Electrocatalytic Behavior of Poly(2,5-dihydroxyaniline) Synthesized by Electropolymerization in Aqueous Solutions

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Poly(2,5-dihydroxyaniline), or poly[imino(2,5-dihydroxy-1,4-phenylene)] ($PAn(OH)_2$), films were prepared by electropolymerization of 2,5-dimethoxyaniline (DMA), followed by electrochemical hydrolysis of methoxyl groups in an acidic solution. The films gave responses characteristic of a hydroquinone/quinone couple in aqueous solutions, suggesting that many hydroquinone units are introduced in the polymer structure. Although the polymer in the reduced state consisted of aniline units with substitutions by hydroxyl groups, its redox process is based on the reaction of hydroquinone/quinone couple in its structure, not on the doping/undoping in the aniline unit. Electrochemical redox processes were examined on the $PAn(OH)_2$-modified platinum electrode. The polymer films showed electrocatalytic activities for such redox reactions as the oxidation of $[Fe(CN)_6]^{4-}$, Fe^{2+}, and $[Co(NH_3)_6]^{2+}$ in aqueous solutions. Some interactions were suggested between the hydroquinone/quinone site or the aniline unit in the polymer and the redox active metal complexes in the solution and/or in the polymer.

There have been many studies on the synthesis of electroconducting polymers with various functional groups and their application to the chemically modified electrodes. Among them, much attention has been directed to the electrocatalytic properties of the resulting polymers and the polymer-modified electrodes. For example, polymers functionalized with ferrocenyl groups were synthesized and their redox properties were investigated.[1—3] Similarly, Fukui et al.[4] prepared quinoid polymers and reported their electrocatalytic behavior in aqueous solutions. More recently, Wang and co-workers[5] have succeeded in synthesizing a conducting polymer having hydroxyl groups by an enzymatic method. However, those polymers need rather specialized and complicated preparation techniques. Another approach to obtain polymers with high catalytic activities is inclusion or physical immobilization of active species in the conducting polymers.[6,7] The preparation of this type of polymers is rather simple, but we do not expect such polymers to keep high catalytic activities over a long term, because of rather weak adhesion of the active sites in the polymer structure.

We have recently proposed a simple method to prepare polymers with hydroquinone units that could act as active sites for electrochemical reactions.[8] That is, poly(2,5-dihydroxyaniline) (poly[imino(2,5-dihydroxy-1,4-phenylene)]; $PAn(OH)_2$) films were synthesized on a platinum (Pt) substrate by electropolymerization of 2,5-dimethoxyaniline (DMA) followed by electrochemical hydrolysis of the methoxyl groups in acidic solutions. Pistoia and Rosati[9] and Storrier et al.[10] have also obtained poly(2,5-dimethoxyaniline) (poly[imino-(2,5-dimethoxy-1,4-phenylene)]; $PAn(OCH_3)_2$) by the anodic oxidation of DMA in aqueous solutions. However, they did not refer to further hydrolysis processes of $PAn(OCH_3)_2$. We found that electropolymerized $PAn(OCH_3)_2$ is easily converted to $PAn(OH)_2$ through the hydrolysis of methoxyl groups in the DMA units during the potential scanning in perchloric acid solutions. The polymer itself exhibited the redox activity which is analogous to that of hydroquinone in aqueous electrolytes.

In the present work, the electrochemically synthesized $PAn(OH)_2$ films have been characterized by spectroscopic and electrochemical methods. Then the electrocatalytic properties of the films are investigated for various types of charge-transfer reactions. In the previous paper,[8] we presented a preliminary result that the $PAn(OH)_2$ film showed an electrocatalytic activity for a simple charge-transfer reaction in an aqueous solution. In this paper, characteristics of the $PAn(OH)_2$-coated electrode as a polymer mediator are described for the redox processes of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$, Fe^{2+}/Fe^{3+}, and $[Co(NH_3)_6]^{2+}/[Co(NH_3)_6]^{3+}$. As a result, a somewhat different mode of electrocatalysis was observed for each redox system. There have been only a few works that compare each electrocatalytic process in different redox systems on the polymer-coated electrode. Thus, in this paper, we will discuss the redox processes on the polymer-coated electrode from the viewpoint of electrochemical mediation of an electroconductive polymer that has active redox sites in its polymer structure.

