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Electrochromism of Polyaniline Film Prepared by Electrochemical Polymerization

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ABSTRACT: Polyaniline films were prepared by galvanostatic oxidation of aniline in 0.1 M H_2SO_4 aqueous solution, and their electrochromic properties were investigated by cyclic voltammetry, spectroelectrochemical measurements, and ESR spectroscopy. Polyaniline films showed multiple color changes (transparent yellow–green–blue) depending on the electrochemical reactions in the potential range −0.2 to 0.8 V vs. SCE. The cyclic voltammogram of a polyaniline film in 0.1 M H_2SO_4 aqueous solution showed two anodic peaks at 0.2 and 0.7 V, together with large capacitive background currents. The color of polyaniline films changed from transparent yellow to green at the anodic peak around 0.2 V and gradually changed from green to dark blue at potentials higher than 0.3 V. The color change from transparent yellow to green is due to the formation of Würster-type radical cations at 0.2 V, and that from green to blue is due to the formation of a diimine structure and doped states with SO_4^{2-} in the polymer at potentials above 0.3 V. The deterioration of electrochromic properties is caused by hydrolysis of the diimine structure formed by oxidation at 0.7 V.

Introduction

Electropolymerized polyaniline films[1-14] have received considerable attention recently owing to their electrical conductivity and wide application in electrochemistry.[15-17] The electrochromic properties of polyaniline films have been investigated for applications in display devices. It has been reported that polyaniline-coated electrodes show reversible color changes (transparent yellow–green–dark blue–black), depending on potential, between −0.2 and 1.0 V vs. saturated calomel electrode (SCE).[18-20] It has been suggested that these color changes are caused by proton addition/elimination reactions[1,2] and anion insertion/elimination reactions.[1,8,13,15,19] However, further investigation is required to clarify the assignment of current peaks in the cyclic voltammograms and the electrochromic mechanism.

In this paper we discuss the electrochromic properties of polyaniline films and the electrochemical reactions which cause the electrochromism on the basis of cyclic voltammograms, electronic absorption spectra, and ESR spectra.

Experimental Section

Materials. Aniline was purified by vacuum distillation. The surface of the Pt electrode was polished with 0.3-μm Al_2O_3 powder and then washed with deionized water and trichloroethylene. For spectroelectrochemical measurements, a tin oxide coated glass was employed as an optically transparent electrode (OTE). Polyaniline films were deposited on these electrodes by galvanostatic oxidation of aniline in 0.1 M H_2SO_4–0.1 M aniline aqueous solutions or by a potential sweep method. The molecular weights of the polyaniline films are about 10 000.[21] Diphenylamine and *p*-phenylenediamine (TOKYO KASEI) were used as monomer model compounds.

Measurements. Cyclic voltammograms were obtained with a potentiostat/galvanostat (HOKUTO HA-201) and a function generator (HOKUTO HB-103). Electrochemical potentials were recorded vs. SCE. Electronic absorption spectra of polyaniline films coated on the OTE were measured in situ in a quartz cell with 0.1 M H_2SO_4 aqueous solution by a spectrophotometer (Shimazu UV-210). ESR (electron spin resonance) measurements were carried out with a JEOL PE-1X-type ESR spectrometer. The *g* values were determined by using the signals of DPPH (1,1-diphenyl-2-picrylhydrazyl free radical) and Mn^{2+} in MgO as standards.

