

Electrochromic Behavior and Stability of Polyaniline Composite Films Combined with Prussian Blue

MITSUYUKI MORITA

Osaka Municipal Technical Research Institute, Morinomiya, Joto-Ku, Osaka 536, Japan

SYNOPSIS

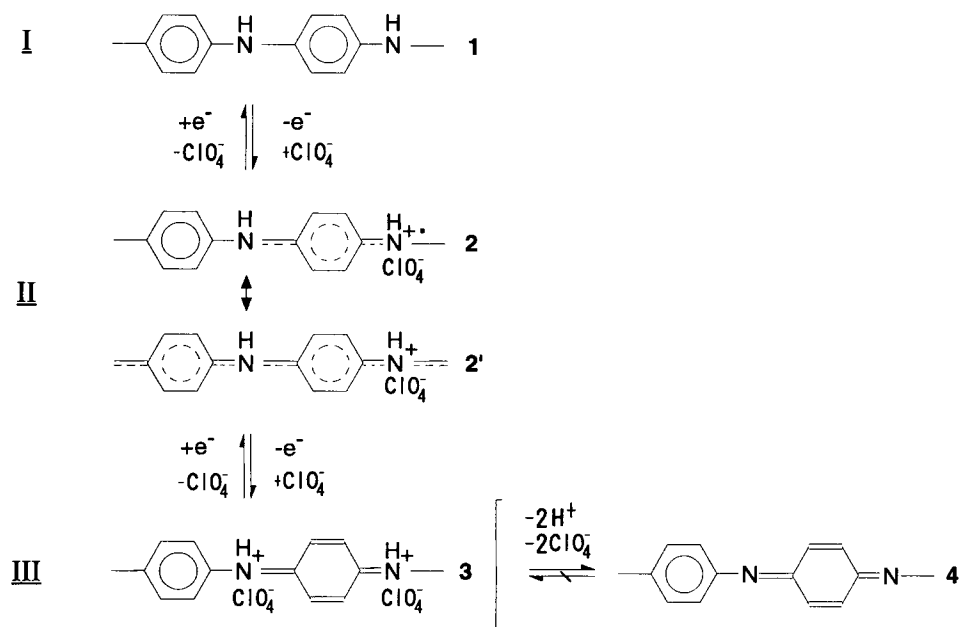
The electrochromic behavior of polyaniline-poly(vinyl alcohol) composite films (CPAn-PVA) combined with electrochemically synthesized Prussian blue films (PB) was investigated in $\text{LiClO}_4 - \text{CH}_3\text{CN}$ nonaqueous aprotic solution. The combination was achieved by chemical deposition of CPAn-PVA on PB. When the combined films (CPAn-PVA-PB) are prepared with the appropriately low quantity of PB, CPAn-PVA-PB showed various visible absorption spectra overlapped roughly with the absorption of the component materials at different applied potentials. CPAn-PVA-PB provided the color change from green to blue at much lower applied potential than did CPAn-PVA. However, the combined PB eliminates protons from the first oxidized polyaniline chains to decrease the electrochemical activity of polyaniline. Therefore, to construct multicolor electrochromic devices by the combination of polyaniline with the other electrochromic materials, it is necessary to select the materials containing no deprotonation activity. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyaniline has attracted much attention as a unique electrically conducting polymer with a multicolor electrochromic property.¹⁻⁷ Polyaniline shows a two-step color change when oxidized electrochemically. Its color is pale yellow in the reduced state, green in the first oxidized state, and blue in the second oxidized state. This electrochromic behavior is observed in nonaqueous electrolyte systems¹⁻⁵ as well as in aqueous electrolyte systems.^{6,7} However, nonaqueous systems have the advantage of aqueous systems when polyaniline is employed in practical applications, because polyaniline is apt to undergo hydrolytic decomposition in a highly oxidized state in aqueous systems.^{8,9} From this viewpoint, we investigated the electrochromic behavior and electrochemical redox and degradation process of polyaniline in nonaqueous systems.¹⁰⁻¹² Electrochemically synthesized polyaniline films are employed in many studies on the electrochemical process of polyaniline. In our studies, however, polyaniline composite films, which were prepared with appropriate matrix poly-

mers by applying a chemical method proposed in our previous paper,¹³ were employed as an electrochromic material, because chemical synthesis is generally suitable for large-scale production in comparison with electrochemical synthesis where the scale of the products depends on the electrode area and it is difficult to generate practically strong thin films of homogeneous polyaniline by the usual chemical synthesis.

Our previous studies also suggested the following redox and degradation mechanisms of polyaniline in nonaqueous aprotic electrolyte system. They are shown in Scheme 1. This scheme shows the case when ClO_4 salts are employed as a supporting electrolyte. In the first oxidation process (I \rightarrow II), the phenyleneamine structure (**1**, pale yellow), the main component of polyaniline in the reduced state, is oxidized to the semiquinone radical cation structure and its delocalized state (**2** and **2'**, green) accompanying insertion of the electrolyte anions. In the second oxidation process (II \rightarrow III), polyaniline undergoes further dopant anion insertion to form the quinonediimine cation structure (**3**, blue). This second oxidation process is different from that in aqueous media where polyaniline is converted directly to the fully quinonediimine structure (**4**,



Scheme 1 Electrochemical redox and degradation mechanism of polyaniline in the $\text{LiClO}_4\text{---CH}_3\text{CN}$ nonaqueous electrolyte system. The bracketed part represents the degradation process.

bluish purple), eliminating protons and anions.^{2,4,6} This mechanism is supported from the other reports on ESR spectroscopy⁶ and on electrogravimetric measurements.^{14,15}

