Comparative Study of Redox Reactions of Polyaniline Films in Aqueous and Nonaqueous Solutions

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ABSTRACT: Electrochemical redox reactions of polyaniline films were investigated in aqueous and nonaqueous solutions, and the mechanism was discussed on the basis of comparison of those reactions in aqueous and nonaqueous media. The polyaniline films were prepared under two different conditions, at a constant current density in an aqueous solution (0.1 M aniline–0.2 M $HClO_4$ aqueous solution) and at a constant potential in a nonaqueous solution (0.1 M aniline–0.1 M $LiClO_4$ acetonitrile solution). Cyclic voltammograms, in situ absorption spectra, conductivity, and spin density were measured for three different cases: redox reactions (i) in aqueous media using polyaniline films prepared in aqueous solution, (ii) in nonaqueous media using polyaniline films prepared in aqueous solution, and (iii) in nonaqueous media using polyaniline films prepared in nonaqueous solution. Cyclic voltammograms showed two pairs of redox peaks in all cases. Even in aprotic solvent, the redox reaction at a lower potential region was quite reproducible on repeated cycles. In situ absorption spectra and ESR spectra indicated the formation of radical cations at the first anodic peak for all cases. The conductivity of polyaniline reached a maximum at the first oxidation peak and decreased by the second oxidation. The conductivity change was correlated with that of the spin density calculated from ESR spectra. The results were similar in both aqueous and nonaqueous solutions. The potential dependence of in situ absorption spectra and conductivity was discussed in terms of a polaron model.

Introduction

Polyaniline films prepared by electrochemical polymerization show high conductivity and electrochemical activity.[1-3] These properties provide many application fields, especially, secondary lithium batteries using polyaniline have received considerable attention recently.[4,5] In a nonaqueous lithium battery, polyanilines as an active material were prepared in aqueous solution. For the improvement of the battery, it is important to reveal electrochemical redox reactions in both aqueous and nonaqueous media.

The mechanism of electrochemical redox reaction of polyaniline has been investigated mainly in aqueous media.[1-3,6-8] In those studies, the effect of pH on the electrochemical activity of polyaniline was emphasized. The outline of the redox reactions and the appearance of the conductivity of polyaniline films are as follows: First the polyamine form is oxidized by a transfer of one proton and one electron and then the diimine structure is formed.[2,3,6-8] The reaction is a so-called proton addition/elimination reaction.[2,7] The conductivity is caused by the addition of protons to the diimine structure. The protonation induces semiquinone radical cations by disproportionation.[9,10] As another explanation for the conductivity, the insertion of anions into the diimine structure (anion doping) has been proposed.[7,8]

On the other hand, the electrochemical redox reaction mechanism of polyaniline in aprotic solution is not so confirmed. In aprotic media, the reversible proton addition/elimination reaction cannot occur, and so another mechanism must be proposed for redox reactions and the conductivity of polyanilines.

In a previous paper,[11] we proposed a mechanism involving the formation of a radical cation instead of proton addition/elimination reactions. We assigned the electrochemical redox reactions of polyaniline films in 0.1 M H_2SO_4 aqueous solution as follows: radical cations at the N-position are formed by the first oxidation at 0.2 V versus SCE and diimine structures are formed by the second oxidation at 0.7 V versus SCE. Recently, Genies et al.[12] and McManus et al.[13] proposed similar mechanisms.

Comparative study of electrochemical redox reactions of polyaniline is a useful method to judge the effect of proton addition/elimination reactions. If protons play a dominant role in redox reactions and the appearance of the conductivity of polyaniline films in aqueous solution, quite different results must be obtained by the measurements in nonaqueous solutions. Whereas if the same reactions occur in both protonic and aprotic solutions, another mechanism such as the formation of radical cations must be considered. In this paper, we will discuss the mechanism for three cases: redox reactions (i) in aqueous media using polyaniline films prepared in aqueous solution, (ii) in nonaqueous media using polyaniline films prepared in aqueous solution, and (iii) in nonaqueous media using polyaniline films prepared in nonaqueous solution.

In some cases, the conductivity of polyanilines has been explained by the bipolaron model.[14] This is based on the independence between the electric conductivity of the polyaniline films and the spin density.[15] In this study, we investigated the correlation between the conductivity and spin density as a function of polarized potential in both aqueous and nonaqueous solutions.

