Redox Behavior and Electrochromic Properties of Polypyrrole Films in Aqueous Solutions

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Polypyrrole films prepared by anodic polymerization of pyrrole on Pt or SnO_2-coated glass show redox behavior in aqueous electrolyte solutions containing a supporting electrolyte alone. Transfer of electrolyte anions into and from the film is involved in the redox reaction similarly with acetonitrile solutions already reported. Insertion of divalent anions into the film occurs in two steps but that of monovalent anions in one step, as judged from corresponding cyclic voltammograms. The change in film color which occurs in the redox reaction of the film was investigated in detail as a function of electrode potential and the charge consumed in the redox reaction. Polypyrrole is a promising material for electrochromic display devices.

Recently many reports have been published concerning electrochemical properties of electroconductive polymers. Among them, polypyrrole has been studied most extensively. Except for earlier reports by Weiss *et al.*,[1–3] most of electrochemical studies have been conducted on films prepared by anodic polymerization of pyrrole in an acetonitrile medium. According to Diaz *et al.*[4–9] polypyrrole-coated Pt electrodes show redox behavior in acetonitrile solutions: Insertion of anionic species into films and elimination of inserted anions from films occur in the oxidation and reduction of films, respectively; the oxidized film contains 0.25 mol of anions in 1 mol of pyrrole rings and exhibits high conductivity. Use was made of this property to stabilize unstable semiconductor electrodes such as *n*-Si and *n*-GaAs in aqueous solutions by coating electrode surface with thin polypyrrole films.[10–15]

Concerning electrochemical properties of polypyrrole films in aqueous solutions, redox behavior of several electroactive species such as $[Fe(CN)_6]^{3-/4-}$ and ferrocene/ferricenium has been investigated by use of Pt or Ta as the electrode substrate and it has been found that the polymer films serve as inert electrodes like Pt electrodes.[7,16–18] Their photoelectrochemical properties were also investigated in relation to the conduction mechanisms.[18] We have studied electrochemical properties of polypyrrole films in aqueous solutions containing a supporting electrolyte alone and found that the films exhibit redox behavior like those reported in acetonitrile solutions. In this paper electrochemical properties of polypyrrole films in aqueous solutions will be reported with particular reference to their redox behavior. Furthermore, it will be shown that the color of polypyrrole films changes with redox behavior. Preliminary results will also be presented on the application to electrochromic display devices which have been obtained with stable inorganic oxides such as WO_3[19–23] and organic materials such as phthalocyanines.[24] The color change of polymer-coated electrodes during the course of their polarization has been described with several polymers,[8,25,26] but no systematic study with focusing on the application to electrochromic display devices seems to have conducted.

Experimental

Preparation of Polypyrrole. Redox reactions of polypyrrole were investigated with its film prepared on a Pt substrate. For this purpose, a flat Pt plate was mounted on a Teflon electrode holder having an exposed electrode area of $1\,cm^2$. An anodic polymerization of pyrrole was carried out in an N_2 atmosphere in acetonitrile containing $0.1\,mol\,dm^{-3}$ pyrrole and $0.3\,mol\,dm^{-3}$ $LiClO_4$ at $0.3\,mA\,cm^{-2}$ for 2 min. By this procedure polypyrrole of *ca.* 90 nm thickness was deposited on the Pt as determined with a multi-reflection interferometer (Mizojiri Kogaku, Model 2). The electrode prepared in this manner is denoted here by PPy/Pt. For the purpose of elemental analysis the film was prepared on a Pt electrode having a large area of *ca.* $20\,cm^2$ under the same conditions as described above except for the electrolysis time which was 20 min, and was teared away from the substrate. The film thickness in this case was *ca.* 220 nm.

Measurements of electrochromic properties of polypyrrole were carried out with a film prepared on a SnO_2–coated glass electrode. The SnO_2-coated glass electrode was prepared in this laboratory by pyrolysis of a spray mixture of $3\,mol\,dm^{-3}$ $SnCl_4$, $0.15\,mol\,dm^{-3}$ $SbCl_5$, and $1.5\,mol\,dm^{-3}$ HCl,[27] and its area was $3.5\,cm^2$. An electrical lead wire was attached to its round rim with silver-epoxy by coating it first with epoxy resin and then with silicone rubber adhesive. The SnO_2–coated glass electrode prepared in this manner had an exposed area of *ca.* $3\,cm^2$, which was used as the substrate for the deposition of polypyrrole. The deposition was performed under the same conditions as in the case of PPy/Pt and the prepared electrode will be denoted here by PPy/OTE.