Results and Discussion

Cyclic Voltammetry. Cyclic voltammograms of the polyaniline-coated Pt electrode in 0.1 M H_2SO_4 aqueous solution are shown in Figure 1. The polyaniline film was prepared by a galvanostatic method at 0.01 mA/cm^2, and the electrode potential was almost constant at 0.6 V during the electrochemical polymerization. In Figure 1 the first cycle shows two sharp anodic peaks at 0.2 and 0.7 V and a weak anodic peak at 0.45 V. With an increase in the electrode potential, the color of the polyaniline film changed from transparent yellow to green at 0.2 V and from green to blue at higher potentials, becoming blue–violet at 0.8 V. These color changes were reversed with decreasing electrode potential. The electrochromic behavior was stable, and there was essentially no change in the voltammogram's shape after 2000 cycles if the potential sweep range was restricted between −0.2 and 0.3 V. However, when the potential sweep range was between −0.2 and 0.8 V, the shape of the voltammogram changed with increasing cycle number as shown in Figure 1; the anodic currents at 0.2 and 0.7 V decreased and that at 0.45 V increased. The reversibility of color change was gradually lost with an increase of the anodic peak at 0.45 V, and the polyaniline film finally became dark blue. It has been reported that the degradation of polyaniline films, which involves the formation of benzoquinone, takes place at potentials higher than 0.7 V.[20] In that report, the anodic and cathodic peaks around 0.45 V were assigned to the oxidation and reduction of a quinoid structure.

Cyclic voltammograms for electropolymerization of polyaniline on a Pt electrode by a potential sweep method between −0.2 and 1.2 V vs. SCE are shown in Figure 2. Typical current peaks,[8] i.e., oxidation of aniline at 0.9 V for the first cycle and three sets of peaks which suggest the electrochemical activity of polyaniline film, are shown. Judging from observations on the deterioration of the polyaniline film, the peaks near 0.4 V in Figure 2 must be caused by a potential sweep to the higher potential, 1.2 V. In the following, we discuss the mechanism of the electrochromic behavior using polyaniline film prepared by the galvanostatic method in order to avoid the complexities caused by deterioration.

In Figure 1, large capacitive background currents appear in the potential range 0.3–0.8 V together with the anodic and cathodic peaks near 0.7 V. It has been pointed out that the capacitive currents are caused by electrochemical reactions involving the insertion and elimination of anions.[19]

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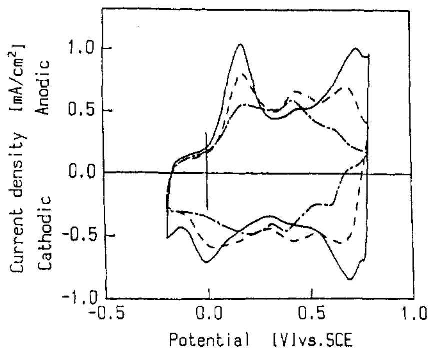


Figure 1. Cyclic voltammograms of the polyaniline-coated Pt electrode in 0.1 M H_2SO_4 aqueous solution: (—) first scan, (- - -) after 20 cycles, (– - –) after 50 cycles; sweep rate, 60 s/V.

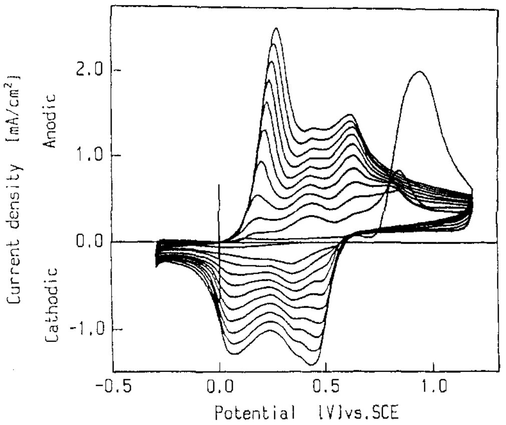
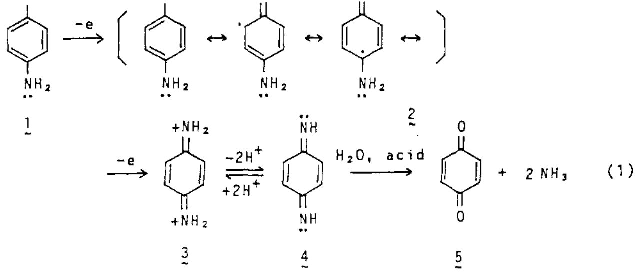


Figure 2. Cyclic voltammograms for electropolymerization of aniline in 0.1 M aniline–0.1 M H_2SO_4 aqueous solution: sweep rate, 60 s/V.