Experimental Section

Materials. Aniline was purified by vacuum distillation. Acetonitrile was dehydrated with diphosphorus pentaoxide and then distilled. Polyaniline films were prepared by the following two procedures: (i) electrochemical polymerization in a 0.1 M aniline–0.2 M $HClO_4$ aqueous solution at a constant current density of 0.02 mA/cm^2 for 5 h; (ii) electrochemical polymerization in a 0.1 M aniline–0.1 M $LiClO_4$ acetonitrile solution at a constant potential of 2.0 V versus SCE for 1 h. In the aqueous system, the solution was degassed and filled with Ar gas before electrolysis. In the nonaqueous system, Ar gas was bubbled into the solution. Pt-coated glass was used for in situ absorption spectrometry as an optically transparent electrode (OTE). For other measurements, a Pt electrode was used. The surface of the Pt electrode was polished with 0.3-μm Al_2O_3 powder and then washed with deionized water, ethanol, and trichloroethylene. Nigrosine

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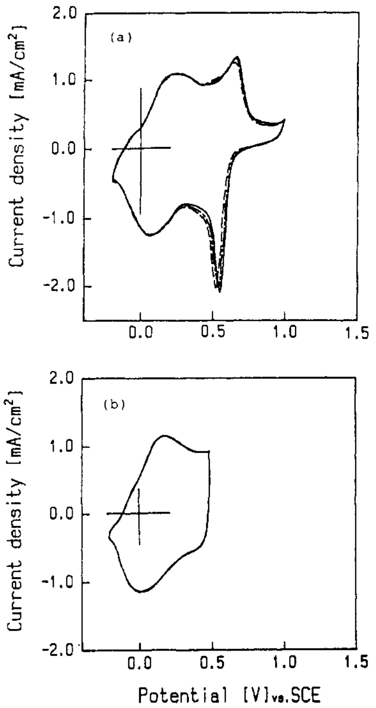

Figure 1. Cyclic voltammograms of polyaniline films in 0.2 M $HClO_4$ aqueous solution at 60 s/V. Preparation conditions: galvanostatic oxidation at 0.02 mA/cm² in a 0.1 M aniline–0.2 M $HClO_4$ aqueous solution for 5 h. (a) Potential was scanned in the range −0.2 to 1.0 V. (b) Potential was scanned in the range 0.2 to 0.5 V.

(Aldrich) was used as an octamer model having a diimine structure.

Measurements. Cyclic voltammograms of polyaniline-coated electrodes were obtained with a potentiostat/galvanostat (Hokuto HA-201) and a function generator (Hokuto HB-103). Electrochemical potentials were recorded versus SCE. In situ absorption spectra were measured in a quartz cell with electrolyte solutions by a spectrometer (Jasco Ubest-30). After the polarization at a certain potential for 5 min, spectra were measured. These measurements were carried out from lower potential to higher potential. ESR measurements were made by using a Varian E-4 spectrometer. The *g* value and spin density were determined from the signal of DPPH (1,1-diphenyl-2-picrylhydrazyl) free radicals as a standard. Polyaniline films were polarized at various potentials and then collected and diluted to 0.5% in KBr as a sample for ESR measurements. The conductivity of polyanilines was measured by a two-probe method. Measurement by a four-probe method was difficult because polyaniline films on a Pt electrode were quite thin and conduction through the Pt is not negligible. Polyaniline powders were loaded into glass capillaries of 1-mm diameter and then either side of the packed polymer in the capillary was connected to the lead wires by Ag paste. All these measurements were carried out at 22 °C.

