodeposited PB film (Fig. 8(b)) scarcely changes after immersion. Since the chlorine atoms in different species can be distinguished by the peak position in XPS, i.e., chlorine atoms in a HTAC surfactant, PB and perchlorate appear at 198, 199, and 208 eV, respectively, the XPS measurements of the cast film clearly indicated the origin of the chlorine atoms. Based on the results of XPS measurements, the incease in the Cl^- content of the cast film by simple immersion in $KClO_4$ can be accounted for by the incorporation of ClO_4^- into the cast film by an exchange with Cl^- in the reverse micelles.

When the iron(III) states are reduced at -0.3 V in a 0.1 mol dm^{-3} $KClO_4$ solution at pH 4.0, the K^+ peak of the cast PB–HTAC–$LiClO_4$ films in the EDX spectra increases, as shown in Fig. 7(c), indicating the incorporation of a large quantity of K^+ ions into the cast films. As for the oxidation of the hexacyanoferrate(II) states of the cast films in which the iron(III) states have been reductively cycled in advance, the oxidation of the hexacyanoferrate(II) sites at $+1.0$ V in $KClO_4$ drives all of the K^+ ions from the cast film, as shown in Fig. 7(d). This oxidation reaction can be

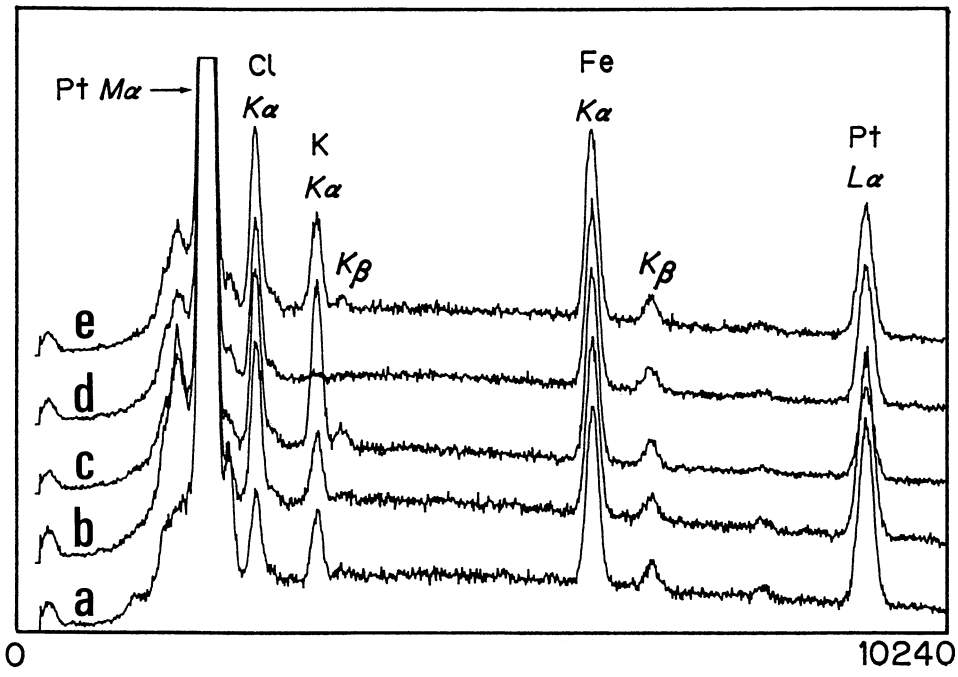

Fig. 7. EDX spectra of the cast PB–HTAC–$LiClO_4$ films on Pt electrodes: (a) as-cast, (b) immersed in 0.1 mol dm^{-3} $KClO_4$, (c) reduced in 0.1 mol dm^{-3} $KClO_4$ three times, (d) oxidized at 1.0 V in 0.1 mol dm^{-3} $KClO_4$, and (e) oxidized at 1.0 V and then re-reduced to Fe(III/II) in 0.1 mol dm^{-3} $KClO_4$. Accelerating voltage=10 kV.