Electrochemical degradation of polyaniline in nonaqueous aprotic media is due to an irreversible formation of the fully quinonediimine structure (4), which is electrochemically inactive in nonaqueous aprotic media,¹⁶ from structure 3 by a gradual elimination of protons and anions in highly oxidized state. Hence, to improve the stability of polyaniline, the following two essential routes are considered: One is to restrict the elimination of protons and anions in the highly oxidized state. To achieve this, I have already proposed that polyaniline be employed as a composite material with some matrix polymers containing an appropriate charge balance.¹² The other is to limit polyaniline employments in the low oxidation potential region. In this route, however, polyaniline provides the monochromic change of the first oxidation process from pale yellow (almost transparent) to green. To construct multicolor electrochromic devices, it is necessary to combine polyaniline with the other electrochromic materials. A few examples¹⁷⁻²⁰ of such combinations have been reported so far. However, these materials were prepared by electrochemical methods, whereas chemical methods have been rarely applied.

In the present article, I report on the electro-

chromic behavior of polyaniline composite films combined with Prussian blue films (PB) as an example of the combination of polyaniline with the other electrochromic materials. The preparation of the samples was carried out applying the chemical method employed in our previous papers.^{10,11} I also report on the stability of the combined films in the electrochemical redox process and discuss the effect of PB combination on the oxidation process of polyaniline.

EXPERIMENTAL

Materials

A reagent grade of poly(vinyl alcohol) (PVA, Wako Pure Chemical Industries, $M_n = 95,000$) was used as a matrix polymer. Guaranteed grades of aniline and acetonitrile were purified before use by reduced pressure or simple distillation after dehydration on molecular sieves (4 Å, $\frac{1}{16}$ in. pellets) for 48 h. Guaranteed grades of $\text{K}_3\text{Fe}(\text{CN})_6$ and FeCl_3 were used without further purification. The other reagents were all of special reagent grade and were used without further purification. A tin oxide-coated electrically conductive glass (TO, Nippon Ito Garasu; 1.1 mm in thickness, 83% in transmittance, 2400 S/cm in conductivity) was employed as an optically

transparent electrode substrate after washing with alkaline detergent and water and drying.

Preparation of Electrochromic Samples

Polyaniline-poly(vinyl alcohol) composite film (CPAn-PVA) was prepared chemically on the T0 substrate by the method described in our previous reports.^{10,11} Prussian blue films (PB) were prepared electrochemically by the previous method reported by Itaya et al.²¹ on the T0 substrate from 0.002 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.002 M $\text{K}_3\text{Fe}(\text{CN})_6$ aqueous solution. The preparation was carried out at room temperature, applying a constant cathodic current density of 4×10^{-5} A/cm² with an Advantest TR 6142 dc voltage/current generator for different periods.

Combination of CPAn-PVA with PB was carried out by deposition of CPAn-PVA on the PB samples employing the above-mentioned preparation method of CPAn-PVA. The CPAn-PVA sample combined with PB is to be called "CPAn-PVA-PB." The area of each electrochromic sample was standardized by cutting to 1.1×2.3 cm.

Measurements

As the pretreatment of the following measurements, each electrochromic sample was immersed in 0.1 M $\text{LiClO}_4 - \text{CH}_3\text{CN}$ electrolyte solution for 2 h. The sample was then set in a glass cell containing 0.1 M $\text{LiClO}_4 - \text{CH}_3\text{CN}$, a Pt wire (2.51 cm² in surface area) as a counter electrode, a saturated calomel electrode (SCE) as a reference, and a N_2 gas introduction tube. The sample was reduced electrochemically at -0.6 V for 30 min after it had been cycled 10 times under N_2 gas bubbling between -0.6 and +0.2 V at 20 mV/s with a Hokuto HA-501G potentiostat and a Hokuto HB-104 function generator. The electrolyte solution was replaced with a fresh one in order to exchange the electrolytes in the sample with LiClO_4 . The electrochemical degradation treatment was carried out by having the sample stand at +0.6 V for 1 h.

For investigation of the electrochromic behavior of the sample, *in situ* visible absorption spectroscopy was carried out as follows: The glass cell containing the pretreated sample and 0.1 M $\text{LiClO}_4 - \text{CH}_3\text{CN}$ was set in a Shimadzu UV-240 spectrophotometer with a reference cell containing the T0 substrate and the electrolyte solution. The sample was polarized sequentially under N_2 gas bubbling with the potentiostat from lower to higher potential. The absorption spectra were measured after the polariza-

tion for 5 min at given applied potentials. This procedure was also applied to the sample that had undergone the electrochemical degradation treatment.

Cyclic voltammograms of the sample were recorded in 0.1 M $\text{LiClO}_4 - \text{CH}_3\text{CN}$ solution on a Riken Denshi F-35 X-Y recorder employing the glass cell described above. The potential was cycled at 20 mV/s between -0.6 V and a given anodic potential.

To investigate and compare the structural changes of the polyaniline in CPAn-PVA and CPAn-PVA-PB when polarized at different applied potentials, *ex situ* FTIR spectroscopy was carried out with a Nicolet 5DX spectrophotometer as follows: The sample film was set in the above-described glass cell with 0.1 M $\text{LiClO}_4 - \text{CH}_3\text{CN}$ solution and polarized under N_2 gas bubbling at a given applied potential for 5 min. After polarization, the sample was taken out and immersed in a large quantity of CH_3CN for 10 s for elimination of the excess electrolyte. Then, it was dried immediately under reduced pressure, scraped off the T0 substrate (in the case of CPAn-PVA) or the PB substrate (in the case of CPAn-PVA-PB), dispersed in KBr, and finally compressed into a tablet. The FTIR spectrum of the tablet was measured and the spectrum of the polyaniline in CPAn-PVA and CPAn-PVA-PB was obtained by subtraction of the PVA spectrum from the tablet spectrum. This procedure was also applied to the sample that had undergone the electrochemical degradation treatment.