Results

Cyclic Voltammetry. Cyclic voltammograms of polyaniline films in aqueous and nonaqueous solutions are shown in Figures 1–3. These were measured with successive scans. Figure 1 shows those of a polyaniline-coated Pt electrode in 0.2 M $HClO_4$ aqueous solution. The polyaniline-coated Pt electrode was prepared in a 0.1 M aniline–0.2 $HClO_4$ aqueous solution. Figure 2 shows those in a 0.1 M $LiClO_4$ acetonitrile solution. The polyaniline-coated Pt electrode was also prepared in a 0.1 M aniline–0.2 $HClO_4$ aqueous solution. Two pairs of redox peaks reported before[2,3,7] appear in Figure 1, and similar redox peaks also appear in nonaqueous solution as shown in Figure 2. In the following, we call the oxidation at the lower anodic peak the first oxidation and that at the higher anodic peak the second oxidation. Similarly, we call the redox reaction at the lower potential region the first redox reaction and that at the higher potential region the second redox reaction. The second anodic peak in the higher potential region shows a difference between aqueous and nonaqueous solutions. In Figure 1a, the second anodic peak at 0.7 V is quite reversible in protonic media. On the other hand, the second anodic peak at 1.2 V is irreversible in aprotic media as shown in Figure 2a. These results suggest that protons participate in the second oxidation reaction. Contrary to this, the first anodic peak at the

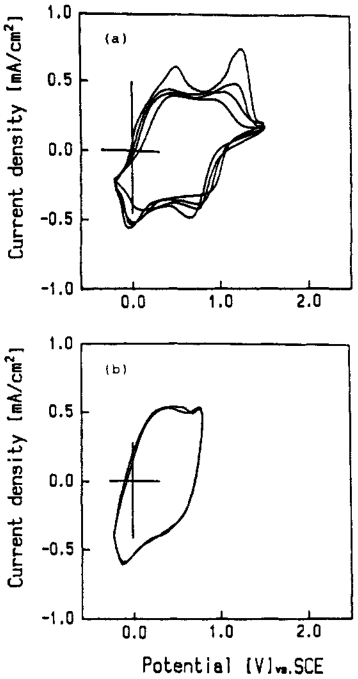

Figure 2. Cyclic voltammograms of polyaniline films in a 0.1 M $LiClO_4$ acetonitrile solution at 60 s/V. Preparation conditions: galvanostatic oxidation at 0.02 mA/cm² in a 0.1 M aniline–0.2 M $HClO_4$ aqueous solution for 5 h. (a) Potential was scanned in the range −0.2 to 1.5 V. (b) Potential was scanned in the range −0.2 to 0.8 V.

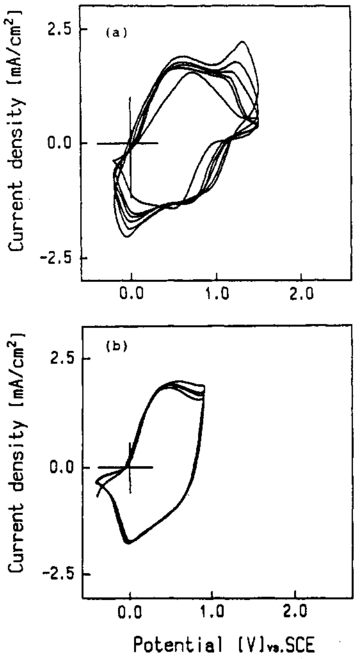

Figure 3. Cyclic voltammograms of polyaniline films in a 0.1 M $LiClO_4$ acetonitrile solution at 60 s/V. Preparation conditions: potentiostatic oxidation at 2.0 V in a 0.1 M aniline–0.1 M $LiClO_4$ acetonitrile solution for 1 h. (a) Potential was scanned in the range −0.2 to 1.5 V. (b) Potential was scanned in the range of −0.2 to 0.8 V.