Experimental

All chemicals were extra pure or guaranteed grade reagents, except for solvent acetonitrile (MeCN, HPLC grade), and were used without further purification. The $PAn(OH)_2$ films were electrochemically prepared on a Pt sheet substrate (apparent surface area: 2.0 cm^2). First, $PAn(OCH_3)_2$ was deposited on the substrate by potential scanning electrolysis in a solution of mixed water/acetonitrile (H_2O/MeCN=50/50 by volume) containing 0.2 mol dm^{-3} of monomer DMA and 0.25 mol dm^{-3} of $(C_2H_5)_4NClO_4$ (TEAP) or $HClO_4$ as a supporting electrolyte. The potential was scanned between 0.0 and +0.9 V vs. SCE with the scan rate (v) of 0.02 V s^{-1}. The amount of the deposit was controlled by the number of the potential scanning (n). This process is essentially the same as those reported by Pistoia and Rosati[9] and Storrier et al.,[10] except for details of experimental conditions. In some cases, controlled-potential electrolysis (potential: +0.65 V vs. SCE, quantity of electricity passed: 0.15 C cm^{-2}) was employed for the $PAn(OCH_3)_2$ deposition. The resulting $PAn(OCH_3)_2$ was electrochemically hydrolyzed by potential scanning between −0.2 and +0.9 V in an aqueous solution of 0.5 mol dm^{-3} $HClO_4$ to form $PAn(OH)_2$. This potential scanning was essential to yield $PAn(OH)_2$ efficiently because the hydrolysis rate, hence the extent of hydrolysis, was very low when the $PAn(OCH_3)_2$ film was simply immersed in the acidic aqueous solution.

The polymer films of $PAn(OCH_3)_2$ and $PAn(OH)_2$ were characterized by UV-vis and FTIR spectroscopies. The UV spectra were measured after dissolving the polymers in acetonitrile solvent. The FTIR measurements were carried out both for polymer films with Pt substrates and for powdered samples. Conductivity of the polymer films were measured on the substrate by a d.c. four-terminal method. The electrocatalytic properties of the polymer-coated Pt electrode were examined by conventional cyclic voltammetry. The electrolytic solution was a pH 7 phosphate or a pH 4 phthalate buffer containing 1×10^{-3}—2×10^{-2} mol dm^{-3} of the redox active species, $[Fe(CN)_6]^{4-}$, Fe^{2+}, and $[Co(NH_3)_6]^{2+}$.

