Electrochemically prepared poly(o-phenylenediamine) – Prussian blue composite film for a three-colour expressible ECD material

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Both Prussian blue (PB) and poly(o-phenylenediamine) (PoPD) were easily electrodeposited as stable films onto a transparent indium tin oxide (ITO) electrode. The voltammogram of the PB film showed a reversible sharp redox peak current at about 0.25 V. Although the colour change was caused by altering the applied potentials, no colour change was seen after about 10^4 repetitions. The PoPD film also showed a reversible redox peak current at about -0.05 V. The redox reaction was accompanied by a readily observable colour change between nearly red (vermilion) and colourless. The PoPD film was electrodeposited onto the PB coated electrode to obtain a PB/PoPD composite film. The voltammogram of the film was comprised of the two redox waves of the individual components. The film retained the electrochromic properties of each component and there was no undesirable interference. By changing the potentials, the film exhibited a continuous variety of colours: colourless (-0.2 V), vermilion (0.1 V) and emerald green (0.6 V). The switching time of the colour change was found to be <600 ms. Compared with the PB film, the composite film lasted longer. About 60% of the colouration remained after 10^5 repetitions since the PoPD worked as a binder which enhanced the adhesion of PB to the electrode surface.

1. Introduction

These days we are inundated with information, requiring many types of displays. Among the various displays, in particular, non-emissive displays such as electrochromic displays (ECDs) and liquid-crystal displays (LCDs), need to be developed because of their reduced glare to human eyes. ECDs are based on the redox reaction of a material that exhibits a colour which depends on its redox state. ECDs have advantages over LCDs since they do not have the limited viewing angle which is inherent to LCDs, and have memory functions. These characteristics are among the basic requirements for display devices.

Many inorganics and organics have been tested for ECD use. In general, the inorganics have less variety in colour change and less adhesion to electrode substrates than organics, although the former are intrinsically more stable than the latter. If composite films consisting of inorganics and organics are prepared and retain the electrochromic properties of each component, not only will reduced variety and adhesion of

the inorganics be improved by the organics but they will also be available as multicolour ECDs. However, such attempts have been very limited.

We have found that some electrically conductive polymers such as polyanilines, show good electrochromic properties [1, 2]. In this study, poly-(o-phenylenediamine) (PoPD), a polyaniline, and Prussian blue (PB) were employed as an organic and inorganic, respectively. These are especially attractive for our objectives, because the redox potentials at which the colour change takes place are sufficiently separate from each other (more than 0.20 V) [3, 4] and, in the coloured state, the colours of PB and PoPD are blue and nearly red (vermilion), which are two of the three primary colours.

The PB/PoPD composite film was obtained by the electrodeposition of PB and PoPD. A voltammogram of the film shows the two redox waves of the components. The film retained the electrochromic properties of each component and there was no undesirable interference. By changing the potentials the film

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colour varied over a continuous range. Furthermore, the composite film lasted longer than the PB film.

2. Experimental procedure

2.1. Chemicals
o-Phenylenediamine (Tokyo Kasei Kogyo Co.) was used after recrystallization from distilled water. Other chemicals were of reagent grade and used as received. Aqueous solutions were prepared using double-distilled water. The film preparation of PB, PoPD and PB/PoPD will be described in Section 3.

2.2. Voltammetric measurements
The voltammetric measurements for the film preparation of PB, PoPD and PB/PoPD and for the redox activities were carried out in a single compartment cell with the usual three-electrode configuration. The counter electrode was a cylindrical piece of platinum 2 cm in diameter and 2 cm long. The working electrode on which the PB, PoPD and PB/PoPD films were electrodeposited was a transparent indium tin oxide (ITO) coated glass plate 0.8 cm wide and 5 cm long. The working electrode was placed axially with respect to the counter electrode. A saturated calomel electrode (SCE) equipped with a KCl salt bridge was used as the reference electrode. All voltammograms were obtained using a Hokuto Denko HA-301 potentiostat connected to a Hokuto Denko HB-104 function generator and to a Rikadenki RW-21 x–y recorder.

2.3. Spectro-electrochemical measurements
The absorption curves of the films were obtained using a Shimadzu UV-2200 spectrophotometer. The arrangement of the electrodes in the cell chamber is schematically depicted in Fig. 1. The coated ITO electrode was placed parallel to the window surface of an ordinary 1 cm UV quartz cell. An Ag/AgCl plate, used as the reference electrode, was placed in a region out of the light path. The cell was purged with pure nitrogen gas before the measurements. A nitrogen atmosphere was maintained in the whole cell chamber during the measurements. In addition, the same potentiostat system as previously described in the former section was used for polarization of the films.