Electrochemical Measurements. Measurements were carried out in a Pyrex beaker type cell. A saturated calomel electrode (SCE) served as a reference electrode. Cyclic voltammograms were obtained by use of a potentiostat (Hokuto Denko HA-104), a function-generator (Hokuto Denko HB-104), and an X–Y recorder (Yokogawa Electric Inc. 3077). An electronic coulometer (Hokuto Denko HF-201) was used as required. For measurements of resistivity of polypyrrole films the four-probe method[28] was applied to a film sample which had been teared away from PPy/Pt by use of an adhesive tape.

Electron Probe X-Ray Microanalysis of Polypyrrole Films. A qualitative analysis of anions contained in polypyrrole films was performed to obtain direct information on the anion transfer into and from films which occur in the course of redox reaction of PPy/Pt electrodes. An energy dispersive electron probe X-ray microanalyzer (EPMA) (Horiba EMAX-1500E) connected to a scanning electron microscope (Hitachi S-450) served for this purpose.

Measurements of Electrochromic Properties. A PPy/OTE working electrode and a counter electrode (*ca.* 1 cm^2 Pt plate) were set in a quartz cell (20×10×40H mm). The cell was connected to a reference electrode (SCE) with a salt bridge and set in an UV-visible spectro-photometer (Shimadzu MPS-5000). The absorbance of polypyrrole films was measured *in situ* in the course of polarization measurements.

Results and Discussion

Redox Behavior of Polypyrrole in Aqueous Solutions. Cyclic voltammograms of PPy/Pt electrodes in 0.5 mol dm^{-3} KCl or 0.5 mol dm^{-3} Na_2SO_4 are shown in Fig. 1. Well-defined peaks are seen both in the anodic and cathodic potential scans. Peak currents increase linearly with increasing sweep rate from 20 to 100 mV s^{-1}, suggesting that these peaks are due to electrochemical reactions of the film itself.[29] In the KCl solution the anodic and cathodic peaks appear at −0.35 and −0.15 V, respectively, and the peak potentials are eventually invariant with sweep rate. On the other hand, two anodic peaks appear in the Na_2SO_4 solution, though the cathodic behavior is almost the same as in the KCl solution. The first peak like a shoulder appears at −0.44 V, whereas the more marked second peak shows a tendency to shift its potential towards the positive direction with increasing sweep rate.

Cyclic voltammograms were obtained in other kinds of electrolytes. The peak potential and current of the cyclic voltammograms obtained at the sweep rate of 50 mV s^{-1} are shown in Table 1. In the case of appearence of two anodic peaks, the peak potential and current at the lower potential are given with the subscript pa-1 and those at the higher potential with pa-2. When only one anodic peak appears the values are given in the column of pa-1. As recognized from this Table, monovalent anions give one anodic peak, while divalint anions give two peaks. The peak potential and current of cathodic waves are little influenced by the kind of electrolyte anions, whereas different situations can be seen in the anodic waves.

The $E_{\text{pa-1}}$ observed in divalent anions is more negative than $E_{\text{pa-1}}$ observed in monovalent anions, but $E_{\text{pa-2}}$ is more positive than the latter. Voltammograms obtained in individual solution were not remarkably varied in the temperature range 0—80°C. It is suggested from cyclic voltammograms obtained in the presence of divalent anions that the oxidation in this case occurs in two steps: In the first step, the surface of polypyrrole film may be oxidized weakly by attracting anions onto the polymer surface; in the following step, anions may be inserted into the film and an oxidation of the film occurs simultaneously. It is seen in Table 1 that $E_{\text{pa-2}}$ depends on the kind of anions; sulfate and hydrophosphate ions give nearly the same $E_{\text{pa-2}}$ except for Li_2SO_4, whereas WO_4^{2-} gives more anodic $E_{\text{pa-2}}$. The discrepancy in the values of $E_{\text{pa-2}}$ seems to be closely related to ionic radii of the anions[30] to be incorporated into the film. The ionic radii of hydrated HPO_4^{2-} and SO_4^{2-} are *ca.* 4 Å, while that of WO_4^{2-} is *ca.* 5 Å. If this difference is serious, it is then suggested that the larger the ionic radius of anions, the more anodic potentials are needed for the incorporation of anions into the film to take place. Experiments aiming at the verification of this hypothesis is in progress and will be reported in future. As to the monovalent anions given in Table 1, the ionic radii of Cl^-, Br^-, and I^- are *ca.* 3 Å and that of ClO_4^{2-} is 3.5 Å, which are smaller than those of the