RESULTS AND DISCUSSION

Electrochromic Behavior and Degradation of the Component Materials

In situ visible absorption spectra of the polyaniline-poly(vinyl alcohol) composite film (CPAn-PVA) that was polarized at different applied potentials in 0.1 M $\text{LiClO}_4 - \text{CH}_3\text{CN}$ nonaqueous aprotic solution are shown in Figure 1. The top spectral change corresponds to the first oxidation process (I \rightarrow II in Scheme 1, pale yellow to green) in the potential region from -0.6 to +0.6 V. In the reduced state from -0.6 to -0.2 V, only one absorption band appears at 330 nm. This is assigned to the phenyleneamine structure (**1**)^{5,22} and there is little absorption within the visible range. As the potential increases until +0.6 V, the absorption at 330 nm decreases, while new absorption bands at 420 nm and 800 nm, which are assigned to the semiquinone radical cation structure (**2**)²³ and its delocalized structure (**2'**),⁵ respectively, increase with ClO_4^- insertion. As shown

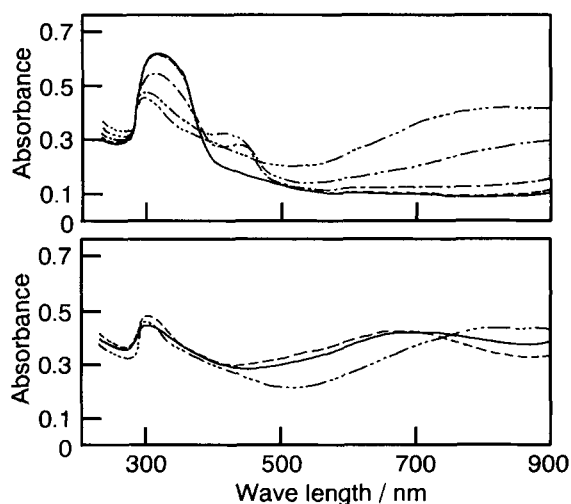


Figure 1 *In situ* visible absorption spectra of the polyaniline-poly(vinyl alcohol) composite film (CPAn-PVA) in 0.1 M LiClO₄-CH₃CN solution in the first oxidation process (top) and the second oxidation process (bottom). The potentials applied in the top spectra are (—) -0.6 V, (---) -0.2 V, (---) +0.1 V, (----) +0.3 V, and (-----) +0.6 V. The potentials applied in the bottom spectra are (-----) +0.6 V, (—) +0.8 V, and (---) +0.9 V.

in the bottom spectra, the absorption at 800 nm shifts to lower wavelength as the potential is increased more positively beyond +0.7 V. This shift is due to formation of the quinonediimine cation structure (3).^{11,12} Hence, the bottom spectral change corresponds to the second oxidation process (II → III, green to blue).

Figure 2 shows cyclic voltammograms of CPAn-PVA in 0.1 M LiClO₄-CH₃CN solution between -0.6 and +0.6 V (top) and between -0.6 and +0.9 V (bottom). The scan rate was 20 mV/s. The top and bottom cyclic voltammetry data show the electrochemical stability of CPAn-PVA in the first oxidation process and in the first and the second oxidation process, respectively. The peak current loss after 50 potential scans is 5.2% in the top voltammetry and 20.8% in the bottom voltammetry. Hence, to ensure good stability, as mentioned in the Introduction, CPAn-PVA must be employed in appropriately low oxidation potentials below +0.6 V.

Figure 3 shows *in situ* visible absorption spectra (top) and cyclic voltammograms (bottom, at 20 mV/s) of an electrochemically synthesized Prussian blue film (PB) between -0.6 and +0.6 V in 0.1 M LiClO₄-CH₃CN solution. The PB sample was prepared at a constant current density of 4×10^{-5} A/cm² for 1 min. As shown in the top spectra of Figure

3, there is little absorption within the visible range below +0.1 V, and the specific absorption near 700 nm increases as applied potential increases. Simultaneously, the film color changes gradually from colorless to blue beyond +0.1 V. This absorption is attributed to an intervalence charge transfer transition from an electric configuration of Fe^{III}Fe^{II}(CN)₆ to Fe^{II}Fe^{III}(CN)₆.²⁴

As shown in the cyclic voltammetry data of Figure 3, PB shows cyclic voltammograms with an extremely broad oxidation peak at ca. +0.17 V. The peak current increases in 13.3% after 50 scans. These results are different markedly from the behavior of PB in aqueous media. Itaya et al.²⁵ reported that the electrochemical reaction of PB proceeds in the presence of the cations such as K⁺, Rb⁺, Cs⁺, and NH₄⁺, but it is blocked in the presence of the cations such as Li⁺, Na⁺, and Ba²⁺ in aqueous media. They also concluded that Li⁺, Na⁺, and Ba²⁺ cannot transport through the open spaces in the crystal of PB because the size of those hydrated cations is larger than that of the channels of the PB crystal lattice, like a zeolite,²⁶ and this effect is the reason for the inactiveness of PB in aqueous solution containing Li⁺, Na⁺, and Ba²⁺. On the other hand, in