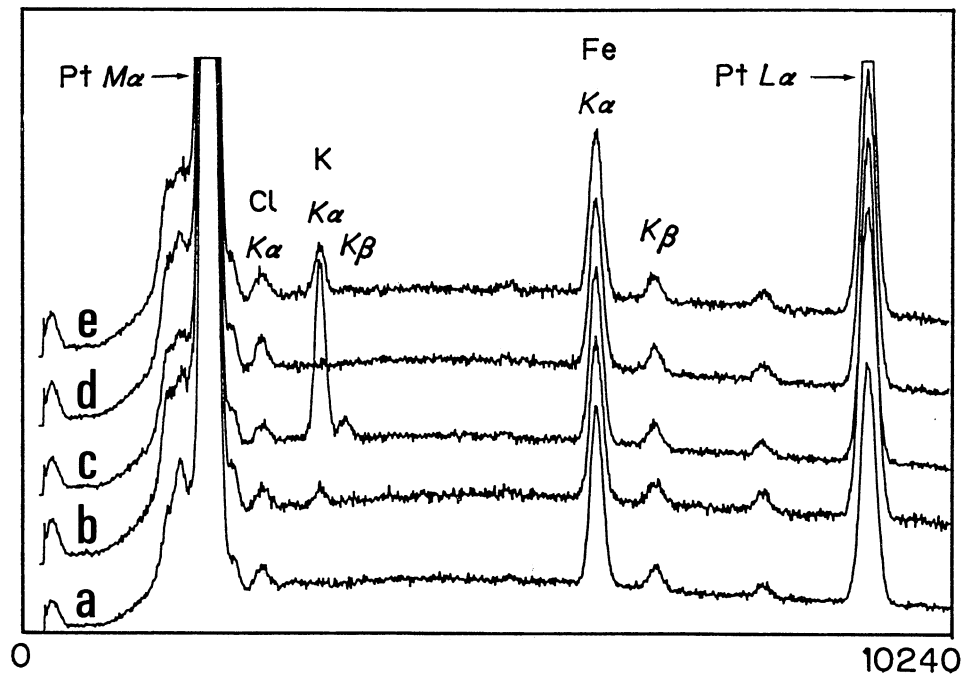

Fig. 8. EDX spectra of the electrodeposited PB films on Pt electrodes: (a) as-grown, (b) immersed in 0.1 mol dm^{-3} $KClO_4$, (c) reduced in 0.1 mol dm^{-3} $KClO_4$ three times, (d) oxidized at 1.0 V in 0.1 mol dm^{-3} $KClO_4$, and (e) oxidized at +1.0 V and then re-reduced to Fe(III/II) in 0.1 mol dm^{-3} $KClO_4$. Accelerating voltage=10 kV.

represented by Eq. 4. Re-reduction back to the Fe (III/II) state reproduces the original K^+ content, as shown in Fig. 7(e). However, the Cl^- content of the cast film is little changed by cyclic electrochemical redox between the Fe(II/II) and Fe(III/III) states.

In a similar investigation concerning an electrodeposited film (Fig. 8(c)—(e)) the contents of both K^+ and Cl^- ions change during the redox cycle in the same manner as for a cast film, as previously reported for 0.5 mol dm^{-3} KCl.[18]

These results have clarified several points concerning the change in the chemical composition of a cast PB–HTAC–$LiClO_4$ film as well as an electrodeposited PB film during the electrochemical reaction: (a) The K^+ content of the as-cast state of a cast PB film is consistent with the "soluble" form of PB, while an electrodeposited PB film does not contain K^+, suggesting an "insoluble" form of PB. (b) The ion exchange between ClO_4^- of the supporting electrolyte and Cl^- of the surfactant probably leads to the micelle swelling and morphological change observed in the SEM micrograph. (c) The fact that ClO_4^- enters into a