Results and Discussion

Preparation and Characterization of $PAn(OH)_2$. Figure 1(a) shows a cyclic voltammogram of $PAn(OCH_3)_2$, prepared under a potentiostatic condition (+0.65 V vs. SCE, 0.2 C cm^{-2}) in H_2O/MeCN containing 0.5 mol dm^{-3} TEAP, measured in an aqueous $HClO_4$ electrolyte (0.5 mol dm^{-3}). Sharp redox peaks appear at about +0.1 and +0.45 V; these are characteristic for conventional polyaniline (PAn)-base films. That is, $PAn(OCH_3)_2$ has a PAn-skeleton structure.[9,10] In addition to this, a couple of broad redox current peaks were observed at about +0.3 V for the initial potential cycles. While the former current peaks based on the redox reactions of the PAn-skeleton decreased gradually with repeating the potential scan, the latter broad current peaks became clear. This variation in the voltammogram with the potential scan suggested that the methoxyl groups in the film were hydrolyzed during the potential scan under the acidic conditions. Figure 1(b) is a voltammogram for the film that was prepared by polymerization of DMA in H_2O/MeCN containing 0.25 mol dm^{-3} $HClO_4$, and was measured in aqueous $HClO_4$. The voltammogram showed a couple of larger broad current peaks at about 0.3 V, accompanied by very small peaks that are based on the redox reactions of PAn. These results mean that the acidic conditions during the polymerization are favorable to prepare polymers that are insoluble in the electrolyte solution and make it more easy to hydrolyze the methoxyl groups in the resulting polymer film. Thus, we will call the polymer after the hydrolysis of $PAn(OCH_3)_2$ in acidic conditions $PAn(OH)_2$. The hydrolysis reaction itself should need no electricity, but the electrochemical redox reaction of the PAn-backbone forwards the transport of protons (hydronium ions) in the polymer bulk, promoting the acid-catalyzed hydrolysis of the methoxyl groups to yield hydroxyl groups. However, the detailed mechanism is not clear for such a hydrolysis reaction in the polymer films. The voltammetric profile of the $PAn(OH)_2$ film shown in Fig. 1(b) is quite similar to that for poly(1,5-dihydroxynaphthalene),[5] which possesses hydroxyl groups in its polymer structure.

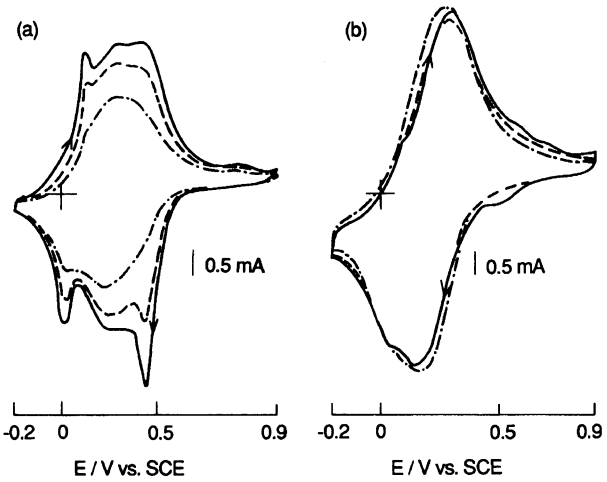

Fig. 1. Cyclic voltammograms for (a) $PAn(OCH_3)_2$ and (b) $PAn(OH)_2$ film electrodes in 0.5 mol dm^{-3} $HClO_4$. The films prepared in (a) H_2O/MeCN (50/50) containing 0.25 mol dm^{-3} TEAP, and (b) H_2O/MeCN (50/50) containing 0.25 mol dm^{-3} $HClO_4$, Scan rate: 0.02 V s^{-1}, —: 1st scan, - - -: 20th scan, −·−: 50th scan.

The potential scanning oxidation of DMA in H_2O/MeCN containing $HClO_4$, followed by the electrochemical hydrolysis in aqueous $HClO_4$, also gave electroactive $PAn(OH)_2$ films whose voltammograms were essentially the same as those shown in Fig. 1(b). Hereinafter, unless otherwise noted, the experimental results will be presented for $PAn(OH)_2$ prepared by the potential scanning method. Quite reproducible current responses were obtained for the polymer films whose thickness (amount of the deposition) was controlled by the number of the potential scannings. Figure 2