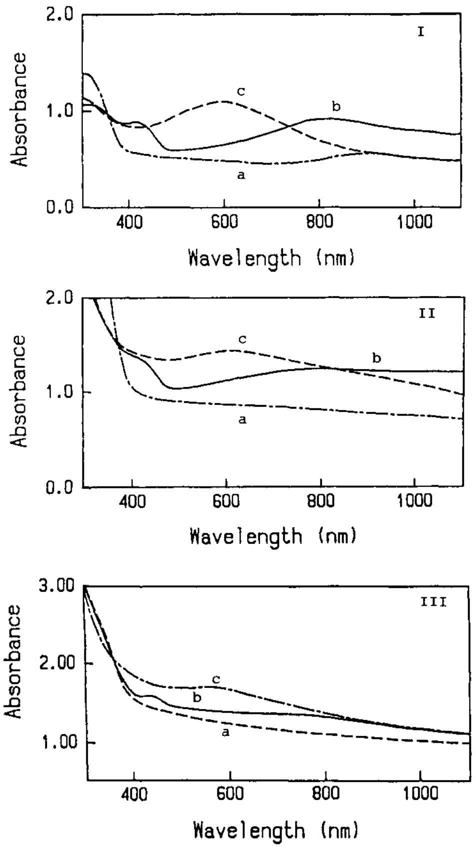

Figure 4. In situ absorption spectra of polyaniline-coated OTE at various potentials. (I) Polyaniline film prepared by galvanostatic oxidation at 0.02 mA/cm^2 in a 0.1 M aniline–0.2 M $HClO_4$ aqueous solution for 5 h, which is polarized in a 0.2 M $HClO_4$ aqueous solution: (a) −0.2 V; (b) 0.2 V; (c) 1.0 V. (II) Polyaniline film prepared by galvanostatic oxidation at 0.02 mA/cm^2 in a 0.1 M aniline–0.2 M $HClO_4$ aqueous solution for 5 h, which is polarized in a 0.1 M $LiClO_4$ acetonitrile solution: (a) −0.2 V; (b) 0.4 V; (c) 1.5 V. (III) Polyaniline film prepared by potentiostatic oxidation at 2.0 V in a 0.1 M aniline–0.1 M $LiClO_4$ acetonitrile solution for 1 h, which is polarized in a 0.1 M $LiClO_4$ acetonitrile solution: (a) −0.2 V; (b) 0.4 V; (c) 1.5 V.

lower potential region is quite reversible in both Figures 1b and 2b. This result suggests that the oxidation reaction at the first anodic peak does not involve the proton-transfer process.

Polyaniline films prepared in aqueous media exist in a protonated structure. These protons may affect electrochemical redox reactions of polyaniline films in aprotic media. Therefore, we tried to prepare a polyaniline film in aprotic media. At the beginning, we electrolyzed a 0.1 M aniline–0.1 M $LiClO_4$ acetonitrile solution by galvanostatic oxidation at a constant current of 0.02 mA/cm^2. In this case, blue oxidized products were eluted and very little polyaniline film was obtained on the Pt electrode. GPC analysis showed that these blue species were oligomers with a molecular weight of about 1000. These molecular weights correspond to those of emeraldine, nigrosine, etc. However, potentiostatic electrolysis at 2.0 V gave a polyaniline film on the electrode. In the electrolysis, polyaniline films were formed on the electrode with the formation of eluted blue species. The film formation is due to the subsequent oxidation of the oligomer species at the higher potential. Polyaniline films prepared by this procedure do not involve a protonated structure. Therefore, in the redox reactions of such polyaniline films in aprotic media, the affect of protons is completely excluded. Figure 3 shows cyclic voltammograms of the system. Two pairs of redox peaks appear in a manner similar to that in Figures 1 and 2. The first anodic peak at 0.3 V is quite reversible as shown Figure 3b; whereas the second anodic peak at 1.2 V in Figure 3a is irreversible. This irreversibility is a characteristic of redox reactions of polyaniline films in aprotic media.

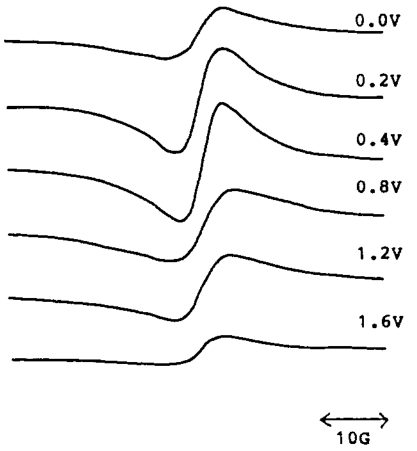

Figure 5. ESR spectra of polyaniline polarized at various potentials in a 0.1 M $LiClO_4$ acetonitrile solution. Preparation conditions: galvanostatic oxidation at 0.5 mA/cm^2 in a 0.1 M aniline–0.2 M $HClO_4$ aqueous solution.