In the following sections, we discuss these current peaks and the mechanism of polyaniline's electrochromism on the basis of cyclic voltammograms, absorption spectra, and ESR spectra.

Comparison with Monomer Model. We selected diphenylamine and *p*-phenylenediamine as monomer model compounds for polyaniline in measurements of cyclic voltammograms. Polyaniline films are known to have an emeraldine-like structure in the polymer backbone.[2,5] Although there are differences between polyaniline and the model compounds in molecular weight and length of resonance, we can get effective information on the assignment of the anodic and cathodic peaks for polyaniline. The cyclic voltammogram of diphenylamine in 0.1 M H_2SO_4 aqueous solution shows one oxidation peak current at 0.7 V (Figure 3). The cyclic voltammogram of *p*-phenylenediamine in Na_2SO_4 aqueous solution shows two oxidation peaks at 0.4 and 0.95 V (Figure 3). Two such oxidation peaks are reported for phenylenediamines in CH_3CN–$NaClO_4$ medium with pyridine.[5] It is known that *p*-phenylenediamine is converted to a diimine by two-step oxidation[22,23] (eq 1). The one-electron oxidation product, i.e., the radical cation of *p*-phenylenediamine, is stable because of resonance 2. In contrast, the two-electron oxidation product, diimine 4, is easily hydrolyzed by inorganic acids and converted to benzoquinone and ammonia. The radical cations of aromatic diamines, such as *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine, are known to be fairly stable, and these radical cations are called Würster's salts.[23-27]



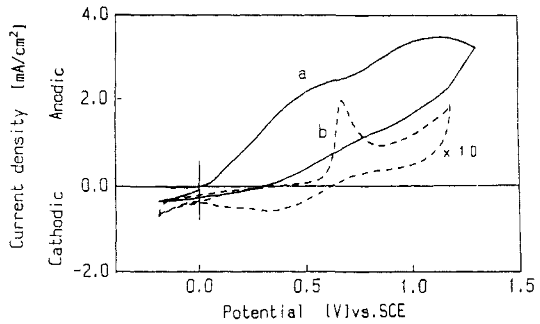


Figure 3. Cyclic voltammograms of model compounds: (a) *p*-phenylenediamine, (b) diphenylamine.

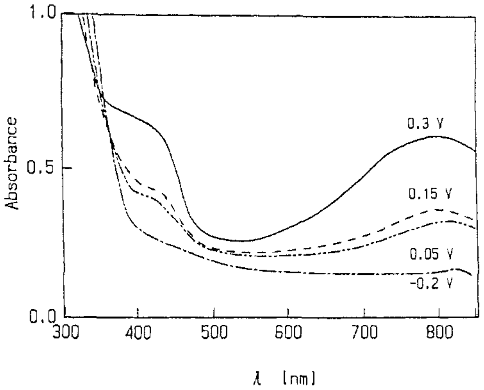


Figure 4. Absorption spectra of the polyaniline-coated OTE in 0.1 M H_2SO_4 aqueous solution.

It has been reported that a diimine structure in the polyaniline backbone is formed by one-step oxidation at 0.2 V vs. SCE.[1,8,13,15,19] However, in view of the results for the monomer model, it appears that the oxidation of polyaniline occurs in two steps and that there are two species, a stable radical cation and an unstable dication (diimine) in the oxidation. Furthermore, if a diimine structure in the polyaniline backbone is formed by a one-step oxidation at 0.2 V, the reported stability of electrochromism, which showed no deterioration up to 10^6 cycles between −0.2 and 0.6 V,[18] could not occur because of the instability of the diimine structure.