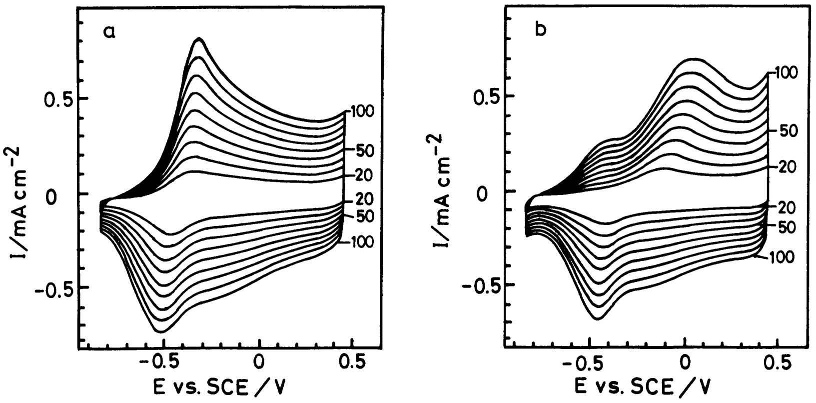


Fig. 1. Cyclic voltammograms of PPy/Pt electrodes at various sweep rates in an interval of dE/dt=10 mV s^{-1}. The number denotes the sweep rate in mV s^{-1}.
(a) in 0.5 mol dm^{-3} KCl (b) in 0.5 mol dm^{-3} Na_2SO_4

TABLE 1. PEAK POTENTIALS AND CURRENTS OF CYCLIC VOLTAMMOGRAMS OF PPy/Pt ELECTRODES OBTAINED AT dE/dt=50 mV s^{-1} IN A VARIETY OF ELECTROLYTES

Electrolyte[a)]	$E_{\text{pa-1}}$/V	$E_{\text{pa-2}}$/V	E_{pc}/V	$i_{\text{pa-1}}$/mA	$i_{\text{pa-2}}$/mA	i_{pc}/mA
0.5 M KCl	−0.31		−0.47	0.36		−0.41
0.5 M KBr	−0.32		−0.46	0.34		−0.38
0.5 M KI	−0.29		−0.56	0.41		−0.36
0.5 M $LiClO_4$	−0.31		−0.48	0.39		−0.30
0.5 M Na_2SO_4	−0.44	0.04	−0.46	0.12	0.35	−0.34
0.5 M K_2SO_4	−0.45	0.02	−0.48	0.09	0.36	−0.35
0.5 M Li_2SO_4	−0.42	0.21	−0.44	0.07	0.38	−0.41
0.5 M Na_2HPO_4	−0.42	0.02	−0.36	0.13	0.41	−0.45
0.5 M Na_2WO_4	−0.42	0.45	−0.49	0.13	0.40	−0.43

a) 1 M=1 mol dm^{-3}.

divalent ions used, and the smaller size of monovalent anions may make the peak potential less positive than the $E_{pa\text{-}2}$ obtained for the divalent anions. In connection to this hypothesis, it seems important to notice that the onset potential of film oxidation is eventually the same between the monovalent and divalent ions.