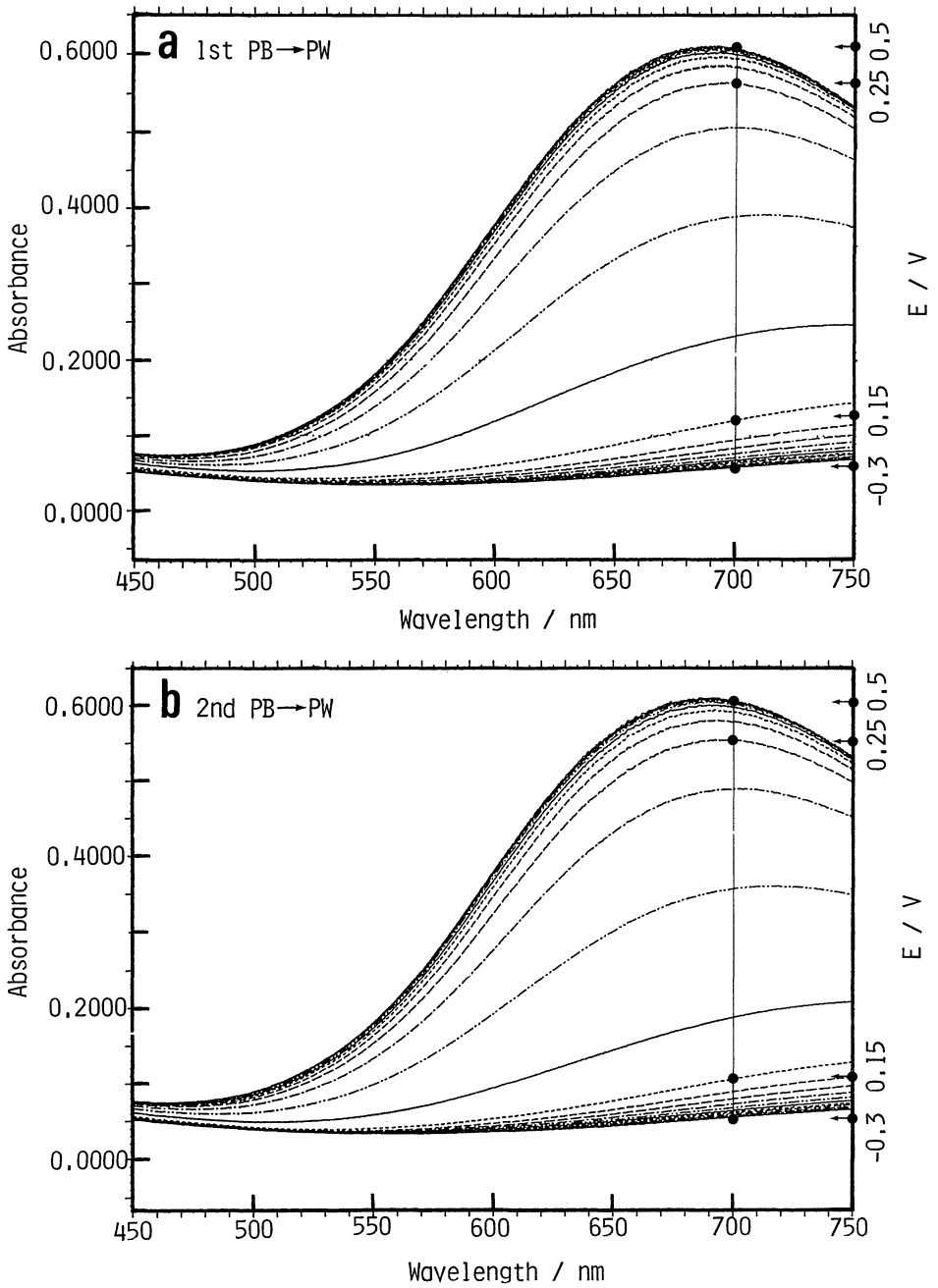

Fig. 9. Visible absorption spectra of the PB–HTAC–$LiClO_4$ film cast on an ITO electrode during the reduction in 0.1 mol dm^{-3} $KClO_4$; (a) the first and (b) the second reduction of PB to PW. Scan speed=2 mV s^{-1}. Spectra were recorded in 25-mV intervals.

reversed micelle upon immersion in a 0.1 mol dm^{-3} $KClO_4$ solution may be accounted for both in terms of a delocalization of the electric charge of ClO_4^-, based on the large molecular size and (probably more importantly) the hydrophobic affinity of the ClO_4^- to the reversed micelle. (d) The absence of a K^+ exchange, observed for a cast PB–HTAC–$LiClO_4$ film during immersion in 0.1 mol dm^{-3} $KClO_4$, may be accounted for by a repulsive force between the strong ionic property of small K^+ ions and a reversed micelle having a hydrophobic environment.

Spectroelectrochemistry. The transient visible spectra of a cast PB–HTAC–$LiClO_4$ film and an electrodeposited PB film on ITO electrodes were taken at closely spaced potential intervals during a negative potential scan from +0.5 to −0.3 V in 0.1 mol dm^{-3} $KClO_4$. The spectra of the cast and electrodeposited films are shown in Figs. 9 and 10, respentively.

Both spectra of the as-cast PB–HTAC–$LiClO_4$ film and the as-deposited PB film are similar to each other, but differ regarding some points. The major difference is in the wavelengths of the maximum absorbance