In the next section we discuss the electrochromic species taking this electrochemical oxidation mechanism into consideration.

Spectroelectrochemical Measurements. Electronic absorption spectra of polyaniline-coated OTE were measured in situ at various potentials (Figures 4 and 5). Figure 4 shows the electronic absorption spectra in the potential range −0.2 to 0.3 V vs. SCE. The absorbances at 430 and 810 nm increase with increasing electrode potential. In the potential range −0.2 to 0.3 V, the changes in the absorption spectra are uniform. However, in the potential range 0.3–0.8 V, the absorption spectra change (Figure 5); the absorbance at 430 nm decreases and the absorption maximum at 810 nm shifts continuously to 610 nm with a potential sweep from 0.3 to 0.8 V. At potentials higher than 0.3 V, the changes in the absorption spectra are complicated. We show the dependence of the absorption maximum, λ_{max}, at the longer wavelength (810 nm

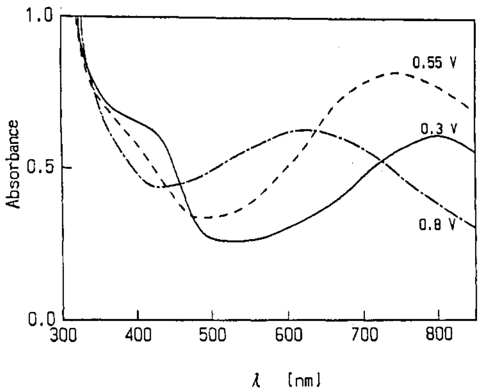


Figure 5. Absorption spectra of the polyaniline-coated OTE in 0.1 M H_2SO_4 aqueous solution.

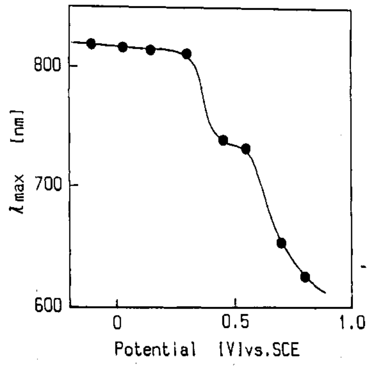


Figure 6. Dependence of λ_{max} of polyaniline-coated OTE on the electrode potential.

at 0.2 V) on the electrode potential in Figure 6. Between −0.2 and 0.3 V, λ_{max} is almost constant at 810 nm. At potentials higher than 0.3 V, however, λ_{max} suddenly drops, showing a shoulder at around 0.5 V. The potentials at which spectral changes occur correspond to peak potentials in the cyclic voltammograms (Figure 1). An anodic peak appears between −0.2 and 0.3 V, and in this potential range, λ_{max} is almost constant. A second weak anodic peak appears between 0.3 and 0.55 V, and at 0.3 V, λ_{max} suddenly drops to 730 nm and shows a plateau in the potential range at around 0.45 V. A third anodic peak appears between 0.55 and 0.8 V, and at 0.55 V, λ_{max} begins to drop again.

The spectral shape in Figure 4, a shoulder at 400 nm and a broad band at longer wavelengths, resembles that for Würster-type radical cations.[23-27] The formation of this radical cation as an intermediate species in the two-step oxidation of polyaniline is expected from results with monomer model compounds. The absorption maximum at 810 nm shows a red shift compared to monomer model compounds; the Würster's salt of *p*-phenylenediamine shows λ_{max} at 460 nm and that of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine shows λ_{max} at 620 nm.[23-27] Such a red shift of λ_{max} in polyaniline must be caused by the stabilization of radical cations in the polymer chain. In the case of monomer models, it is known that the substitution of H on nitrogen by a methyl group, which has an electron-releasing effect, induces a red shift.[23,29] In the case of polyaniline, the radical cation must be stabilized by electron resonance in the polymer chain.