Effects of the electrolyte concentration on cyclic voltammograms were investigated in KCl solutions. According to the results obtained, the peak potentials and currents were not appreciably varied with the concentration of electrolytes as long as it was higher than 10^{-3} mol dm^{-3}. In more dilute solutions, however, the voltammograms were deformed owing to IR drop in the electrolyte.[31]

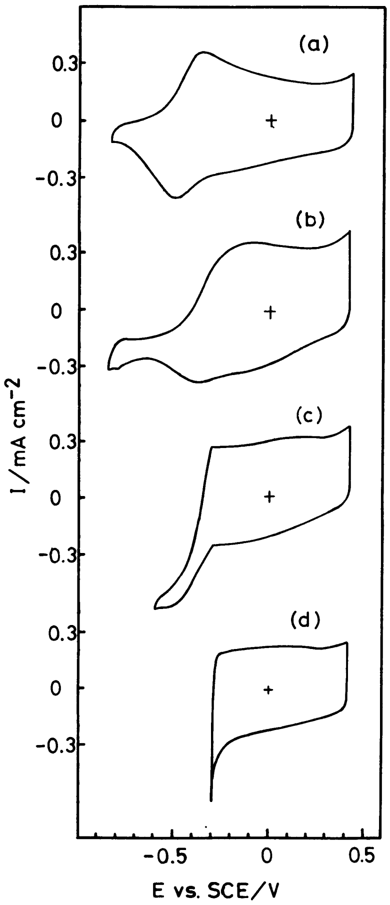


Fig. 2. Effects of solution pH on cyclic voltammograms of PPy/Pt electrodes in 1 mol dm^{-3} chloride solutions.
pH=(a) 5.5, (b) 2.0, (c) 1.5, (d) 0.6. dE/dt=50 mV s^{-1}.

Figure 2 shows effects of pH on the redox behavior of polypyrrole. The concentration of Cl^- anions was kept constant in this case. As noticed from Fig.2, the redox behavior appears in solutions having pH values higher than 2.0. In solutions of lower pH, hydrogen evolution becomes predominant, resulting in shadowing the redox behavior of polypyrrole itself.

It was reported in acetonitrile solutions[8] that the redox behavior is due to anion insertion into polypyrrole films and elimination of inserted anions from the film. In order to confirm whether or not this is true in aqueous solutions, anionic species in the film were analyzed by EPMA. The results are shown in Fig. 3. Figure 3-(a) is the spectrum of a PPy/Pt electrode prepared in the acetonitrile solution. A peak assignable to chlorine is seen, which gives the evidence that ClO_4^- is inserted into the film in the course of anodic polymerization. This electrode was kept in 0.5 mol dm^{-3} KI aqueous solution for 2 min at −0.85 V which is enough to cause the cathodic process of redox reaction, and then washed with water. Then the chlorine peak disappeared, as shown in Fig. 3-(b). When this sample was again kept for 2 min in the same solution at 0.45 V *vs.* SCE to cause the anodic process of redox reaction, peaks of iodine appeared as shown in Fig. 3-(c). Similar results of the occurrence of replacement of anionic species were obtained in other electrolytes such as KBr, Na_2SO_4, and Na_2HPO_4. Thus, it is evident that the redox reaction is accompanied with the anion transfer into and from the film.

Resistivity measurements and elemental analyses on polypyrrole films were carried out both for the original film prepared in the acetonitrile solution and for films polarized afterwards in 0.5 mol dm^{-3} KCl aqueous solution for 2 min at −0.85, 0, or 0.45 V *vs.* SCE.