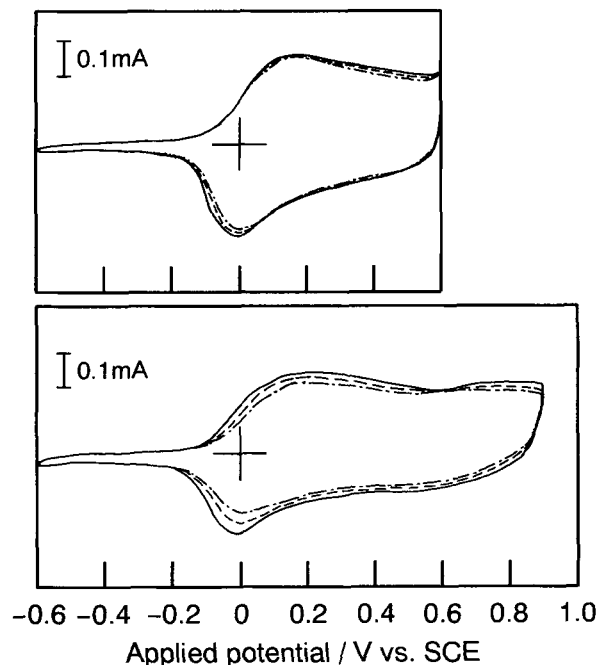


Figure 2 Cyclic voltammograms of CPAn-PVA in 0.1 M LiClO₄-CH₃CN solution between -0.6 and +0.6 V in the first oxidation process (top) and between -0.6 and +0.9 V in the first and the second oxidation process (bottom) on (—) the 1st, (---) the 20th, and (---) the 50th scan. Scan rate is 20 mV/s.

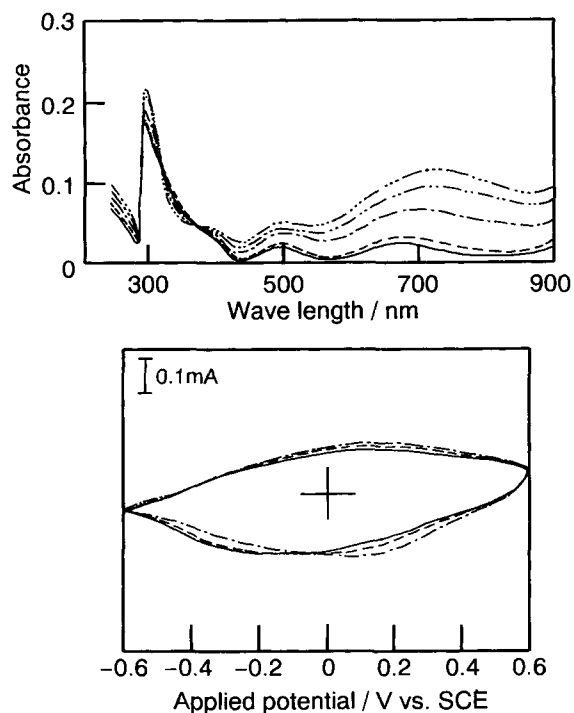
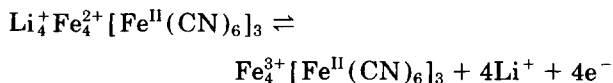


Figure 3 *In situ* visible absorption spectra (top) and cyclic voltammograms (bottom) of a Prussian blue film (PB) in 0.1 M LiClO₄—CH₃CN solution. The potentials applied in the top spectra are (—) -0.6 V, (---) -0.2 V, (- - -) +0.1 V, (- - - -) +0.3 V, and (- - - - -) +0.6 V. The voltammograms are recorded at 20 mV/s on (—) the 1st, (---) the 20th, and (- - -) the 50th scan.

the present CH₃CN nonaqueous solution, it is considered that the size of the solvated Li⁺ is smaller than that in water because alkaline metal cations have lower solvation energies in CH₃CN than in water.^{27,28} The size of the Li⁺ cation solvated with CH₃CN is possibly smaller than the channels of the PB lattice, so that PB is electrochemically active in the CH₃CN solution of Li⁺.

Hence, in the present LiClO₄—CH₃CN system, it is suggested that PB (Fe³⁺[Fe^{II}(CN)₆]₃) undergoes the following redox reaction accompanying reversal lithium insertion-elimination process in the same way in aqueous media²⁵ containing the cations such as K⁺, Rb⁺, Cs⁺, and NH₄⁺:



Electrochromic Behavior and Degradation of CPAn-PVA-PB

The top graph of Figure 4 shows *in situ* visible absorption spectra of a CPAn-PVA-PB combined film

in 0.1 M LiClO₄—CH₃CN at the applied potentials from -0.6 to +0.6 V. The sample was prepared with the PB synthesized by charging electricity for 1 min. The spectral change of the CPAn-PVA-PB seems roughly an overlapped spectral change of CPAn-PVA (Fig. 1, top) and PB (Fig. 3, top). As the result of the spectral changes, the color of the CPAn-PVA-PB film is pale yellow (almost transparent) below 0 V, becomes green over +0.1 V, and gradually changes to blue beyond +0.3 V. To investigate in detail the effects of the quantity of the combined PB on the electrochromic behavior of CPAn-PVA-PB, changes in the transmittance ratio at 540 nm (green)/480 nm (blue) are plotted in the top graph of Figure 4 as a function of the applied potential, employing the CPAn-PVA-PB samples prepared with the PBs synthesized electrochemically for dif-