2.4. Measurements of the switching time and lifetime of the colour change
The switching time and lifetime of the colour change of the films were estimated from plots of both the current and absorbance response to the applied square-wave potentials. The potentials were controlled with the potentiostat system previously described except for the recorder. The transient current response was recorded using a Rikadenki R-61K x–t recorder with wave memory functions. The transient absorbance response at the maximum absorption wavelength was detected by amplifying the direct voltage signals
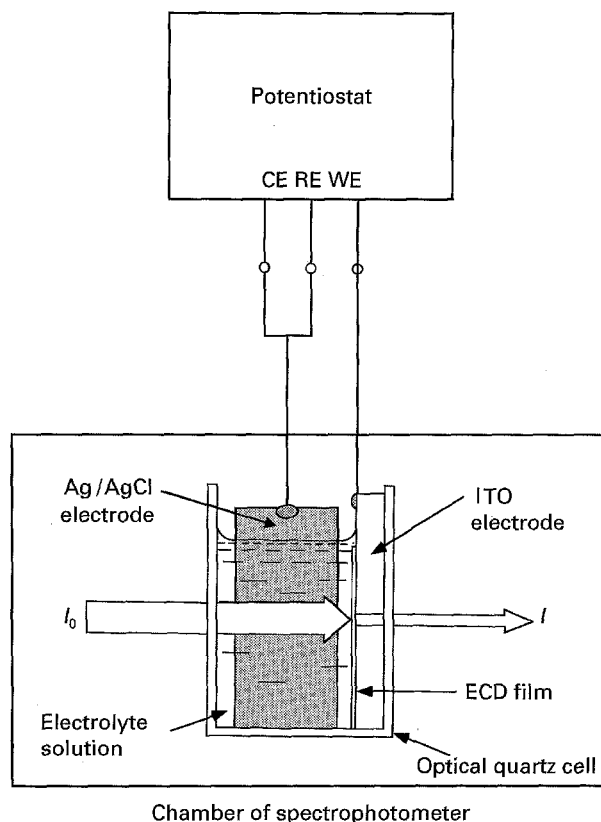

Figure 1 Schematic drawing of the arrangement of the filmed ITO electrode and the Ag/AgCl electrode in the spectrophotometer cell chamber.

from the photomultiplier of the spectrophotometer. The signals were also recorded using the x–t recorder.

2.5. Morphological observation
The morphology of the obtained film was observed using a Hitachi S-2300 scanning electron microscope (SEM) and the film thickness was determined from the SEM observations. The film was electrodeposited onto a 0.5 cm square platinum plate for the observations.

3. Results and discussion

3.1. Preparation and electrochromism of the PB film
The PB film was deposited onto the ITO electrode by a modification of the literature method [5] from a nitrogen-purged 0.5 M KHSO$_4$ solution containing 2 mM of both K$_3$[Fe(CN)$_6$], and Fe$_2$(SO$_4$)$_3$, by potential cycling from +0.8 V to −0.2 V versus SCE at 100 mV s^{-1}. Fig. 2a shows the cyclic voltammograms in the film forming process. The blue PB film formed on the electrode surface exhibits a sharp redox peak current at about 0.25 V. The increase in the current with the number of potential cyclings shows the gradual growth of the film. A brighter blue film is obtained by increasing the number of cycles. Unfortunately, however, the i–R drop of the film increases the peak potential separation of the cyclic voltammogram and the switching time of the colour change. To obtain the best film for ECD use, the potential cycling was stopped at 60 cycles (film thickness: 1.8 μm).
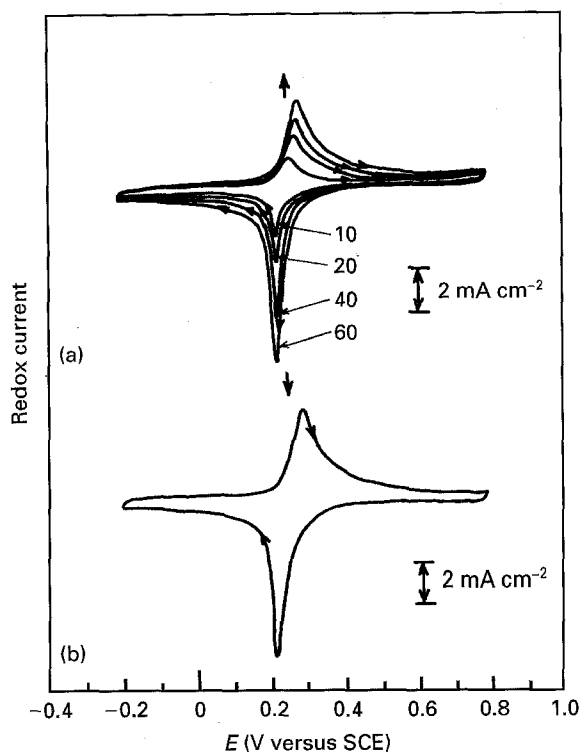
Figure 2 (a) Cyclic voltammograms in the film forming process of Prussian blue (PB). Sweep rate: 100 mV s^{-1}. Solution: 0.5 M KHSO$_4$ containing 2 mM K$_3$[Fe(CN)$_6$] + 2 mM Fe$_2$(SO$_4$)$_3$. (b) Cyclic voltammogram showing the redox activity of the deposited PB film. Sweep rate: 100 mV s^{-1}. Solution: 0.1 M KCl + 0.1 M HCl.

Figure 3 Effect of the polarizing potential on the absorption spectra of the PB film. Potential values, referred to a Ag/AgCl electrode, are shown in the figure.