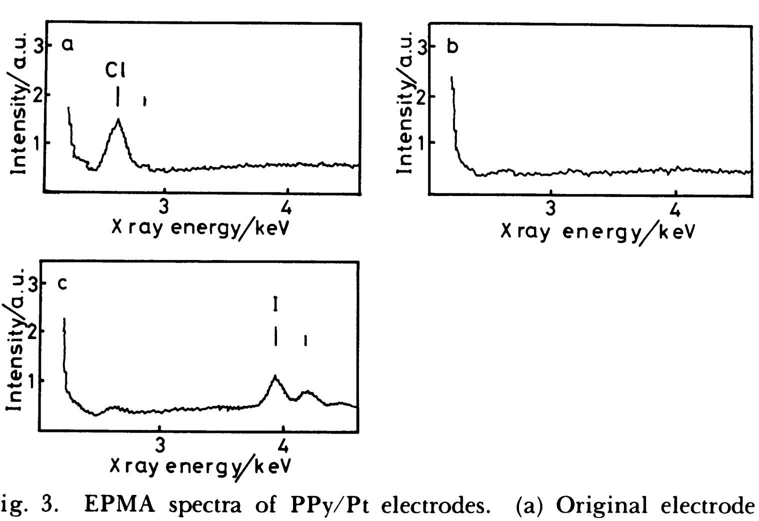


Fig. 3. EPMA spectra of PPy/Pt electrodes. (a) Original electrode prepared in 0.1 mol dm^{-3} $LiClO_4$/acetonitrile. (b) Reduced at −0.85 V *vs.* SCE in a 0.5 mol dm^{-3} KI aqueous solution for 2 min. (c) Successively oxidized at 0.45 V *vs.* SCE in the same solution for 2 min.

Prior to the measurements and analyses films were washed thoroughly with twice distilled water. The value of resistivity was found to be invariable for a few days in air. The observed results are shown in Table 2. In this table, the results of elemental analyses are given in relative molar ratio of each element to nitrogen. As expected, the original film has a low resistivity. When this film was polarized at −0.85 V in 0.5 mol dm^{-3} KCl aqueous solution, an elimination of a large part of the inserted ClO_4^- occurs and the resisitivity is enhanced. With an increase in anodic polarization, the incorporation of Cl^- anions into the film becomes appreciable as expected. Simultaneously, the resistivity becomes lowered. Judging from the results from the elemental analyses, the inserion of Cl^- is not completed at 0 V *vs.* SCE which is enough positive to the peak potential of voltammogram (see Fig. 1-(a)). It is noticed in the voltammogram that relatively large anodic currents flow in the potential region betweeen 0 and 0.45 V. At a glance, they seem to be attributable to capacitive currents,[9] but according to the results obtained that the content of Cl^- was increased by changing the polarization potential from 0 to 0.45 V *vs.*SCE, anodic oxidation of polypyrrole with insertion of anions still occurs in this potential region.

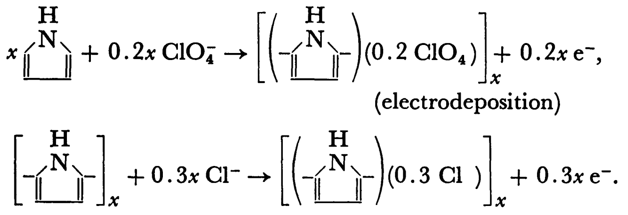
Another interesting point to be noticed is that the molar ratio of Cl^- was higher for the film polarized at 0.45 V in 0.5 mol dm^{-3} KCl than for the original film which contained the incorporated ClO_4^-. This result suggests that the charge involved in the redox process in 0.5 mol dm^{-3} KCl is higher than the excess charge retained in the film in the course of anodic polymerization of pyrrole. According to a literature,[8] 2.25 mol of electrons are involved in the electropolymerization of 1 mol of pyrrole, and 2 mol of electrons are consumed in the polymer chain formation. The extra amount of electrons is consumed in the ionization of film and the equivalent amount of anions is incorporated at that time. Judging from the results given in Table 2, our sample had an excess charge of 0.2 mol per mol of pyrrole when prepared in the acetonitrile solution, but more than 0.25 mol of electrons were found to be involved in the aqueous redox processes, as described below.

Table 2. Elemental analysis and resistivity of polypyrrole films polarized at different potentials in a 0.5 mol dm^{-3} KCl aqueous solution

E	Molar ratio to nitrogen				Resistivity
V *vs.* SCE	C	H	N	Cl	ohm cm
−0.85	4.06	3.33	1.00	0.03	3.9×10^{4}
0.00	4.03	3.28	1.00	0.15	1.2×10^{-2}
0.45	4.04	3.30	1.00	0.30	3.2×10^{-3}
Original	4.02	3.29	1.00	0.20	3.8×10^{-3}

According to the results with the original sample given in Table 2, 2.2 mol of electrons per mol of pyrrole are involved in the deposition of polypyrrole, whereas the results with the film polarized at 0.45 V suggest that 0.3 mol of eletrons can be used in the aqueous redox processes. The amount of charge consumed in the preparation of the PPy/Pt electrode was 36 mC cm^{-2}. When this sample was subjected to an anodic potential sweep from −0.8 to 0.4 V under the same conditions as chosen in the experiment shown in Fig. 1-(a), the charge of 4.8 mC cm^{-2} was consumed. Therefore, if such an assumption is made that 0.3 mol of electrons is involved in the aqueous redox processes, the charge capable of participating in the redox processes will be 36 mC cm^{-2}×0.3/2.2=4.9 mC cm^{-2}, which is in fair agreement with the charge obtained in the course of anodic sweep.