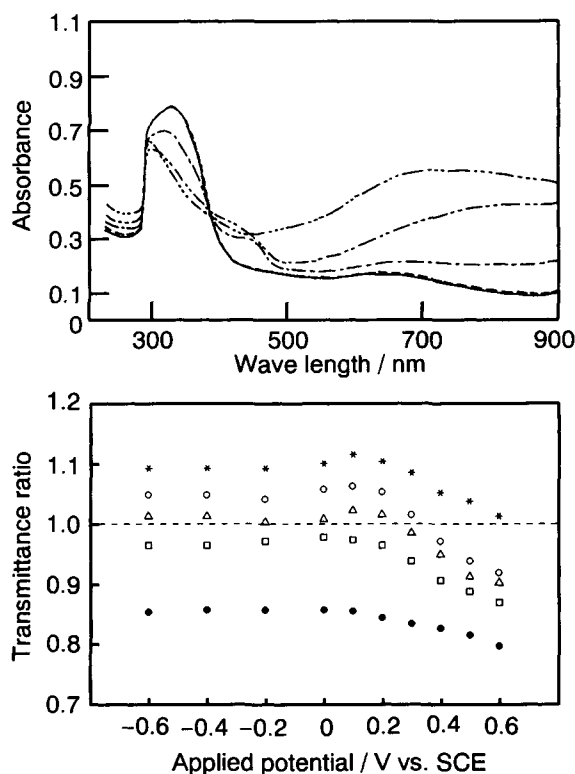


Figure 4 *In situ* visible absorption spectra of a CPAn-PVA film combined with PB (CPAn-PVA-PB) (top) and changes in the transmittance ratio at 540/480 nm of the CPAn-PVA-PB samples prepared with the PBs synthesized for different charging periods (bottom) in 0.1 M LiClO₄—CH₃CN solution. The potentials applied in the top spectra are (—) -0.6 V, (---) -0.2 V, (- - -) +0.1 V, (- - - -) +0.3 V, and (- - - - -) +0.6 V. The charging periods of the PBs employed in the bottom graph are (*) 0 min; CPAn-PVA, (O) 1 min, (Δ) 2 min, (□) 3 min, and (●) 4 min.

ferent charging periods. This transmittance ratio indicates roughly the relative intensity of the green to blue color. As shown in the graph, CPAn-PVA does not display a blue color below +0.6 V. However, as the quantity of the combined PB increases, the color changes from green to blue at lower applied potentials and, finally, the color of the combined films changes to blue in cathodic potentials. This suggests that the potential of the electrochromic change of CPAn-PVA-PB will be controllable by the quantity of the combined PB (i.e., the charging period at the synthesis of PB). It will be an advantageous factor for construction of electrochromic devices because operating potential can be lowered, if both components, CPAn-PVA and PB, are not influenced for the worse by the combination.

Figure 5 shows cyclic voltammograms of a CPAn-PVA-PB combined film in 0.1 M LiClO₄—CH₃CN at 20 mV/s in the applied potential region between -0.6 and +0.6 V. The combined film was prepared with the PB synthesized electrochemically for 1 min. The shape of the cyclic voltammograms does not seem to be the overlapped ones of CPAn-PVA and PB, especially in high potential region beyond +0.4 V. The electrochemical stability in this region is much lower than that of the components. For instance, the peak current loss after 50 scans is 20.4% and this value is larger than that of CPAn-PVA and PB. This current loss is likely to be due to an en-

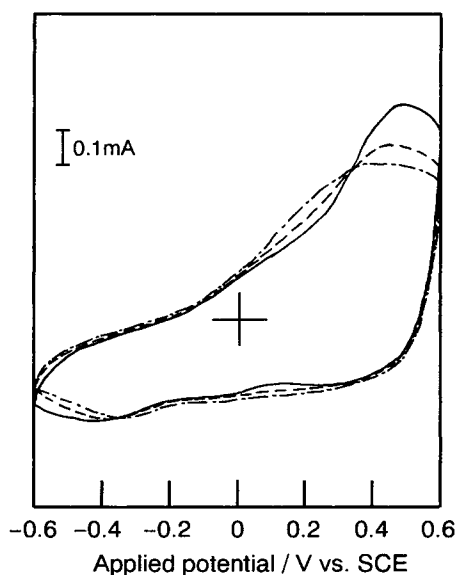


Figure 5 Cyclic voltammograms of CPAn-PVA-PB in 0.1 M LiClO₄—CH₃CN solution at 20 mV/s between -0.6 and +0.6 V on (—) the 1st, (---) the 20th, and (-·-·) the 50th scan.

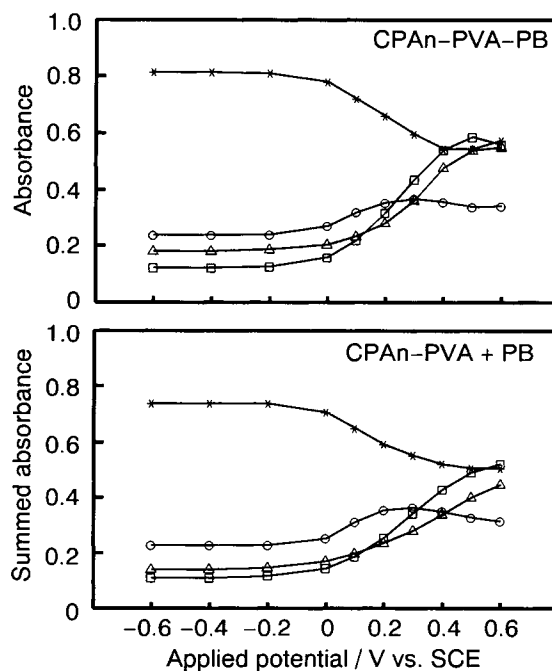


Figure 6 Changes in the specific absorbances of CPAn-PVA-PB (top) and the summed specific absorbances of CPAn-PVA and PB (bottom) for the pristine samples at (*) 330 nm, (O) 420 nm, (Δ) 680 nm, and (\square) 800 nm as a function of applied potential.

hanced degradation of the CPAn-PVA component because the current-increasing regions are corresponding to the current-increasing region of the PB (as shown in Fig. 3, bottom). Hence, polyaniline undergoes some degradative interaction with PB in the CPAn-PVA-PB combined film.