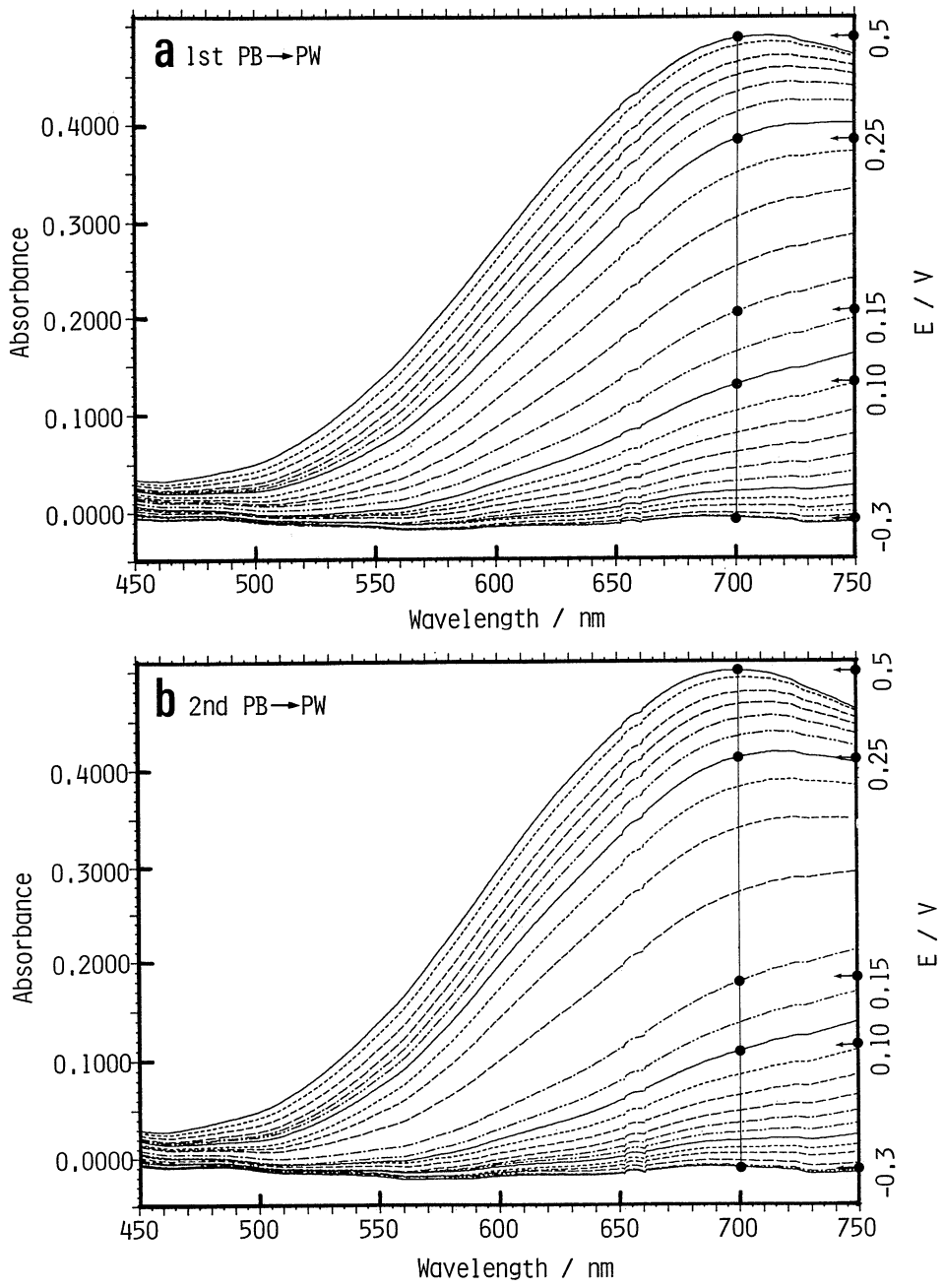

Fig. 10. Visible absorption spectra of the electrodeposited PB film on an ITO electrode during the reduction in 0.1 mol dm^{-3} $KClO_4$; (a) the first and (b) the second reduction of PB to PW. Scan speed= 2 mV s^{-1}. Spectra were recorded in 25-mV intervals.

(λ_{max}), which are in the 690 and 715 nm regions for the cast and electrodeposited films, respectively. The λ_{max} of the cast PB–HTAC–$LiClO_4$ film remained unchanged after voltammetric scanning (compare the first (a) and second (b) scans in Fig. 9). On the contrary, the λ_{max} of the electrodeposited film shifts from about 715 nm to a lower wavelength of about 695 nm after initial reduction cycle (compare (a) and (b) in Fig. 10). This is consistent with the spectroelectrochemical data of Mortimer and Rosseinsky[19] who showed a shift in the spectra of an electrodeposited PB film after the first reduction cycle. The spectral shift was proposed to be due to a partial conversion of an "insoluble" PB into a "soluble" PB. The absence of a λ_{max} shift for the cast PB film directly supports the idea that cast films comprise only "soluble" PB, as mentioned above.

Figures 11 and 12 show how the 600, 645, 701, and 745 nm absorbances change with a reductive applied potential in a $KClO_4$ electrolyte for a cast PB–HTAC–$LiClO_4$ film and an electrodeposited PB film, respectively. The absorbances are normalized to the highest initial value for ease of comparison. In the case of a cast film, the absorbance–potential response (Fig. 11) is the same at each wavelength and remains unchanged during subsequent scans in a $KClO_4$ electrolyte (compare (a) and (b) in Fig. 11). Each absorbance change is very sharp and centered at +0.18 V, agreeing with the sharp central peak in the voltammogram in a $KClO_4$ electrolyte (Fig. 4a). In the case of an electrodeposited film, the initial absorbance–potential response (Fig. 12a) is different at each wavelength centered at between +0.4 and −0.1 V, agreeing with the broad peak in the initial voltammogram shown in Fig. 4b. Upon a subsequent scan (Fig. 12b), the absorbance change at each wavelength was slightly sharper than the first scan and centered at +0.17 V, but still tailed between +0.1 V and −0.1 V. This feature is clearly associated with the +0.17 V sharp central peak and the 0.0 V shoulder in the voltammetry in $KClO_4$ shown in Fig. 4b, the 2nd scan.