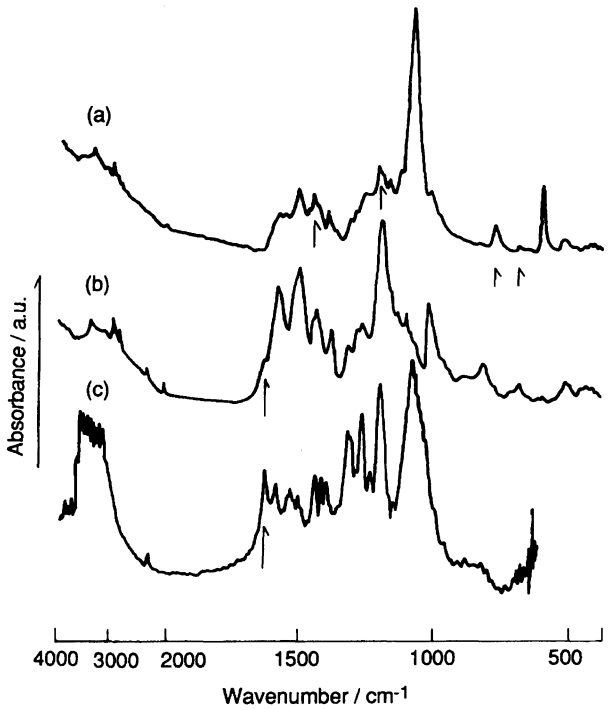

Fig. 2. IR spectra for the polymer. (a) $PAn(OCH_3)_2$ (prepared in H_2O/MeCN (50/50) containing TEAP), (b) $PAn(OH)_2$ (prepared in H_2O/MeCN (50/50) containing $HClO_4$, followed by electrochemical hydrolysis), (c) $PAn(OH)_2$ (the same as B, reflection spectrum).

shows the IR spectra of the polymers. On the spectrum of $PAn(OCH_3)_2$ (spectrum **a**; prepared potentiostatically from H_2O/MeCN containing 0.5 mol dm^{-3} TEAP), characteristic absorption peaks for the methoxyl groups were observed at 1210, 1460, and 3000 cm^{-1}; such peaks were superimposed on the absorption spectrum of conventional PAn. On the other hand, the spectrum of $PAn(OH)_2$ (spectrum **b**; polymerized in H_2O/MeCN containing 0.25 mol dm^{-3} $HClO_4$, followed by hydrolysis in aqueous $HClO_4$) had an absorption peak at 1650 cm^{-1} which is peculiar to quinone units in the polymer, together with the peaks based on the methoxyl and imino groups. The relative absorption intensity for the quinone units was much higher in the reflection spectrum (spectrum **c**) than in the transmission spectrum (spectrum **b**), and those of the methoxyl groups were rather low in the reflection spectrum. These results suggest that the hydroquinone/quinone units are concentrated rather in the surface region of the polymer film and that some methoxyl groups remain unhydrolyzed in the bulk of the film.

The UV-vis absorption spectra of $PAn(OCH_3)_2$ and $PAn(OH)_2$ have well characterized the structures of these polymers. The spectra of $PAn(OCH_3)_2$ oxidized electrochemically (at +0.125 V) and reduced (at −0.20 V) were similar to those of the usual PAn in oxidized and reduced states, respectively.[8,11,12] That is, the oxidized $PAn(OCH_3)_2$ showed characteristic absorption for the anion doped PAn (λ_{max} = 340 and 415 nm), and the reduced $PAn(OCH_3)_2$ was in the undoped state. The spectrum of the oxidized $PAn(OH)_2$ (+0.90 V) consisted of that of *p*-benzoquinone (λ_{max} = 295 nm), and the spectrum for the reduced $PAn(OH)_2$ (−0.20 V) was almost the same as that of oxidized $PAn(OCH_3)_2$. Thus, the reduced $PAn(OH)_2$ film has an anion-doped PAn structure and the oxidized is regarded as poly(aminoquinone), or poly[imino(2,5-dioxo-2,5-dihydro-1,4-phenylene)].[13] Proposed structures of the polymers are shown in Fig. 3.[8]