Effects of the Combined PB on the Oxidation Process of Polyaniline in CPAn-PVA-PB

To evidence the interaction between polyaniline and PB in CPAn-PVA-PB, changes in the specific absorbances of CPAn-PVA-PB (top) and the summed specific absorbances of CPAn-PVA and PB (bottom) as a function of applied potential are shown in Figure 6 for the pristine samples and in Figure 7 for the degraded samples. The data are calculated from the *in situ* visible absorption spectra of the samples employed in Figures 1, 3, and 4. The degradation treatment of the samples was carried out by standing them at +0.6 V for 1 h. The measured absorbances are specific of the reduced polyaniline (330 nm), of the first oxidized polyaniline (420 nm and 800 nm), and of the second oxidized polyaniline (680 nm), which absorption is overlapped with that

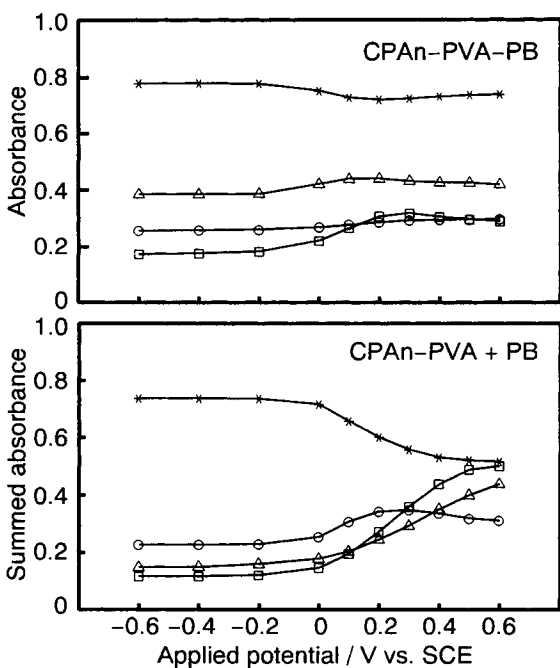


Figure 7 Changes in the specific absorbances of CPAn-PVA-PB (top) and the summed specific absorbances of CPAn-PVA and PB (bottom) for the electrochemically degraded samples at (*) 330 nm, (○) 420 nm, (Δ) 680 nm, and (□) 800 nm as a function of applied potential.

of the oxidized PB. As shown in Figure 6, the specific absorption change of the pristine sample of CPAn-PVA-PB resembles as a whole that of the summed specific absorbances of the components, CPAn-PVA and PB. However, particularly, the specific absorbance at 800 nm in the top graph increases at lower applied potential than that in the bottom graph and decreases slightly beyond +0.4 V. The specific absorbance at 680 nm of the combined film increases continuously to a larger degree than the summed absorbance. This suggests that the oxidation process of the polyaniline is activated in CPAn-PVA-PB. After the degradation treatment, as shown in Figure 7, the change of the specific absorbances of CPAn-PVA-PB by potential applying becomes smaller, and, in particular, the absorbances at 420 nm and 800 nm do not increase greatly while the absorbance at 680 nm has already increased. This suggests that the inactive quinonediimine component forms largely to decrease the electrochemical activity of the polyaniline. On the other hand, the summed specific absorbance change by potential applying is maintained after the degradation treatment, i.e., the electrochemical activity of the component materials does not change when they undergo the degradation treatment separately. Hence, it is strongly presumed

that polyaniline undergoes some interaction with PB to lose its electrochemical activity in CPAn-PVA-PB.

Ex situ FTIR spectroscopy was performed with CPAn-PVA and CPAn-PVA-PB at different applied potentials and the results were compared to investigate the effects of the combined PB on the electrochemical oxidation process of polyaniline in CPAn-PVA-PB. The employed CPAn-PVA-PB sample was the same as shown in Figures 4–7. The polyaniline spectra were derived by subtraction of the PVA spectrum from the sample spectra. The results for CPAn-PVA and CPAn-PVA-PB in the wavenumber region between 1400 and 1700 cm^{-1} , which is attributed to ring stretching vibration mode of the benzene rings, are shown in Figures 8 and 9, respectively. The asterisks represent the data after the electrochemical degradation treatment. As shown in Figure 8, the IR spectrum of polyaniline in CPAn-PVA has two definite peaks at ca. 1500 and 1590 cm^{-1} at -0.6 V. As applied potential increases, broad absorptions increase between 1500 and 1590 cm^{-1} , and, subsequently, the intensity of the 1590 cm^{-1} peak increases, accompanying the decrease of the broad absorption.

According to previous reports^{3,29,30} employing

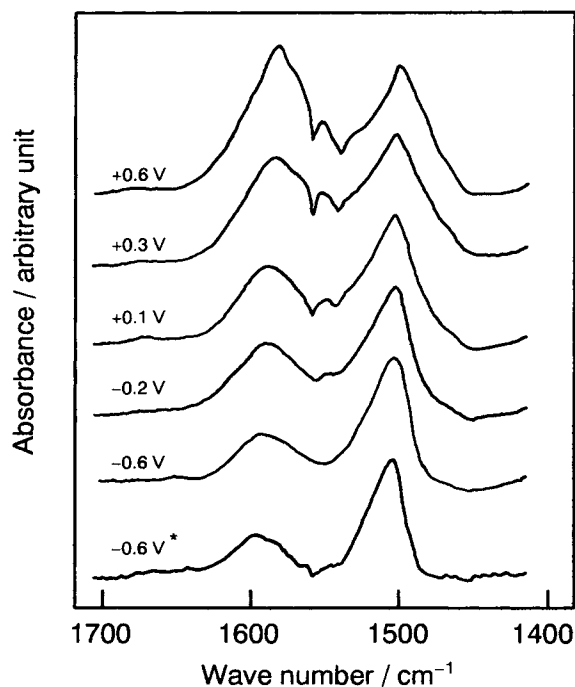


Figure 8 *Ex situ* FTIR absorption spectra of the polyaniline in CPAn-PVA at different applied potentials. The asterisk represents the sample after the electrochemical degradation treatment.