The results of Figs. 11 and 12 are consistent with the voltammetric and compositional results mentioned above, i.e., cast films maintain a soluble form structure, even after a reduction cycle. On the contrary, in electrodeposited films, some parts of the PBs in the insoluble form probably change to a soluble form structure after the reduction cycle; other parts, however, retain their insoluble form. The consistency of the absorbance–potential response with the voltammetric result suggests that a cast PB–HTAC–$LiClO_4$ film contains single species in which a unique electrochemical iron(III) site participates in the cyclic electrochemical reduction. In contrast, plural species are suggested in an electrodeposited PB film as a

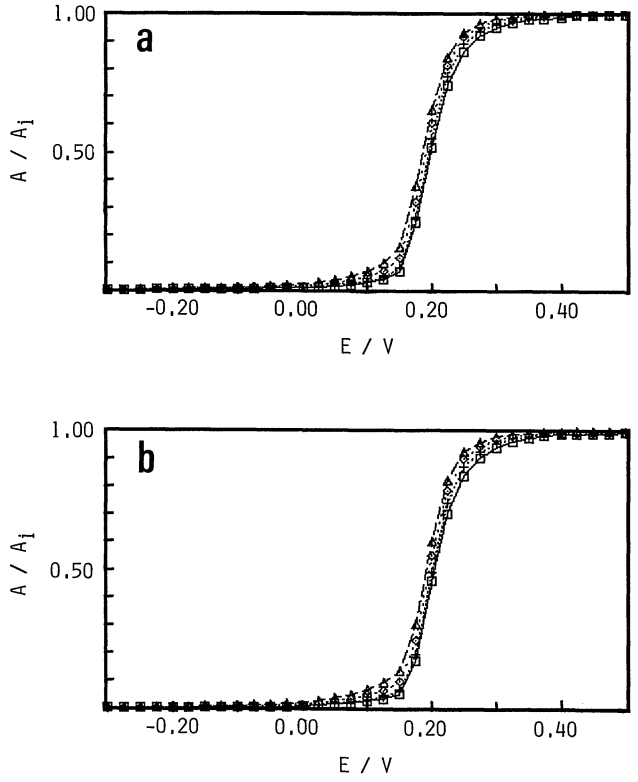

Fig. 11. Normalized absorption vs. potential curves of the cast PB–HTAC–$LiClO_4$ film in 0.1 mol dm^{-3} $KClO_4$ at (□) 600, (+) 645, (◇) 701, and (△) 745 nm: (a) The first and (b) the second reduction.

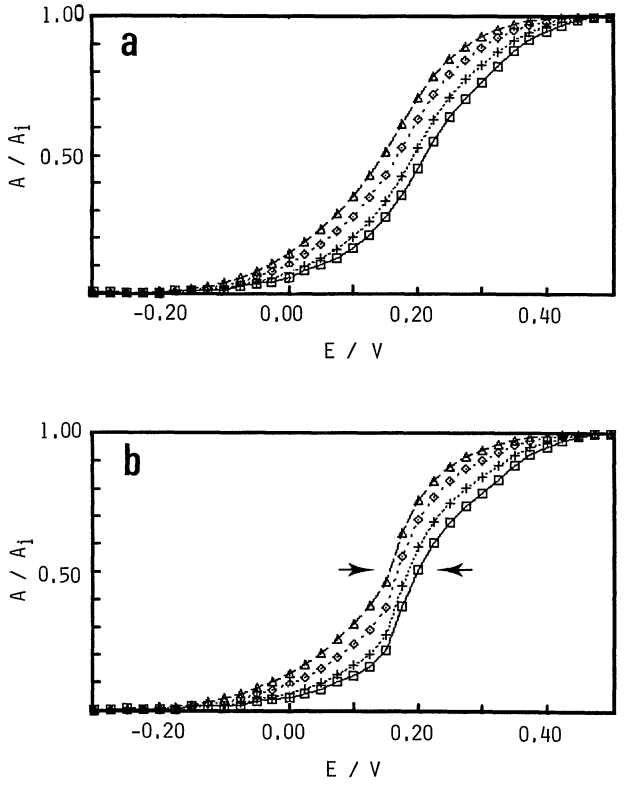

Fig. 12. Normalized absorption vs. potential curves of the electrodeposited PB film in 0.1 mol dm^{-3} $KClO_4$ at (□) 600, (+) 645, (◇) 701, and (△) 745 nm: (a) The first and (b) the second reduction.

mixture of nonequivalent electrochemical iron(III) sites. This somewhat complicated behavior appears to be attractive, but difficult to explain.