Typical d.c. conductivities of the films were 5.5×10^{-2} S cm^{-1} for oxidized (Quinone type) and 2.0×10^{-2} S cm^{-1} for reduced (Hydroquinone type) $PAn(OH)_2$. In these cases, the film thickness was controlled by the number of potential scanning for film preparation (n); it was found to be about 10 μm for the film of n = 2 from SEM observation. A cyclic voltammogram for $PAn(OH)_2$ in the pH 7 buffer is shown in Fig. 4, together with that of *p*-benzoquinone (0.1 mol dm^{-3}) measured on a bare Pt electrode in the pH 7 buffer. Most of conventional PAn's prepared by electrochemical methods are electroinactive in aqueous solutions with pH 4 or higher.[12,14—16] However, the present $PAn(OH)_2$ film was electroactive in the pH 7 buffer solution. The comparison with the voltammogram of *p*-benzoquinone shows that the redox couple around 0 V must be based on the reactions at hydroquinone/quinone (QH_2/Q) sites in the polymer. The peak separation of the redox couple in the polymer film was somewhat smaller than that in *p*-benzoquinone in the solution. There may be a small difference in the electrochemical reversibility between the QH_2/Q sites immobilized in the PAn-based polymer and the QH_2/Q

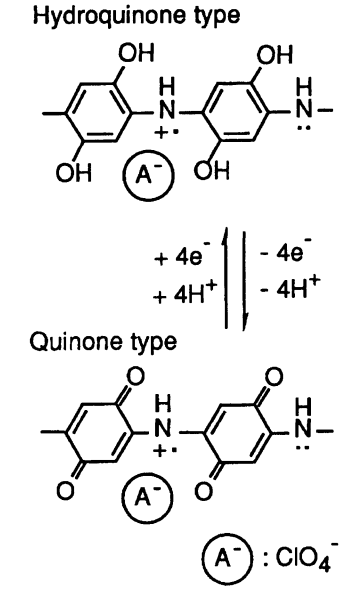

Fig. 3. A possible scheme for the redox reaction of $PAn(OH)_2$.

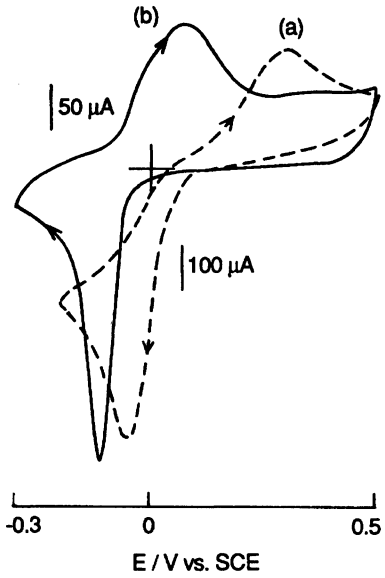

Fig. 4. Cyclic voltammograms for (a) bare Pt in pH 7 buffer solution containing 0.1 mol dm^{-3} *p*-benzoquinone and (b) PAn(OH)$_2$-coated Pt in pH 7 buffer solution. Scan rate: 0.01 V s^{-1}, The number of potential scanning for film preparation (n): 2.

couple in the bulk solution.

Figure 5 shows a variation in the quantity of electricity for the anodic peak in the voltammogram (q_a) with the number of potential scannings in the electropolymerization of the film (n). The quantity of electricity for film preparation was proportional to the n value. In other words, the film thickness linearly increased with increasing n. The q_a value, which represents the amount of the active QH_2/Q site in the polymer, increased almost linearly with n for relatively thin films ($n<3$; the thickness less than about 15 μm). However, the q_a value tended to saturate for thicker films. This

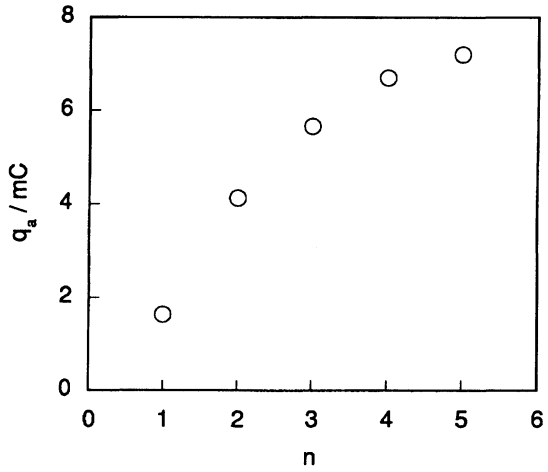

Fig. 5. Variation in q_a with the number of potential scanning for film preparation (n). q_a: the quantity of electricity for anodic peak current (−0.3 — +0.25 V vs. SCE) obtained from the voltammetry shown in Fig. 4.

observation is consistent with the spectroscopic results shown in Fig. 2, suggesting that the quinone sites are concentrated in the surface region of the polymer and that some of methoxyl groups remains unhydrolyzed in the bulk of the film.