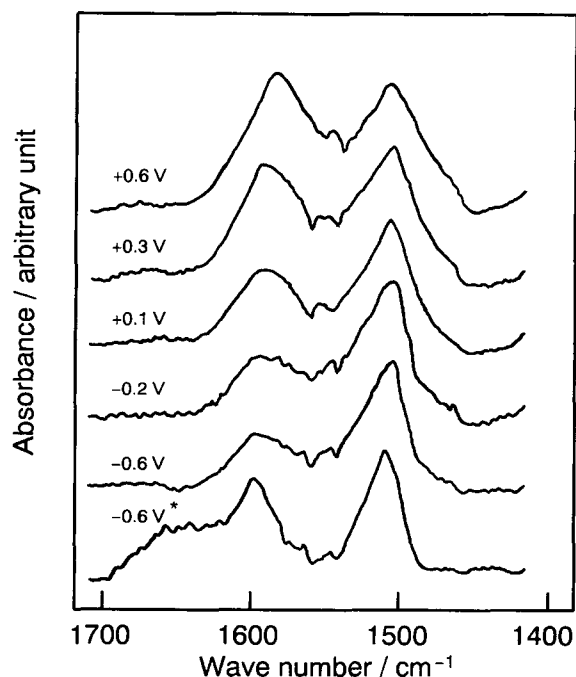


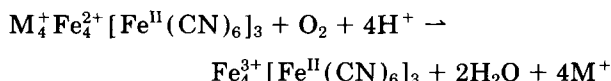
Figure 9 *Ex situ* FTIR absorption spectra of the polyaniline in CPAn-PVA-PB at different applied potentials. The asterisk represents the sample after the electrochemical degradation treatment.

aqueous media, the peaks at ca. 1500 and 1590 cm^{-1} are assigned to the ring stretching of the benzenoid and the semiquinoid structural components of polyaniline, respectively. The benzenoid component corresponds to the phenyleneamine structure (**1**) described in Scheme 1. In the present nonaqueous medium, however, the semiquinoid component involves various structures over wide energy levels from the semiquinone radical cation structure (**2**) and its delocalized state (**2'**) to the quinonediimine cation structure (**3**). From the IR data employing aniline tetramer and polymer,³ it is known that the semiquinoid peak shifts to a higher wavenumber (i.e., higher energy state) as the polyaniline structure is closer to the fully quinoid structure. Hence, it can be expected that the intermediate oxidized states of polyaniline from **1** to **3** involving **2** and **2'** appear between 1500 and 1590 cm^{-1} . In Figure 8, the broad absorption between 1500 and 1590 cm^{-1} remains rather intensively at +0.6 V. It suggests that the second oxidation process of polyaniline does not proceed largely in CPAn-PVA below +0.6 V. Considering that the spectrum at -0.6 V does not change after the degradation treatment, the oxidation process is reversible and polyaniline is stable below +0.6 V.

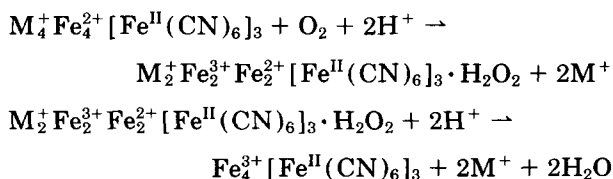
As shown in Figure 9, the IR spectrum of the polyaniline in the pristine sample of CPAn-PVA-

PB changes in almost the same way as the pristine CPAn-PVA by potential applying. However, the spectrum at -0.6 V for the electrochemically degraded CPAn-PVA-PB sample is largely different from that of CPAn-PVA. It has a new broad absorption between 1600 and 1700 cm^{-1} . This broad absorption is assigned to the fully quinoid component^{31,32} of polyaniline, which is corresponding to the quinonediimine structure (**4**). Hence, the degradation of the polyaniline in CPAn-PVA-PB is due to the irreversible formation of the electrochemically inactive quinonediimine component. This reaction is likely to occur beyond +0.2 V because the degradation of the polyaniline was not observed in the pretreatment procedure of cycling the applied potential from -0.6 to +0.2 V. Considering that the semiquinoid peak change in CPAn-PVA-PB, especially the intensity of the peak at 1590 cm^{-1} , is not greatly different from CPAn-PVA for the pristine samples, it is suggested that the formation of the quinonediimine structure occurs in the first oxidation process, i.e., the structure **2** or **2'** is directly converted to **4** through the deprotonation process.

In the previous study reported by Itaya et al.,³³ the reduced form of PB has a catalytic activity for the reduction of molecular oxygen and of hydrogen peroxide in aqueous acidic electrolytes in the following two possible mechanisms (M = alkaline metals):



and



Now I would like to propose that the degradation of polyaniline in CPAn-PVA-PB is caused by these catalytic reactions of PB. As shown in Figures 2 and 3, the cyclic voltammograms of PB have rather higher and much broader peaks than those of polyaniline. This suggests that the electrochemical oxidation process of PB proceeds more slowly than that of polyaniline, because the oxidation process of PB requires the elimination of the cations out of the narrow channels of the PB lattice. Hence, there is possibly the reduced state PB and the oxidized-state polyaniline in the potential region from +0.2 to +0.6 V. In such a state, it is considered that the

reduced PB eliminates protons from the first oxidized polyaniline (**2** and **2'**) chains instead of the acidic protons in aqueous media by the catalytic activity to the oxygen molecules dissolved slightly in the present electrolyte solution. As a result, polyaniline is gradually converted to the inactive structure **4** and loses its electrochemical and electrochromic activity. As the quantity of the combined PB increases, it is also considered that the slightly oxidized polyaniline is expected to undergo this interaction even below +0.2 V, and, finally, the polyaniline has been already degraded in the pretreatment procedure, as shown in the bottom graph of Figure 4.