In Situ Absorption Spectroscopy. In situ absorption spectra of polyaniline-coated OTE are compared in Figure 4. Figure 4I is similar to the absorption spectra of polyaniline films in aqueous solutions previously reported.[7,11,13] Absorption spectra in nonaqueous solution are shown in Figure 4II,III. Figure 4II shows those of polyaniline-coated OTE prepared in a 0.1 M aniline–0.2 M $HClO_4$ aqueous solution. Figure 4III shows those of polyaniline-coated OTE prepared in a 0.1 M aniline–0.1 M $LiClO_4$ acetonitrile solution. In these figures, absorption spectra were measured at three representative potentials. These absorption spectra were measured in the order from a to c. In the first spectrum, a polyaniline-coated OTE was sufficiently reduced at the lower potential than that of the first anodic peak. In the second spectrum, b, it was electrochemically oxidized at a slightly higher potential than that of the first anodic peak in the cyclic voltammograms. In the third spectrum, c, it was oxidized at a slightly higher potential than that of the second anodic peak. The irreversibility in color changes was caused by applying a potential higher than that of the second anodic peak.

The tendency toward spectral change with polarization potential is similar for the three cases, I, II, and III, in Figure 4. In the first oxidation, a peak at 420 nm and a broad absorption at the near-IR region appear. These absorptions were decreased by the second oxidation, and a new peak at 600 nm appears as shown Figure 4. In these measurements, the thicknesses of the polyaniline films are ca. 2 μm, which was determined from a working curve of the weight of films against the amount of electricity passed. A scanning electron micrograph of the polyaniline films showed an increase in heterogeneous structure with increasing film thickness. With increasing inhomogeneity, the spectral change with applied potential became unclear and the absorption peak at 600 nm remained, even in the reduction state at −0.2 V.

Conductivity and Spin Density. Figure 5 shows ESR spectra of the polyaniline prepared in aqueous solution. The polyaniline was polarized at various potentials for 30 min in a 0.1 M $LiClO_4$ acetonitrile solution, collected from the Pt electrode, and then dispersed into KBr at 0.5 wt %. The same procedure was applied to other systems. These procedures were repeated from lower potential to

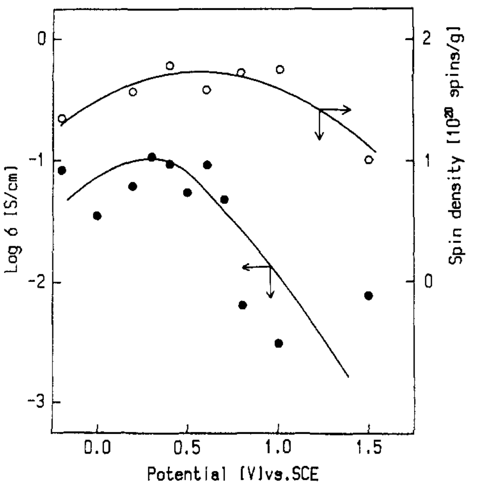

Figure 6. Dependence of the conductivity and the spin density on potentials. Polyaniline was prepared in a 0.1 M aniline–0.2 M $HClO_4$ aqueous solution and then polarized in a 0.2 M $HClO_4$ aqueous solution.

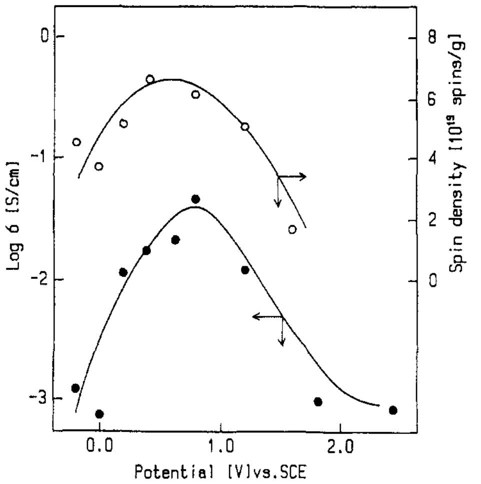

Figure 7. Dependence of the conductivity and the spin density on potentials. Polyaniline was prepared in a 0.1 M aniline–0.2 M $HClO_4$ aqueous solution and then polarized in a 0.1 M $LiClO_4$ acetonitrile solution.

higher potential. The line widths of ESR spectra in Figure 5 were somewhat broad compared to those for the bulk polyaniline[16] because the dilution by KBr weakens the spin exchange interaction. The intensity of the ESR signal in Figure 5 increased by the oxidation at 0.2 V and then decreased by the oxidation at 1.2 V; these oxidation potentials correspond to those of the anodic peak potentials in Figure 2.