Electrocatalytic Behavior of PAn(OH)$_2$. The electrocatalytic activity of the resulting PAn(OH)$_2$-coated Pt electrode was examined for simple charge transfer reactions. Typical voltammetric behavior of $[Fe(CN)_6]^{4-}$ (1×10^{-3} mol dm^{-3}) in the pH 7 buffer is shown in Fig. 6, where the redox response for $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ on PAn(OH)$_2$ is compared with that on a bare Pt electrode (curve **a**). As the redox potential of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ on Pt is more positive than that of QH_2/Q site in the polymer by about 0.15 V, the voltammogram of PAn(OH)$_2$ in the solution containing $[Fe(CN)_6]^{4-}$ (curve **c**) showed a summation of the responses for QH_2/Q site in the polymer (curve **b**) and $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ in the solution (curve **a**).

After the potential scanning in the $[Fe(CN)_6]^{4-}$ solution, the voltammogram for PAn(OH)$_2$-coated Pt in the pH 7 solution without redox active species (curve **d**) gave higher anodic and cathodic currents

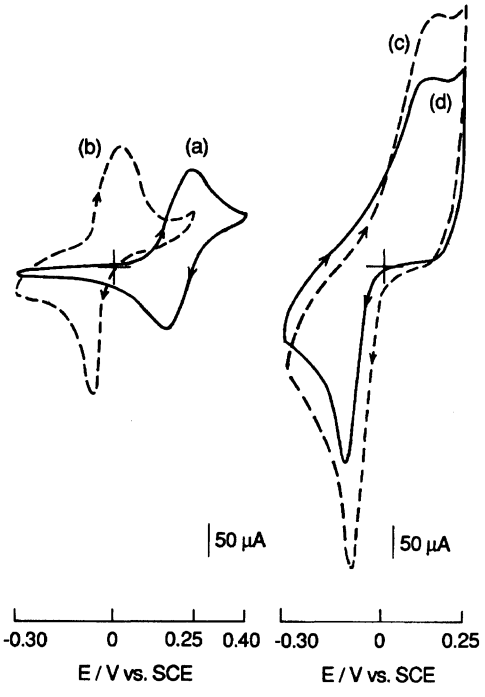

Fig. 6. Cyclic voltammograms for (a) bare Pt in pH 7 buffer solution containing 1×10^{-3} mol dm^{-3} $K_4[Fe(CN)_6]$, (b) PAn(OH)$_2$-coated Pt in pH 7 buffer solution, (c) PAn(OH)$_2$-coated Pt in pH 7 buffer solution containing 1×10^{-3} mol dm^{-3} $K_4[Fe(CN)_6]$, and (d) PAn(OH)$_2$-coated Pt in pH 7 buffer solution after the potential scanning in the solution containing 1×10^{-3} mol dm^{-3} $K_4[Fe(CN)_6]$. Scan rate: 0.01 V s^{-1}, The number of potential scanning for film preparation (n): 1.

than those before the potential scanning in the $[Fe(CN)_6]^{4-}$ solution (curve **b**). This means that the Fe(II/III) species are incorporated in the $PAn(OH)_2$ film after the potential scanning in the solution containing $[Fe(CN)_6]^{4-}$. The electrostatic incorporation of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ have already been reported for PAn-based polymers.[17—19] The anodic peak potential on curve **c** is less positive than that on curve **a**, and the peak current is much higher than that observed for original $PAn(OH)_2$. Thus, the redox reaction of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ in the film would proceed through the redox sites (QH_2/Q) in the polymer, or some electromediation of $PAn(OH)_2$ would occur for the anodic oxidation of $[Fe(CN)_6]^{4-}$ incorporated in the polymer film.