These results undoubtedly support the validity of the reactions



(electrodeposition)

(redox reaction in 0.5 mol dm^{-3} KCl)

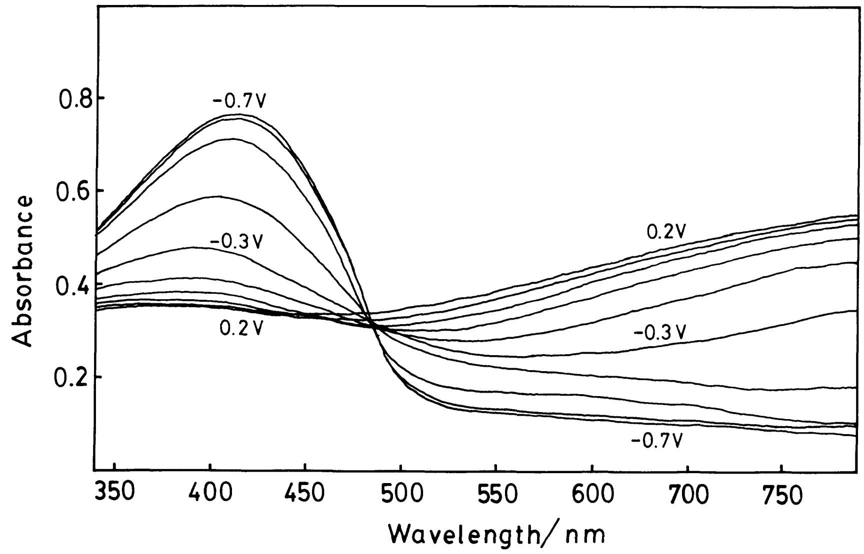


Fig. 4. Absorption spectra of a PPy/OTE electrode obtained *in situ* at different potentials in a 0.1 V interval in 0.5 mol dm^{-3} KCl.

Resistivity measurements were carried out for polypyrrole films prepared in the presence of other kinds of anions and almost the same values as shown in Table 2 were obtained. Judging from these results, electrical properties are primarily determined by charged conditions of polypyrrole which are controlled not by the kind but by the amount of incorporated anions.

Electrochromic Properties of Polypyrrole. It was reported[8,26] that the color of polypyrrole is variable with redox behavior in acetonitrile solutions. It was found that the same was true in aqueous solutions. The color change is reproducible and seems to be applicable to electrochromic display devices.

Visible absorption spectra of a PPy/OTE electrode, obtained under steady states at several different potentials, are shown in Fig. 4. Polymer films with incorporated Cl^- exhibit a brown-black color and show no appreciable absorption peaks. However, when the film is reduced, it turns yellow as recognized from an increase in absorption at wavelengths shorter than 500 nm. The absorption is thought to be assignable to the π-π^* transition of polypyrrole.[18] The coloring occurs noticeably at −0.1 V *vs.* SCE and is enhanced with an increase in cathodic potential up to −0.7 V, beyond which no appreciable increase in absorbance appears.

The change in the absorbance of polypyrrole films with electrolysis charge was pursued *in situ* in 0.5 mol dm^{-3} KCl. The films used were those prepared by anodic oxidation at 0.3 mA cm^{-2} for 2, 4, or 6 min in acetonitrile containing 0.1 mol dm^{-3} pyrrole and 0.3 mol dm^{-3} $LiClO_4$ and were initially reduced at −0.7 V in the solution for measurement. The absorbance of these films was then measured *in situ* during the course of anodic oxidation at 0.3 mA cm^{-2}. Results are given in Fig. 5-(a) as a function of the quantity of electricity consumed in the oxidation. The electrode potential values of the film in the initial and final stages (−0.7 and 0.4 V) and an intermediate stage (−0.2 V) are also given in the figure. In the final stage almost all the charges capable of being retained must have been accumulated in the film, as judged from the results given in Table 2. Fig. 5-(b) shows absorbances at these potetials as a function of the quantity of electricity consumed in the film preparation (Q_d) which is a measure of the film thickness. It is seen from this figure that the absorbance is proportional to the film thickness.