The shift of λ_{max} in Figure 5 suggests that a significant change in the electronic energy level is induced by the oxidation of polyaniline in the potential range 0.3–0.8 V. The continuity of the shift (no appearance of an isosbestic point) suggests that the change in the electronic state takes place over the entire polymer chain.

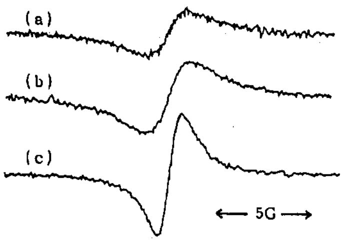


Figure 7. ESR spectral changes after polarization (a) at −0.2 V for 5 min, (b) at 0.3 V for 5 min, and (c) at 0.8 V for 5 min.

Electron Spin Resonance Spectroscopy. From the above results, the following mechanism is proposed. In the first step of the oxidation of polyaniline, Würster-type radical cations are formed, and in the second step, diimine structures are formed in the polymer backbone. In this section we examine this proposal by ESR measurements; the radical cation is paramagnetic and the diimine is diamagnetic.

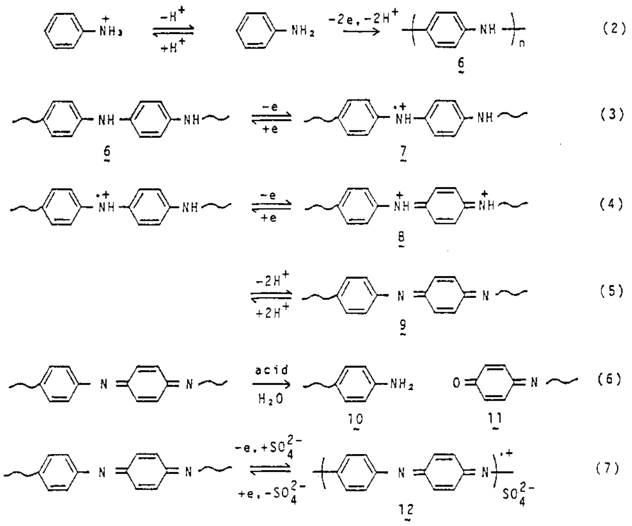
Polyaniline-coated (6.2×10^{-6} mol) Pt electrodes ($3 \times 0.2 \times 2$ cm) were prepared by the galvanostatic method at 0.01 mA/cm^2 and polarized at a given potential for 5 min, and the ESR measurements were then carried out. The ESR spectra of polyaniline (Figure 7) show a single peak with a *g* value of 2.0036, which is almost the same as that of DPPH. The *g* value is not dependent on the polarization potential of the polyaniline-coated electrode and indicates that the radical site is on nitrogen.

The change in radical concentration with polarization can be estimated by comparison of the areas under the integral curves of the ESR signals (Figure 7). During the first oxidation step (at 0.2 V in Figure 1 and the change from (a) to (b) in Figure 7), the radical concentration becomes 2.5 times greater. This increase confirms the formation of radical cations, which are assigned a stable Würster-type structure. During the second oxidation step (at 0.7 V in Figure 1 and the change from (b) to (c) in Figure 7), the radical concentration (c) decreases to 64% of (b): the broad ESR signal has a larger integral area than the sharp ESR signal, while the amplitude of differential plots is almost the same. This decrease in radical concentration confirms the formation of the diimine structure in polyaniline during the second oxidation step.

In Figure 7, (a) shows the existence of radical species at −0.2 V, where polyaniline exists in a reduced state. This is explained as follows: with an increase in film thickness, the reversibility of the color change of polyaniline film decreases, and even at −0.2 V the film shows considerable blue–green color. This result is due to radical species trapped at deep sites away from the surface of the polyaniline-coated electrode.