It is well-known that PB is electroreduced to form colourless Prussian white (PW). Alkali metal or ammonium ions are indispensable for the formation of PW. Among the cations, the potassium ion gives the fastest formation of PW [3, 6]. On the other hand, PB shows high stability in acidic solution, while it deteriorates in neutral solution [7]. A 0.1 M hydrochloric acid solution containing 0.1 M KCl was, therefore, selected as the electrolyte solution for the electrochemical measurements in this paper. Fig. 2b shows the cyclic voltammogram of the PB film obtained. The shape of the voltammogram and the relationship between the current peak and the scan rate are somewhat similar to that reported by Neff and his co-workers [8, 9]. The redox peak current at about 0.2 V is ascribed to the following reaction [3]

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4K^+ + 4e^- \rightleftarrows K_4Fe_4^{II}[Fe^{II}(CN)_6]_3$$

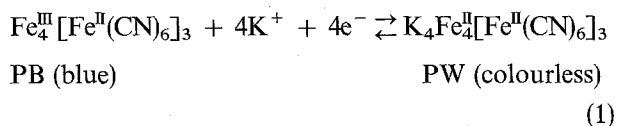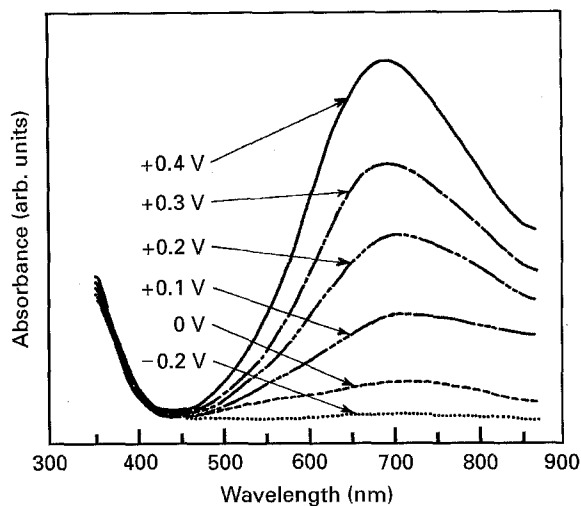PB (blue)   PW (colourless)

(1)

Fig. 3 shows the effect of the polarizing potential on the absorption spectra of the PB film. A band observed at about 700 nm is assigned to an optical transition from an electric configuration of Fe^{III}Fe^{II}(CN)$_6$ to Fe^{II}Fe^{II}(CN)$_6$ [10]. As indicated, the film is completely decolorized at -0.2 V (versus Ag/AgCl/0.2 M Cl$^-$). No hydrogen evolution was observed as long as the ITO was used as the substrate. As expected, the intensity of the colour increases with increasing potential. During the decoloration pro-

cess, the maximum absorption wavelength shifts to a slightly higher wavelength. The shift implies an etching mechanism whereby a portion of the PB film is slowly converted to an authentic soluble form [6, 11, 12]. The conversion degrades the ECD properties of the PB film as will be described in Section 3.4.

3.2. Preparation and electrochromism of the PoPD film

The PoPD film can be deposited onto electrode substrates by the electro-oxidation of o-phenylenediamine using any electrolysis mode [4, 13]. The most stable PoPD film is formed by a potential cycling electrolysis [4, 14] although the reason is not yet well understood. The cyclic voltammogram during the electrodeposition of the film is shown in Fig. 4a. During the first positive scan, monomeric o-phenylenediamine is electro-oxidized, exhibiting a distinct irreversible current peak at about 0.70 V versus SCE. As soon as the current flowed, red powdery products appeared near the electrode's surface. The products continued to diffuse away from the surface to the bulk while the potential cycling was repeated. After about 100 cycles, the deposition of a vermilion film was clearly seen on the electrode's surface. The film thickness was controlled by altering the number of potential cyclings, but a film thicker than 1 μm was not obtainable. The limitation is probably caused by the low electrical conductivity of PoPD being 1.2×10^{-3} S cm^{-1} [14]. The potential cycling was repeated up to the 300th cycle to prepare the best PoPD film for ECD use. The film thickness was 0.8 μm.