The spin density of polyaniline was determined by comparison of the area under the integral curves of the ESR signals with DPPH as a standard. The potential dependence of the spin density and the conductivity of polyanilines is shown in Figures 6–8. In these figures, sufficient correlation is seen between the conductivity and the spin density. They increased by the first oxidation and decreased by the second oxidation in both aqueous and nonaqueous media.

Discussion

Results from cyclic voltammograms and in situ absorption spectra suggest that similar redox reactions occur in both protonic and aprotic media; two pairs of redox reactions were observed in cyclic voltammograms, and absorption at 420 nm appeared by the first oxidation and that at 600 nm appeared by the second oxidation in a similar manner.

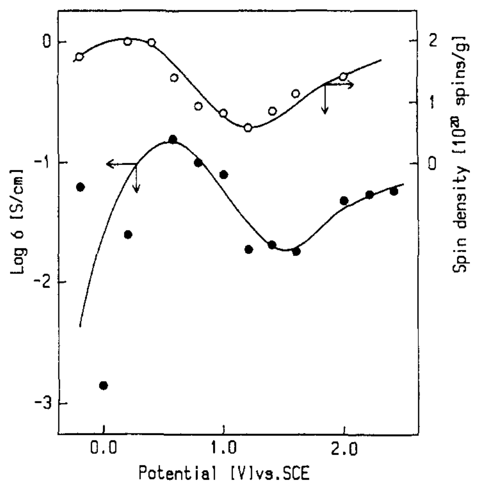

Figure 8. Dependence of the conductivity and the spin density on potentials. Polyaniline was prepared in a 0.1 M aniline–0.1 M $LiClO_4$ acetonitrile solution and then polarized in a 0.1 M $LiClO_4$ acetonitrile solution.

In the comparison of cyclic voltammograms between redox reactions of polyaniline films in aqueous solution and those in nonaqueous solution, two further significant features appeared. First, the first redox reaction is quite reversible in both aqueous and nonaqueous solutions. Second, the second redox reaction is reversible in aqueous solution and irreversible in nonaqueous solutions. The former suggests that the first redox reaction does not involve the proton-transfer process. The later suggests that the second redox reaction involves it.

In the previous paper,[11] we assigned the peaks of polyaniline films in 0.1 M H_2SO_4 aqueous solution as follows: The absorption maximum at 420 nm by the first oxidation is due to a radical cation at the N-position.[17,18] The absorption maximum at 600 nm by the second oxidation is due to the formation of a diimine structure. The measurement of absorption spectra of nigrosine which is an octamer model of polyaniline showed an absorption maximum at 600 nm in aqueous solution. Recently, Genies et al.[12] and McManus et al.[13] made a similar assignment in the absorption spectra of polyaniline. Glarum et al.[16] showed a similar assignment by in situ ESR spectra. Harada et al.[19] also showed a similar assignment on the basis of vibrational spectra. These mechanisms for electrochemical redox reactions of polyaniline films via the radical cation (first oxidation) and the diimine structure (second oxidation) are in disagreement with hitherto proposed mechanisms, i.e., the formation of diimine at the first oxidation and the protonation of the diimine structure (or insertion of anions into the diimine structure).[1-3,6-11]

The formation of a radical cation by the first oxidation is supported by ESR measurements. In Figures 6–8, the spin density reached a maximum at the potential of the first anodic peak. The decrease in the spin density by further oxidation suggests the formation of diamagnetic species by the second oxidation. This tendency is similar in both protonic and aprotic media.

We summarized the redox reaction mechanism of polyaniline films in Figure 9. The first oxidation step is expressed in eq 1. This assignment is supported by the following facts; the absorption peak of aromatic amines at 420 nm, no influence of protons on this oxidation step, and the maximum spin density at this oxidation state. The second oxidation step is expressed by eq 2 and 3. This is supported by the absorption peak of the diimine structure at 600 nm and the decrease in spin density by the second oxidation. Furthermore, the irreversibility of the second