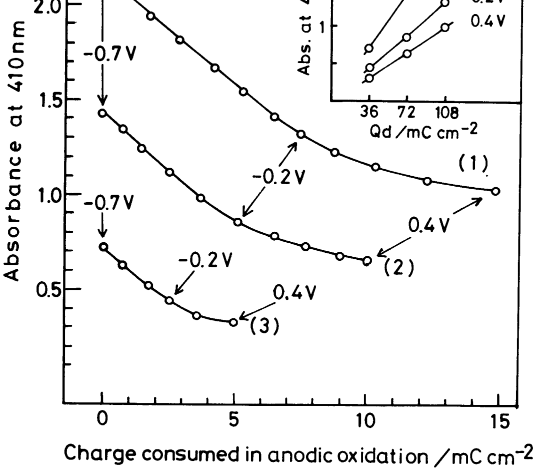


Fig. 5. (a) Absorbance at 410 nm of PPy/OTE having different film thickness as a function of the charge consumed in anodic oxidation at 0.3 mA cm^{-2} in 0.5 mol dm^{-3} KCl. (b) Absorbance at 410 nm of PPy/OTE at −0.7 V, −0.2 V, −0.4 V, in 0.5 mol dm^{-3} as a function of charge consumed for film preparation (Q_d).
The film preparation was carried out in acetonitrile containing 0.1 mol dm^{-3} pyrrole and 0.3 mol dm^{-3} $LiClO_4$ at 0.3 mA cm^{-2} for 2 min (Q=36 mC cm^{-2}) (1), for 4 min (Q_d=72 mC cm^{-2}) (2), and for 6 min (Q_d=108 mC cm^{-2}) (3).

According to Fig. 5-(a), for the films different in thickness linear relations with the same gradient are established between the absorbance and the charge consumed in the anodic oxidation of film in 0.5 mol dm^{-3} KCl as long as the electrode potential is more negative than −0.2 V. However, the rate of absorbance change becomes declined at potentials positive to −0.2 V. This behavior is in qualitatively agreement with the results shown in Fig. 4. The quantity of electricity consumed in the linear part is half the total charge capable of being stored, although with this amount of charge the absorbance at 410 nm changes by *ca.* 80% of the total change.

Relations for the linear part in Fig. 5-(a) are formulated as follows:

$$Abs = -0.119Q_c + 0.72 \text{ (for } Q_d = 36 \text{ mC cm}^{-2}\text{)}, \qquad (1)$$

$$Abs = -0.121Q_c + 1.44 \text{ (for } Q_d = 72 \text{ mC cm}^{-2}\text{)}, \qquad (2)$$

$$Abs = -0.120Q_c + 2.16 \text{ (for } Q_d = 108 \text{ mC cm}^{-2}\text{)}, \qquad (3)$$

where *Abs* denotes the absorbance at 410 nm and Q_c the charge consumed in the anodic oxidation. Since the absorbance is proportional to the quantity of electricity consumed in the film preparation, these equations may reduce to one equation

$$Abs = -0.12Q_c + 0.02Q_d. \qquad (4)$$

Since the total amount of charge capable of being stored is $0.3/2.2 \times Q_d$ as stated above and half the charge is involved in the linear portion of the absorbance change (from −0.7 to −0.2 V), the upper limit of Q_c in the above equation is then $0.07Q_d$.