The cyclic voltammogram showing the redox activity of the PoPD film is indicated in Fig. 4b. The reversible redox peak current at about -0.05 V is due to the redox reaction of the PoPD electrodeposited film. Oyama and co-workers reported [15] that the IR spectrum of PoPD suggested a unit ladder structure having phenazine rings and [16] that, on the
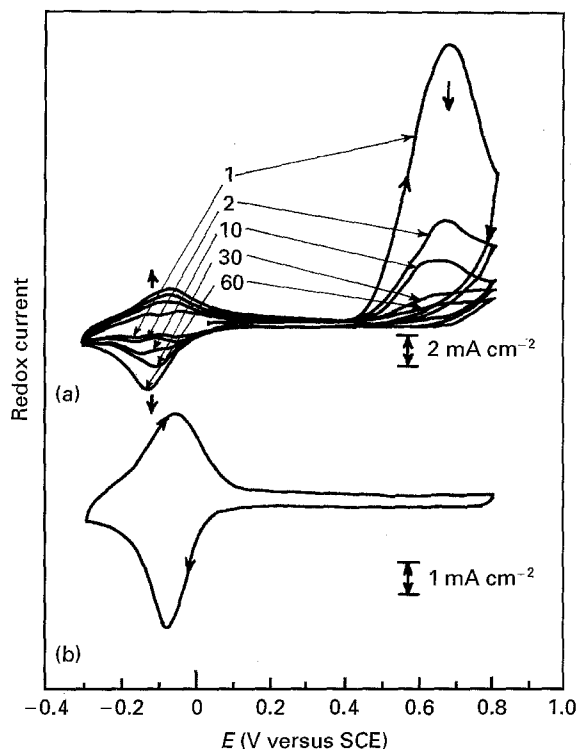
Figure 4 (a) Cyclic voltammograms in the film forming process of poly(o-phenylenediamine) (PoPD). Sweep rate: 100 mV s^{-1}. Solution: 1.0 M H$_2$SO$_4$ containing 50 mM o-phenylenediamine + 0.5 M KHSO$_4$. (b) Cyclic voltammogram showing the redox activity of the deposited PoPD film. Sweep rate: 100 mV s^{-1}. Solution: 0.1 M KCl + 0.1 M HCl.

basis of the structure, the following redox reaction occurred

$$+ 2nH^+ + 2ne^- \rightleftharpoons$$

(2)
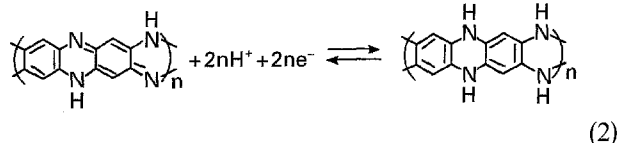
However, we have shown, from the IR and ^{1}H-NMR spectra and the elemental analysis of PoPD [17], that the PoPD polymeric backbone has a 1,4-substituted structure. We believe that the redox reaction is similar
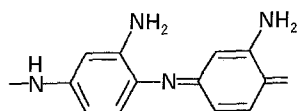
to that of polyaniline [18, 19] and not only protonation but also anion doping takes place. This is supported by the fact that the redox potential strongly depends on the concentration of dissolved anions [20]. The redox reaction is still unknown and further studies are needed to fully characterize it.

Although the redox reaction has not been fully elucidated yet, there is no doubt that the PoPD polymer chain has successive oxidized states as shown in Fig. 5. The cation sites in the oxidized states form the polaron and/or bipolaron bands inside a π–π^* energy gap. The vermilion colour of PoPD originates from these bands. The absorbance of the bands at 480 nm increases when the PoPD film is oxidized higher (Fig. 6).
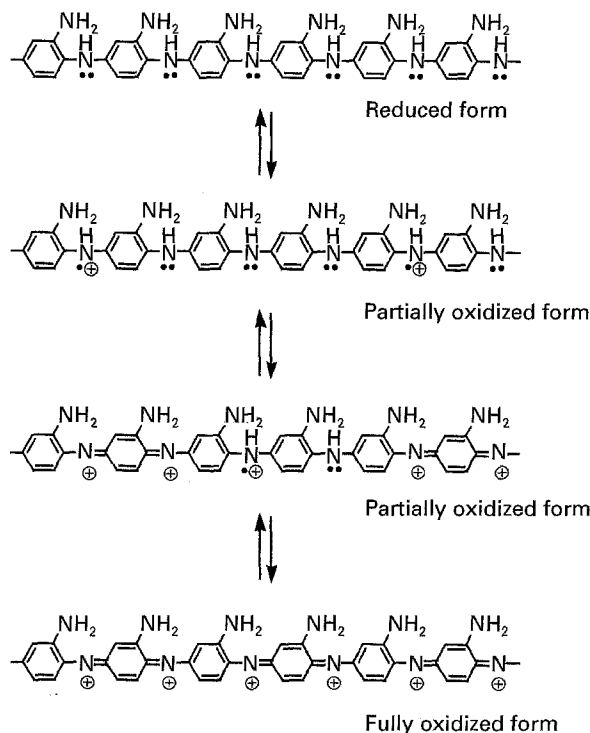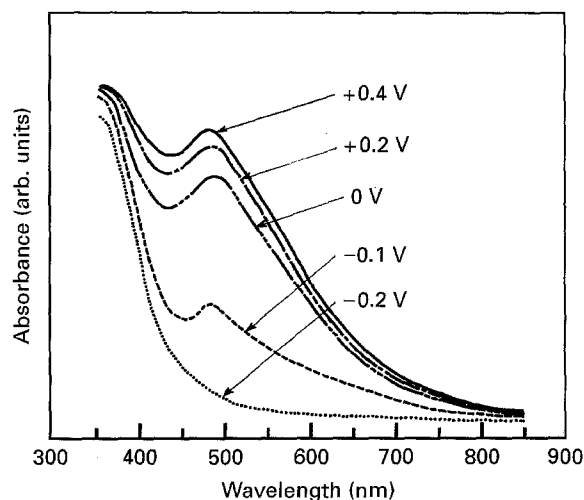

Figure 5 Proposed oxidation states of PoPD.