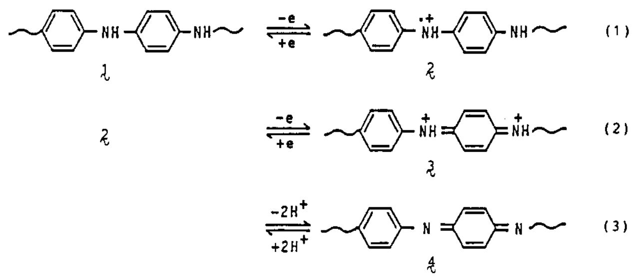

Figure 9. Electrochemical redox reactions of polyaniline films.

redox reaction in aprotic media supports this assignment. In eq 3, two protons are eliminated from the dication structure **3** by the oxidation and two protons must be added to the diimine structure **4** by the reduction. In aprotic media, the reduction reaction is irreversible because of the absence of a proton source.

Interpretation of the redox reactions of polyaniline has been in confusion because there has not been a clear recognition of the existence of two independent factors, i.e., potential and pH. In other words, they are expressed as electrochemical redox reactions with applied potential and chemical redox reactions with proton addition/elimination conditions, respectively. Recently, McManus et al.[13] and Genies et al.[20] suggested that the properties of polyaniline can be expressed by a three-dimensional relationship using potential and pH functions. In this paper we can separate the two factors by using an aprotic media in which proton addition/elimination reactions are negligible in comparison with what occurs in acidic media. Figure 9 shows electrochemical redox reactions occurring under applied potential. In aqueous solutions, there is another type of redox reaction caused by proton addition/elimination, and there is a pH dependence in the redox reactions of polyaniline. High acidity increases conductivity[13,20] and enhances the electrochemical activity of polyaniline films.

The electric conductivity of polyaniline films has been explained by the protonation of the diimine structure **4**[4,9,10] or the formation of the bipolaron.[14] However, the polyaniline film prepared in aprotic media exhibits significant conductivity as shown in Figure 8. In studies reported before, conductivity by the bipolaron mechanism has been confirmed by the independence of the conductivity on the spin density of polyaniline.[14,15] In other words, therefore, it is necessary to introduce the bipolaron model, which explains the appearance of the conductivity by diamagnetic structure. However, our results in Figures 6–8 clearly exhibit the correlation between the conductivity and the spin density. These results suggest the polaron model.[21-23] The polaron model has been proposed for polyaniline on the basis of the absorption spectra.[12] At the first oxidation state where the conductivity is maximum, a broad absorption appears at the near-IR region together with the absorption of radical cations as shown in Figure 4. The formation of a radical cation creates a defect in the polyaniline structure. Such a defect induces energy levels which are symmetrically located between the valence band and the conduction band of polyaniline. The broad absorption is due to the transition from the edge of the valence band to the half-occupied polaron level. The conductivity of polyaniline is due to such a transition, which can be induced by the lower energy. The broad absorption covers from the near-IR region to the IR region.

In Figure 8, the increases in the conductivity and spin density appear at a potential higher than the second oxidation potential. One possible explanation is the doping of ClO_4^- ion into the diimine structure. However, the increase was only observed for polyaniline prepared by potentiostatic oxidation at 2.0 V in nonaqueous solution but was not observed for that prepared by galvanostatic oxidation in aqueous solution as shown in Figures 6 and 7. In the potentiostatic oxidation, the polyaniline film was formed by the further oxidation of the eluted oligomer species with a diimine structure, as indicated by GPC analysis. The different structure may be involved in the polyaniline prepared by potentiostatic oxidation in nonaqueous solution.

Conclusions

Polyaniline films show similar electrochemical redox reactions in both aqueous and nonaqueous solutions. By the first oxidation, a radical cation at N-position is formed. By the second oxidation, a diimine structure is formed via the dication structure. These assignments were clearly suggested by a comparative study in both media with cyclic voltammograms and in situ absorption spectra. The conductivity and spin density of polyaniline films show good correlation. They become maximum at the first oxidation state in both aqueous and nonaqueous solutions. The appearance of the conductivity is explained by the polaron model. Polaron levels are induced by the formation of radical cations (defects) in the degenerate structure of the polymer. This model well explains the broad absorption band at a wavelength longer than the near-IR region.

Registry No. $HClO_4$, 7601-90-3; $LiClO_4$, 7791-03-9; Pt, 7440-06-4; polyaniline, 25233-30-1; aniline, 62-53-3.

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