The spectral changes for the oxidation of cast PB–HTAC–$LiClO_4$ and the electrodeposited PB films in $KClO_4$ are illustrated in Figs. 13 and 14, respectively. The absorbance–potential response for the oxidation are plotted at 600, 645, 701, and 745 nm in Figs. 15 and 16 in a similar way to that in Figs. 11 and 12 for the reduction. The difference in patterns between Figs. 15 and 16 for the oxidation is less distinct than that between Figs. 11 and 12 for the reduction. Nevertheless, the absorbance response of the cast PB–HTAC–$LiClO_4$ film in Fig. 15 is quick and singly centered at about

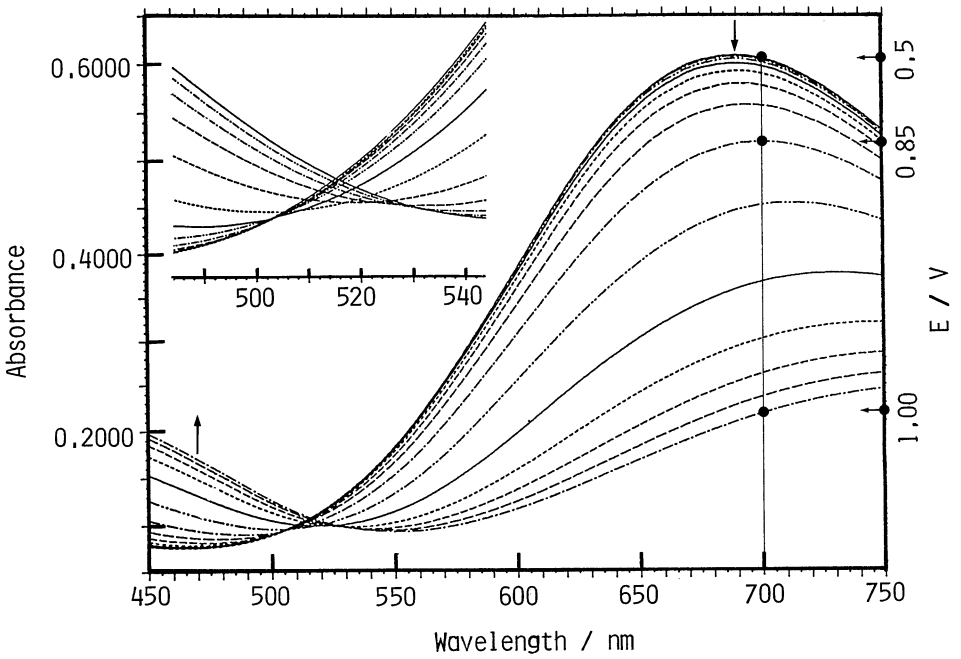

Fig. 13. Visible absorption spectra of the PB–HTAC–$LiClO_4$ film cast on an ITO electrode during the oxidation from PB to BG in 0.1 mol dm^{-3} $KClO_4$. Scan speed=2 mV s^{-1}. Spectra were recorded in 25-mV intervals.