Figure 6 Effect of the polarizing potential on the absorption spectra of the PoPD film. Potential values, referred to the Ag/AgCl electrode, are shown in the figure.

3.3. Preparation and electrochromism of the PB/PoPD composite film

To obtain the PB/PoPD composite film, o-phenylenediamine was electro-oxidized under the same electrolysis condition as previously described using the PB filmed ITO electrode. Fig. 7a shows cyclic voltammograms during the film growth of PoPD on the PB film electrode. During the first cycle, monomeric o-phenylenediamine is oxidized and exhibits a distinct irreversible current peak at about 0.9 V versus SCE. New anodic and cathodic peaks, which are ascribable to the redox reaction of the deposited PoPD film, appear at −0.02 V after the first cycle. These peak currents continue to increase after each subsequent cycle. In contrast to this, the redox peak

currents of PB and the anodic current of o-phenylenediamine gradually decrease with each cycle. This behaviour is strongly related to the electrical conductivity of the PoPD film. The conductivity has the following potential dependence [14]: although the film has a high conductivity within the potential range between −0.2 and 0.1 V, it loses this high conductivity above 0.2 V. In other words, the electrical resistance above 0.2 V can no longer be neglected. As a result, the currents of PB and o-phenylenediamine are suppressed by the deposited film. Also, the PB film obstructs the transport of K^+ ions toward the PB film which are required for the redox reaction of PB (Equation 1). The potential cycling was further continued up to 60 cycles for the preparation of the PB/PoPD composite film electrode. The film thickness in the dry state was 2.2 μm.

The redox wave of the obtained composite film is shown in Fig. 7b. The wave is comprised of the two redox waves of the components. One is the wave at about 0.2 V due to the redox reaction of PB (Equation 1). The other is the wave at −0.02 V, attributed to the redox reaction of PoPD.

Fig. 8 shows the optical absorption spectra of the PB/PoPD composite film in situ at various electrode potentials. By changing the anodizing potential, the film exhibits a continuous variety of colours; colourless (−0.2 V), vermilion (0.1 V) and emerald green (0.6 V). Judging from the spectra, the composite film retains the electrochromic properties of each component separately and there is no undesirable interference. If the redox potentials of each component had not been sufficiently separated from each other, the colour variety could not have been obtained. In fact, a PB/polyaniline composite film cannot express such a colour variety because the redox potentials of each component are very close to each other [5]. In addition, the PB/PoPD composite film was obtainable on various electrode substrates with any shape and/or pattern. An attempt to form the three letters of "ECD" with the film was successful (Fig. 9).

3.4. Switching time and lifetime of the colour change
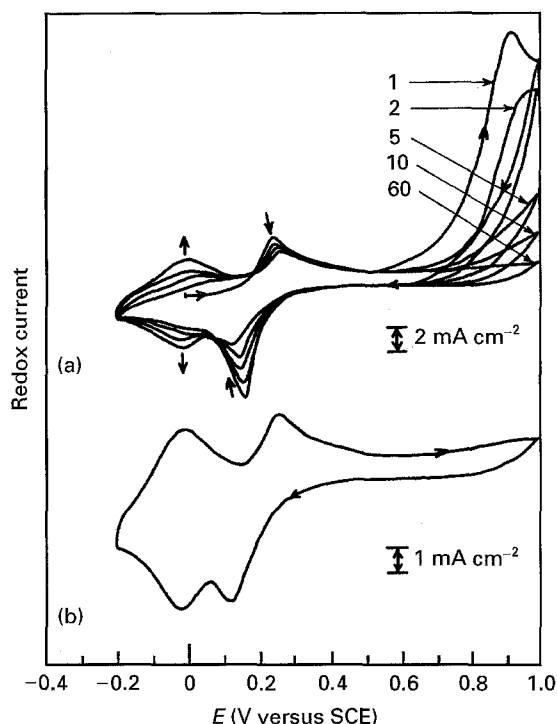We have already measured the switching time and lifetime of the PoPD film for the colour change; the

Figure 7 (a) Cyclic voltammograms in the film forming process of PoPD on the PB film electrode under the same electrolysis conditions as shown in Fig. 4. (b) Cyclic voltammogram showing the redox activity of the PB/PoPD composite film. Sweep rate: 100 mV s⁻¹. Solution: 0.1 M KCl + 0.1 M HCl.
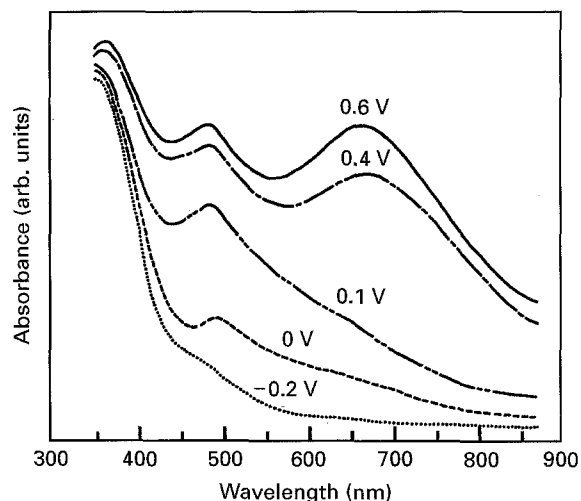