CONCLUSION

The CPAn-PVA-PB combined films were prepared by the chemical method to deposit CPAn-PVA on PB. When CPAn-PVA-PB is prepared with the appropriately low quantity of PB, the combined film is a material that shows a multicolor electrochromic behavior from pale yellow to green and blue, applying a much lower applied potential than to CPAn-PVA. The color change from pale yellow to green and from green to blue is caused by the first oxidation process of polyaniline and the oxidation of PB, respectively. If the electrochemical stability of polyaniline could be maintained by the combination with PB, this combination method will be effective for construction of the electrochromic devices operated at low applied potentials. However, in fact, the combined PB eliminates protons from the first oxidized polyaniline chains to decrease the electrochemical activity of polyaniline. Therefore, to construct multicolor electrochromic devices by the combination of polyaniline with the other electrochromic materials, it is necessary to select the materials containing no deprotonation activity.

REFERENCES

1. T. Kobayashi, H. Yoneyama, and H. Tamura, *J. Electroanal. Chem. Interfac. Electrochem.*, **177**, 281 (1984).
2. A. Watanabe, K. Mori, Y. Iwasaki, Y. Nakamura, and S. Niizuma, *Macromolecules*, **20**, 1793 (1987).
3. L. W. Shacklette, J. F. Wolf, S. Gould, and R. H. Baughman, *J. Chem. Phys.*, **88**, 3955 (1988).
4. R. Jiang and S. Dong, *J. Chem. Soc. Faraday Trans. 1*, **85**, 1585 (1989).
5. D. E. Stilwell and S. Park, *J. Electrochem. Soc.*, **136**, 427 (1989).
6. A. Watanabe, K. Mori, M. Mikuni, Y. Nakamura, and M. Matsuda, *Macromolecules*, **22**, 3323 (1989).
7. M. A. Rodrigues, M. Paoli, and M. Mastragostino, *Electrochim. Acta*, **36**, 2143 (1991).
8. D. E. Stilwell and S. Park, *J. Electrochem. Soc.*, **135**, 2497 (1988).
9. D. Seeger, W. Kowalchuk, and C. Korzeniewski, *Langmuir*, **6**, 1527 (1990).
10. M. Morita and I. Hashida, *J. Polym. Sci. Part B Polym. Phys.*, **29**, 1567 (1991).
11. M. Morita and I. Hashida, *Makromol. Chem.*, **193**, 921 (1992).
12. M. Morita, *Makromol. Chem.*, **194**, 1513 (1993).
13. M. Morita and I. Hashida, *J. Appl. Polym. Sci.*, **41**, 1073 (1990).
14. K. Okabayashi, F. Goto, K. Abe, and T. Yoshida, *J. Electrochem. Soc.*, **136**, 1986 (1989).
15. H. Daifuku, T. Kawagoe, N. Yamamoto, T. Ohsaka, and N. Oyama, *J. Electroanal. Chem.*, **274**, 313 (1989).
16. F. Ueda, K. Mukai, I. Harada, T. Nakajima, and T. Kawagoe, *Macromolecules*, **23**, 4925 (1990).
17. M. T. Nguyen and L. H. Dao, *J. Electrochem. Soc.*, **136**, 2131 (1989).
18. M. G. Kanatzidis, C. Wu, H. O. Marcy, and C. R. Kannewurf, *J. Am. Chem. Soc.*, **111**, 4139 (1989).
19. N. Leventis and Y. C. Chung, *J. Electrochem. Soc.*, **137**, 3321 (1990).
20. P. K. Schen, H. T. Huang, and A. C. C. Tseung, *J. Electrochem. Soc.*, **139**, 1840 (1992).
21. K. Itaya, H. Akahoshi, and S. Toshima, *J. Electrochem. Soc.*, **129**, 1498 (1982).
22. P. M. McManus, S. C. Yang, and R. J. Cushman, *J. Chem. Soc. Chem. Commun.*, 1556 (1985).
23. S. A. Alkatis and M. Grätzel, *J. Am. Chem. Soc.*, **98**, 3549 (1976).
24. M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).
25. K. Itaya, T. Ataka, and S. Toshima, *J. Am. Chem. Soc.*, **104**, 4767 (1982).
26. F. Herren, P. Fischer, A. Ludi, and W. Hälg, *Inorg. Chem.*, **19**, 956 (1980).
27. I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 870 (1957).
28. M. K. Chantooni, Jr. and I. M. Kolthoff, *J. Am. Chem. Soc.*, **89**, 1582 (1967).
29. J. Tang, X. Jing, B. Wang, and F. Wang, *Syn. Met.*, **24**, 231 (1988).
30. Y. Furukawa, F. Ueda, Y. Hyodo, I. Harada, T. Nakajima, and T. Kawagoe, *Macromolecules*, **21**, 1297 (1988).
31. N. S. Sariciftci, H. Kuzmany, H. Neugebauer, and A. Neckel, *J. Chem. Phys.*, **92**, 4530 (1990).
32. T. Ohsaka, Y. Ohnuki, N. Oyama, G. Katagiri, and K. Kamisako, *J. Electroanal. Chem.*, **161**, 399 (1984).
33. K. Itaya, N. Shoji, and I. Uchida, *J. Am. Chem. Soc.*, **106**, 3423 (1984).

Received June 16, 1993
Accepted October 5, 1993