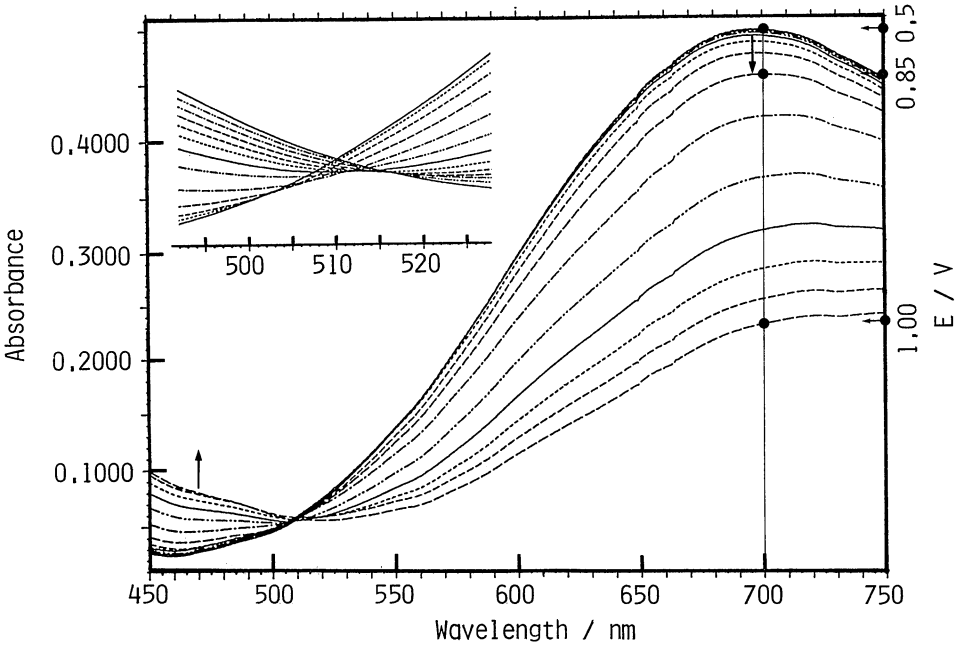

Fig. 14. Visible absorption spectra of the electrodeposited PB film on an ITO electrode during the oxidation from PB to BG in 0.1 mol dm^{-3} $KClO_4$. Scan speed=2 mV s^{-1}. Spectra were recorded in 25-mV intervals.

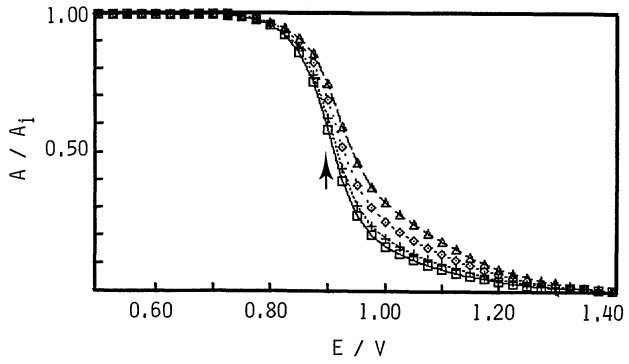

Fig. 15. Normalized absorption vs. potential curves of the cast PB-HTAC-$LiClO_4$ film in 0.1 mol dm^{-3} $KClO_4$ at (□) 600, (+) 645, (◇) 701, and (△) 745 nm for oxidation.

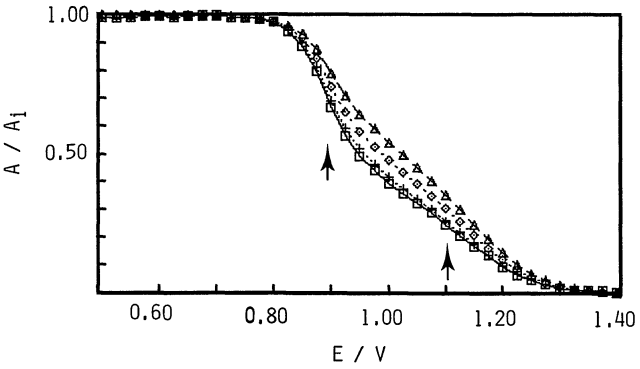

Fig. 16. Normalized absorption vs. potential curves of the electrodeposited PB film in 0.1 mol dm^{-3} $KClO_4$ at (□) 600, (+) 645, (◇) 701, and (△) 745 nm for oxidation.

+0.89 V, while the electrodeposited PB film in Fig. 16 shows an additional change centered at about +1.1 V in addition to the main change at about +0.89 V.

On the other hand, the spectrum of the fully oxidized form of the cast film at +1.4 V was different from that of the electrodeposited film. The spectral change with the application of a potential in the cast film (Fig. 13) is also faster than in the electrodeposited film (Fig. 14). The extent of the oxidation between +0.5 and +1.0 V is about 80% of the full oxidation for the cast film, while the electrodeposited film is oxidized by about 50%. Although a reasonable explanation for the oxidation has not been yet offered, the inset of Fig. 13, as well as the inset of Fig. 14, indicates that spectral changes with the application of the oxidative potential give two isosbestic points, as previously reported,[18,20] and that the transition from one isosbestic point to the other occurs at +0.89 V of the applied potential. The spectral changes giving the two isosbestic points are common to both the cast (Fig. 13) and electrodeposited (Fig. 14) films, and the applied potential giving the two isosbestic points (+0.89 V) is consistent with the main oxidation peaks from PB to BB in the cyclic voltammograms (Fig. 3) of both the cast and electrodeposited films. Although the reason for two isosbestic points is not clear yet, the common spectral change suggests that the change arises from the oxidation of a soluble form of PB both in the cast and the electrodeposited films. The oxidation shoulder wave of the electrodeposited film at +1.1 V observed in Fig. 3b may be attributed to the peculiar oxidation of the insoluble form of PB in the electrodeposited film. Though this specific change in oxidative voltammetry can not be readily resolved, some unknown species (nonequivalent complicated iron sites) probably exist only in the electrodeposited PB film. It is so hard for the species to be oxidized that the potential required for full oxidation is more positive than that for the simple species in the cast PB-HTAC-$LiClO_4$ film.