Figure 8 Effect of the polarizing potential on the absorption spectra of the PB/PoPD film. Potential values, referred to the Ag/AgCl electrode, are shown in the figure.
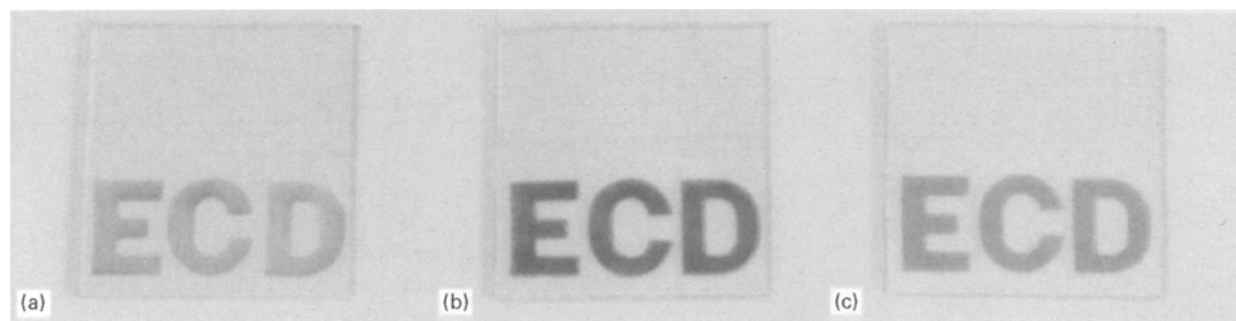

Figure 9 Electrochromism of the PB/PoPD composite film electrodeposited to form the three letters of "ECD". (a) PB film at 0.4 V, (b) PB/PoPD film at 0.1 V, and (c) PB/PoPD film at 0.6 V.

switching time is less than 10 ms and the lifetime is at least 10^5 repetitions [1]. In Fig. 10, the current and absorbance responses of the PB and PB/PoPD films on the ITO electrode is indicated versus the square-wave potential pulse at both the initial stage (full line) and after 2×10^3 repetitions of the pulse polarization (dotted line). The absorbance was monitored at 680 nm for each film. From both responses, the switching time is found to be 500 ms for the PB film and 600 ms for the PB/PoPD film. After 2×10^3 repetitions, the composite film still shows the bright colour change, while the PB film has greatly deteriorated.

To estimate the lifetime of the films, the absorbance difference between the coloured and uncoloured state (ΔA) was monitored at 680 nm. Fig. 11 shows the change in $\Delta A/\Delta A_0$, ΔA_0 being ΔA at the first repetition. No colour change was observed for the PB film electrode when the number of repetitions (N) exceeded 10^4, and the electrode remained permanently blue. Compared with the PB film electrode, the PB/PoPD film electrode lasted longer. About 60% of the colour remained after 10^5 repetitions. This improvement in

the lifetime reflects the better adhesion between PoPD and the electrode substrate than that between PB and the substrate. In other words, PoPD works as a binder. This is supported by the SEM observation of the films (Fig. 12). The PB film has a granular surface (a), while the PoPD film has a featureless smooth one (b). The PB/PoPD film shows almost the same surface as that of the PB film because the PoPD layer is much thinner than the predeposited PB film. Although there are several cracks in the PB film, the composite film has no cracks. The cracks are caused by the drying process. In the composite film, the binder effect of PoPD probably prevents the formation of cracks.

3.5. Effect of solution pH on colour tone

There is no doubt that the polymeric backbone of PoPD has amine and/or imine nitrogen atoms. These nitrogen atoms are probably protonated in acidic solution, and the electronic structure of PoPD is changed. As expected, the colour tone of the PoPD film is changed by the environmental solution pH (Fig. 13b). The maximum absorption wavelength (λ_{max}) in the coloured state linearly decreased with solution pH. This shift is not accompanied by any appreciable change in absorption intensity. On the other hand, λ_{max} of the PB film is constant regardless of the solution pH since the redox reaction includes no proton (Equation 1).