Cyclic voltammograms and absorbances at 410 nm of a PPy/OTE electrode are shown in Fig. 6 for the cases of 0.5 mol dm^{-3} KCl and 0.5 mol dm^{-3} Na_2SO_4. In the KCl solution the absorbance changes quite smoothly with variation in electrode potentials and the change in absorbance shows a hysteresis in the direction of potential sweep. A similar trend of change in absorbance appears also in the Na_2SO_4 solution. In both solutions the absorbance *vs.* potential relations show inflections at the potentials where the voltammograms show their peaks. Thus, two inflections are noticed in the voltammograms obtained on the anodic potential scan in 0.5 mol dm^{-3} Na_2SO_4. These results are closely related to the fact that the change in absorbance is brought about by the redox processes of polypyrrole.

Response behavior of absorbance to pulsed poten-

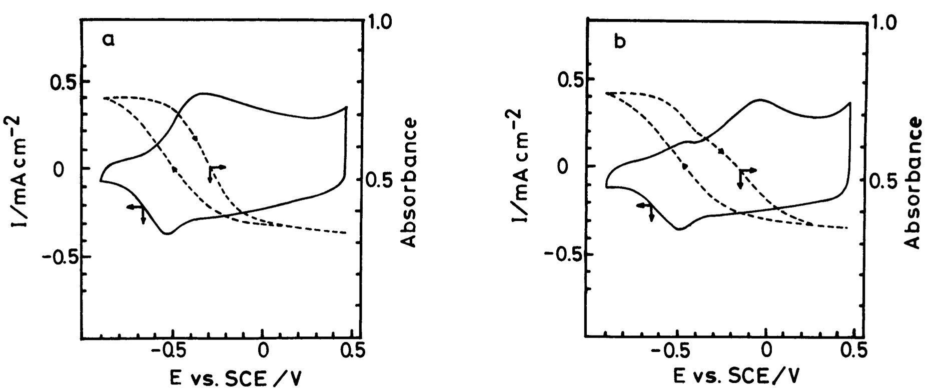


Fig. 6. Change in absorbance at 410 nm obtained *in situ* in the measurements of cyclic voltammograms. (a) in 0.5 mol dm^{-3} KCl (b) in 0.5 mol dm^{-3} Na_2SO_4. dE/dt=50 mV s^{-1}.

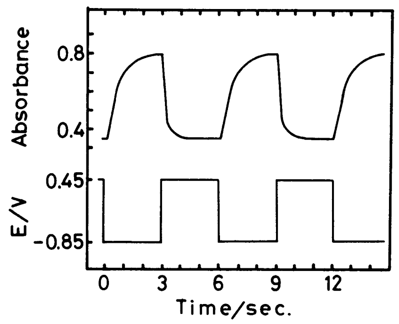


Fig. 7. Response behaviors of the absorbance change of the PPy/OTE electrode to repeated potential pulses of −0.85 V and 0.45 V *vs.* SCE in 0.5 mol dm^{-3} KCl. Absorbance was measured at 410 nm.

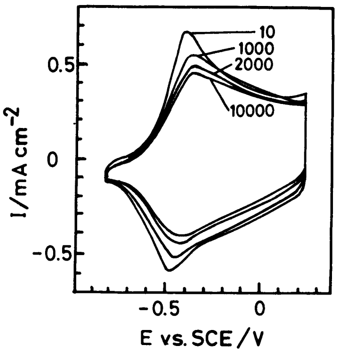


Fig. 8. Change in cyclic voltammograms of PPy/Pt electrode with the number of potential sweep cycles in 0.5 mol dm^{-3} KCl. The number in the figure denotes the cycle number. dE/dt=50 mV s^{-1}.

tials were investigated in 0.5 mol dm^{-3} KCl at 410 nm with a potential pulse of −0.85 or 0.45 V. Results are shown in Fig. 7. The response to the anodic pulse is faster than that to the cathodic one. The slowness of the cathodic response must be related to the fact that the polymer becomes resistive on application of −0.85 V. However, improvement of the response will be possible by appropriate choice of the film thickness, electrode area, and conductive substrate. Stability tests on the redox processes of polypyrrole were investigated in 0.5 mol dm^{-3} KCl with the PPy/Pt electrode. Results are shown in Fig. 8. The shape of voltammograms taken at the sweep rate of 100 mV s^{-1} becomes ill-defined with an increase in potential sweep cycles, but no appreciable change in film color is noticed to the naked eye during 10000 potential sweeps. These results suggest that polypyrrole is a promising candidate as a material for electrochromic display devices.

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