Another notable feature of the ESR spectra is the change in peak-to-peak width ΔH_{msl} (gauss). The spectra of (a) and (b) in Figure 7 show almost the same ΔH_{msl} (2.18 G) and that of (c) shows a different ΔH_{msl} (1.25 G). This suggests that another type of radical cation is formed in the second oxidation step. Now we point out that large capacitive background currents appear in the cyclic voltammogram in Figure 1; these capacitive currents are attributed to anion insertion/elimination in the electrochemical reaction.[9,12,17] The change in the peak-to-peak width, ΔH_{msl}, must reflect the doping of polyaniline by inserted SO_4^{2-}. In such a doped state, the mobility of electrons in polyaniline is considerable judging from its electrical conductivity. The narrowing of the ESR spectra may be caused by "electron-transfer narrowing".[28]

Mechanism of Polyaniline's Electrochromism. We propose a mechanism for polyaniline's oxidation/reduction



as expressed by eq 2–7. The polyaniline structure **6** is formed by a two-electron reaction of aniline (eq 2).[2,4–6] In more acidic media, a large portion of the amine groups in the polymer must be protonated with SO_4^{2-}. However, express the polyaniline structure as **6** to simplify the following scheme.

Judging from the reaction of *p*-phenylenediamine, the first oxidation step of **6** is expressed by eq 3. In this oxidation, a stable Würster-type radical cation, **7**, is formed. In *p*-phenylenediamine, this reaction occurs at ca. 0.4 V (Figure 3), whereas in polyaniline the anodic peak at 0.2 V is assigned to the formation of **7**. The shift to lower potential may be due to the stabilization of the radical cation by resonance in the polyaniline structure. The second step of the oxidation forms dication **8** (eq 4), which is immediately converted to diimine **9** (eq 5). The anodic peak current caused by the reaction of eq 4 appears at 0.7 V for polyaniline. Diimine **9** is easily hydrolyzed by acid and converted to the quinoid form **11** (eq 6). This hydrolysis must be more predominant at higher potentials. This is the reason that the anodic peak at 0.4 V (Figure 1), which is assigned to the oxidation of a quinoid structure, appears when the potential sweep extends to 0.8 V in the cyclic voltammograms.

It has been reported that the electrochemical activities of polyaniline films decrease with increasing solution pH.[1,19] This is explained by considering the stability of radical cation **7** as a function of pH; the stability of radical cations of aniline derivatives increases in more acidic media.[17,29,30]

Together with the oxidation of eq 6, SO_4^{2-} insertion/elimination (doping-undoping) takes place (eq 7). Elemental analysis shows that polyaniline prepared by a potentiostatic method at 0.8 V has about one SO_4^{2-} anion per 12 unit.

We explain the electrochromic behavior of polyaniline films as follows. It is known that Würster-type radical cations produced by oxidation of aromatic diamines show an absorption shoulder near 400 nm and a broad absorption at longer wavelengths.[23,27] The absorption shoulder at 430 nm and the broad absorption around 800 nm (Figure 4) are assigned to the the radical cation **7**. The absorbance of **7** (Figure 4) increases with an increase of oxidation current at 0.2 V (Figure 1). The decrease in the absorbance at 430 nm at potentials higher than 0.3 V (Figure 5) reflects a decrease in the concentration of **7** due to its conversion into dication **8**. Diimine structure **9** is formed, and the doped state **12** is formed by the insertion of SO_4^{2-} anion. The absorptions of diimine **9** and the doped state **12** gradually increase with a potential sweep toward 0.8 V, and the absorption overlaps the absorption of **7**. This spectral overlapping causes the shift of λ_{max} shown in Figures 5 and 6.

In conclusion, the color change from transparent yellow to green is due to the formation of Würster-type radical cations by the oxidation at 0.2 V, and that from green to blue is due to the formation of a diimine structure and the doped state at potentials higher than 0.3 V. The deterioration of electrochromic properties is caused by the hydrolysis of the diimine structure formed by oxidation at 0.7 V.

Registry No. Polybutadiene, 106-50-3; **6**, 25233-30-1; diphenylamine, 122-39-4.

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