For the composite film, the absorption band of PoPD shows almost the same change as illustrated in Fig. 13b. It is interesting to find that the PB band is also changed by solution pH. In a more acidic environment, i.e. below pH 2.5, the band wavelength decreases, exhibiting an electronic interaction between PoPD and PB. The interaction probably originates from the positively charged sites (protonated nitrogen sites) of the PoPD polymeric backbone. Therefore, not only the colour tone, but even the change in colour
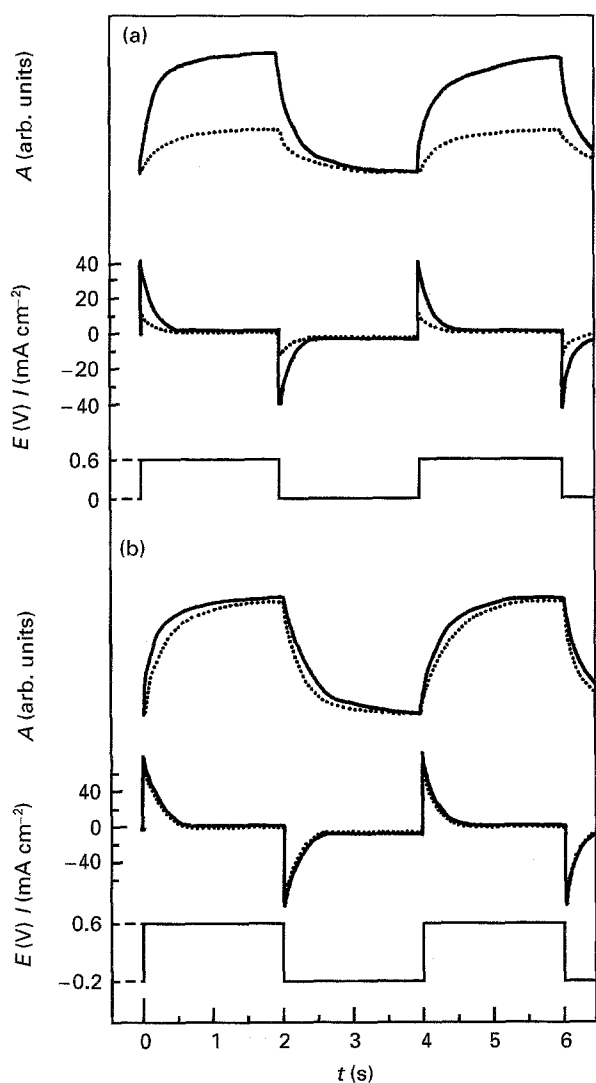

Figure 10 Current (I) and absorbance (A) responses of the PB film (a) and PB/PoPD film (b) on the ITO electrode. The square-wave potential–time profile is shown by the lower curve of each figure. (—): first repetition. (. . .): after 2×10^3 repetitions. The absorbance was monitored at 680 nm.
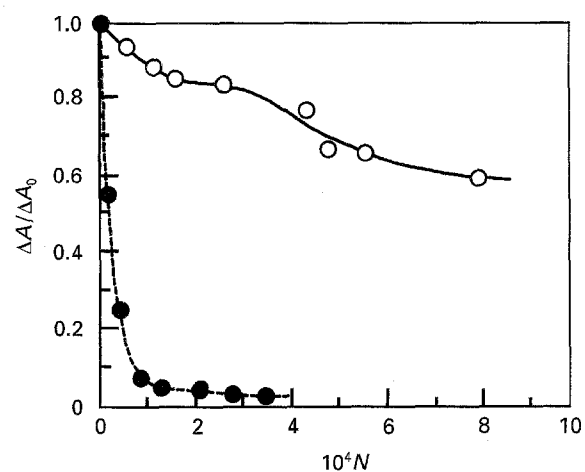

Figure 11 Persistence of coloration–discoloration of the (O) PB/PoPD composite and (●) PB film electrodes in 0.1 M HCl containing 0.1 M KCl. The stability test in colour change was carried out using a repetitive square-wave potential pulse with a 0.5 Hz interval between −0.2 and 0.6 V. The ratio of the absorbance change at 680 nm (ΔA) to that at the initial pulse (ΔA_0) is plotted versus the number of repetitions (N).
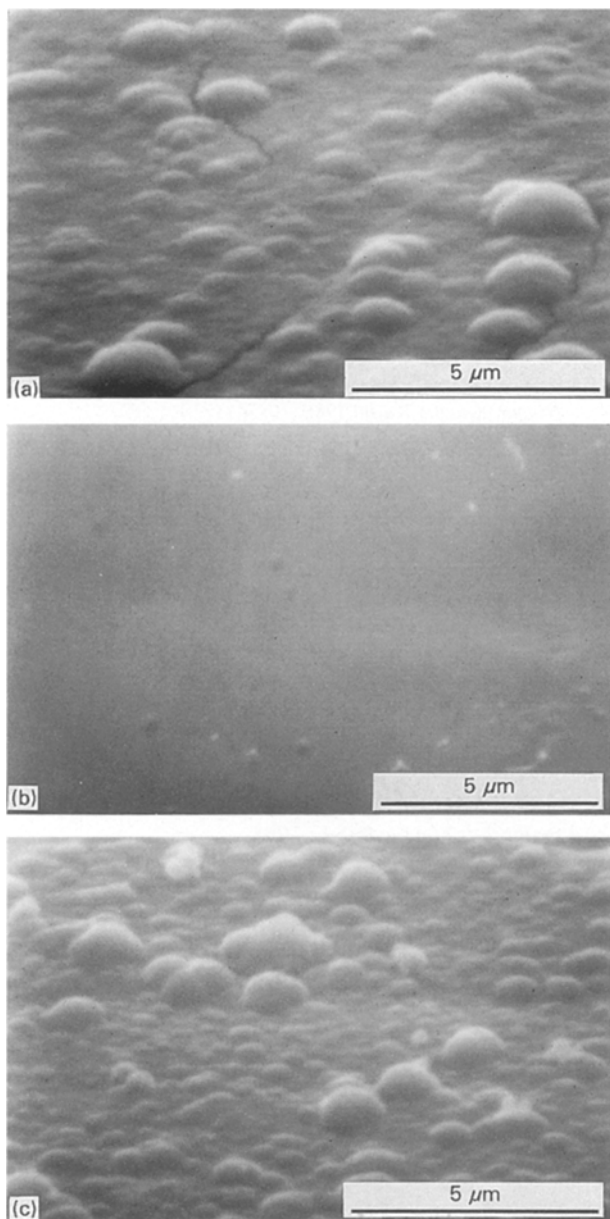
Figure 12 Scanning electron microphotographs of the surfaces of the PB (a), PoPD (b) and PB/PoPD (c) films.