Conclusion

For the practical usage of the PB films, a simplified method of preparing a uniform film with large area and long-term stability is required. The casting of a colloidal PB dispersion in an organic solution provides an effective answer to this request.

According to the present experiments concerning the extraction of colloid PB dispersion, only cationic surfactants can extract PB colloids from an aqueous solution. PB composite films can be prepared onto ITO and Pt electrodes with a novel, simplified casting method by using an extracted PB solution. Particularly, when the ratio of $Fe^{II}/(Fe^{II}+Fe^{III})$ is larger than 0.5, the extraction of PB is considerably effective. This extraction result suggests that only the "soluble" form of PB can be extracted by an organic solution containing cationic surfactants.

The electrochemical behavior of cast films was compared with those of electrodeposited films. Some new facts found in the present investigation are listed:

1) The electrochromism of a cast film was observed to be similar to that of an electrodeposited PB film in a $KClO_4$ solution. The electrochromic response was improved by the addition of $LiClO_4$ to the cast film.

2) Cyclic voltammograms of a cast PB-HTAC-$LiClO_4$ film measured in a $KClO_4$ solution was simpler and more symmetrical than that of an electrodeposited PB film.

3) EDX (and some XPS) measurements show that as-cast films contain K^+ ions, which suggests a "soluble" form of PB, while electrodeposited films do not contain K^+ ions, which suggests an "insoluble" form of PB.

4) The λ_{max} of a cast film remains unchanged, even after successive scans, while that of an electrodeposited film shifts to lower wavelength after the first reduction cycle.

Although some points are not readily resolved in oxidative voltammetry, the present method provides a promising prospect for preparing a simple, stable, and

useful PB cast film.

The authors wish to express their sincere thanks to Dr. Masao Kaneko in Riken for his helpful discussion, as well as Dr. Masanori Owari at Institute of Industrial Science, The University of Tokyo (EDX) and Dr. Mitsuhiro Adachi at Engineering Research Institute, The University of Tokyo (SEM) for their technical assistance. This work was supported by the Grant-in Aid for Scientific Research on Priority Area of "Macromolecular Complexes" Nos. 62612002, 63612003, and 01612002 from the Ministry of Education, Science and Culture.

References

1) V. D. Neff, *J. Electrochem. Soc.*, **125**, 886 (1978).
2) D. Ellis, M. Eckhoff, and V. D. Neff, *J. Phys. Chem.*, **85**, 1225 (1981).
3) K. P. Rajan and V. D. Neff, *J. Phys. Chem.*, **86**, 4361 (1982).
4) K. Itaya, H. Akahoshi, and S. Toshima, *J. Electrochem. Soc.*, **129**, 1498 (1982).
5) K. Itaya, A. Tatsuaki, and S. Toshima, *J. Am. Chem. Soc.*, **104**, 4767 (1982).
6) K. Itaya, K. Shibayama, H. Akahoshi, and S. Toshima, *J. Appl. Phys.*, **53**, 804 (1982).
7) N. Toshima, R.-J. Lin, and M. Kaneko, *Chem. Lett.*, **1990**, 485.
8) R.-J. Lin and N. Toshima, *Kobunshi Rombunshu*, **47**, 825 (1990).
9) P. M. Hoang, S. Holdcraft, and B. L. Funt, *J. Electrochem. Soc.*, **132**, 2129 (1985).
10) K. Itaya, I. Uchida, and V. D. Neff, *Acc. Chem. Res.*, **19**, 162 (1986).
11) H. J. Buser, D. Schwarzenbach, W. Petter, and A. Ludi, *Inorg. Chem.*, **16**, 2704 (1977).
12) R. E. Wilde, S. N. Ghosh, and B. J. Marshall, *Inorg. Chem.*, **9**, 2512 (1970).
13) M. Kaneko, X.-H. Hou, and A. Yamada, *J. Chem. Soc., Faraday Trans. 1*, **82**, 1637 (1986).
14) M. Armand, *Solid State Ionics*, **9/10**, 745 (1983).
15) R.-J. Lin and N. Toshima, unpublished results.
16) P. J. Peerce and A. J. Bard, *J. Electroanal. Chem. Interfacial Electrochem.*, **114**, 89 (1980).
17) E. Laviron and L. Roullier, *J. Electroanal. Chem. Interfacial Electrochem.*, **115**, 65 (1980).
18) C. A. Lundgren and R. W. Murray, *Inorg. Chem.*, **27**, 933 (1988).
19) R. J. Mortimer and D. R. Rosseinsky, *J. Chem. Soc., Dalton Trans.*, **1984**, 2059.
20) N. Toshima, R.-J. Lin, and M. Kaneko, *Chem. Lett.*, **1989**, 1099.