Figure 13 Effect of solution pH on the maximum absorption wavelength (λ_{max}) of the PB (a) and PoPD (b) films.

Figure 14 Effect of solution pH on λ_{max} of the PB/PoPD composite film. (a) Absorption band of PB. (b) Absorption band of PoPD.

can be controlled by a slight change in working conditions.

4. Conclusions

1. The PB film electrodeposited onto the ITO electrode showed a sharp redox peak current at about 0.25 V. The film was completely decolorized at −0.2 V (versus Ag/AgCl/0.2 M Cl⁻), and the intensity of the colour increased with increasing potential.

2. The PoPD film electrodeposited on the ITO electrode also showed a reversible redox peak current at about −0.05 V. The coloured state of the film was vermilion, which decolorized at −0.2 V.

3. The PB/PoPD composite film was prepared by coating the PB film electrode with PoPD. The redox wave of the obtained composite film was comprised of the two redox waves of the individual components. One was the wave at about 0.2 V due to the redox reaction of PB and the other was the wave at −0.02 V
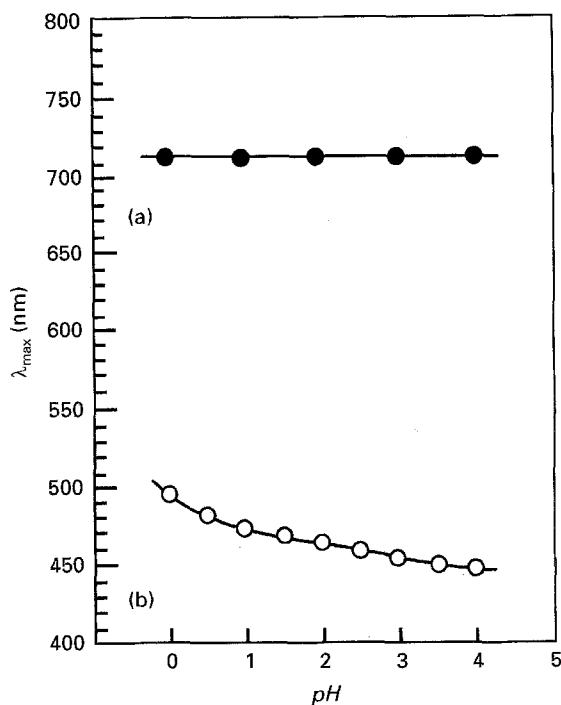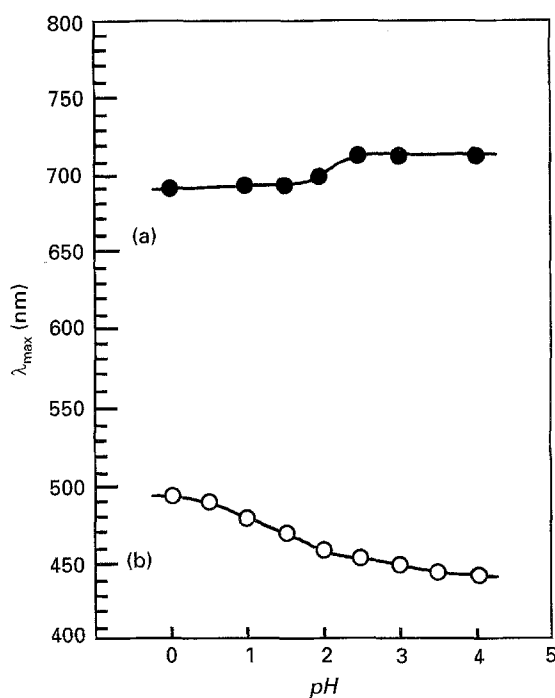
attributed to the redox reaction of PoPD. By changing the anodizing potential, the film exhibited a continuous variety of colours: colourless (−0.2 V), vermilion (0.1 V) and emerald green (0.6 V). The film retained the electrochromic properties of each component and there was no undesirable interference.

4. From both the current and absorbance responses, the switching time was found to be 500 ms for the PB film and 600 ms for the PB/PoPD film. No colour change was observed for the PB film electrode when the number of repetitions (N) exceeded 10^4, after

which the electrode remained permanently blue. Compared with the PB film electrode, the PB/PoPD film electrode lasted longer. About 60% of the colouration remained after 10^5 repetitions.

5. The colour tone of the PB/PoPD film was changed by the environmental solution pH. The maximum absorption wavelength in the coloured state linearly decreased with the solution pH. This shift was not accompanied by any appreciable change in absorption intensity.

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