Figure 7 is a plot of the quantity of electricity for the oxidation of $[Fe(CN)_6]^{4-}$ incorporated in the film (q_{FeCN}) against the number of the potential scanning for $PAn(OH)_2$ preparation (n). The q_{FeCN} value was obtained by subtraction of the electricity for curve **b** from that for curve **c** in Fig. 6, and should be a measure of the catalytic activity for the $[Fe(CN)_6]^{4-}$ oxidation at the electrode in question. In this plot, q_{FeCN} at $n=0$ means the electricity observed for a bare Pt electrode in the solution containing 1×10^{-3} mol dm^{-3} $[Fe(CN)_6]^{4-}$ (curve **a** in Fig. 6). The q_{FeCN} value on $PAn(OH)_2$-coated Pt was much higher than that on bare Pt. This is because the reaction site was spread in all three-dimensions in the polymer layer. The quantity of electricity for $[Fe(CN)_6]^{4-}$oxidation, however, tended to saturate for the films with the n values of 2 or higher. As the q_{Fe} value should correspond to the activity of the incorporated $[Fe(CN)_6]^{4-}$ (the amount of the electroactive ions), the relation in Fig. 7 suggests following two possibilities; 1) the incorporation of $[Fe(CN)_6]^{4-}$ during the potential scanning is restricted rather in the surface region of the polymer, or 2) only the incorporated species in the Pt substrate/$PAn(OH)_2$ interface region is electroactive and the remainder far from the interface is inactive. In either case, Fig. 7 demonstrates that the reaction region extends over at least about 10 μm, which is the thickness of the $PAn(OH)_2$ film with $n=2$.

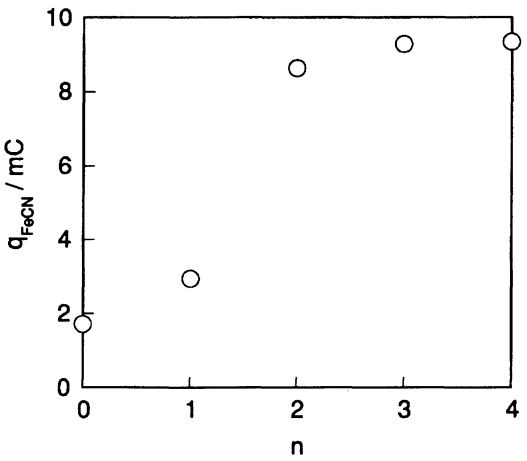

Fig. 7. Variation in q_{FeCN} with the number of potential scanning for film preparation (n). q_{FeCN}: the quantity of electricity for anodic peak current (−0.3 — +0.25 V vs. SCE) obtained from the voltammetry shown in Fig. 6(d).

Figure 8 shows the voltammograms of $PAn(OH)_2$ in the pH 4 solutions with and without 2×10^{-2} mol dm^{-3} of $FeSO_4$ (curves **b** and **c**, respectively). The anodic and cathodic reactions of Fe^{2+}/Fe^{3+} on a bare Pt electrode make current peaks at +0.25 and +0.14 V, respectively. The voltammogram on the $PAn(OH)_2$-modified Pt electrode showed negligibly low current peaks at those potentials for the direct Fe^{2+}/Fe^{3+} reactions on Pt. On the other hand, the broad current peaks at +0.12 V (anodic) and at −0.05 V (cathodic), based on the reactions of QH_2/Q in the polymer, were increased by the presence of $FeSO_4$ in the solution. These observations lead to an expectation that the charge transfer reactions of the Fe^{2+}/Fe^{3+} couple occur through the reactions of the QH_2/Q sites in the polymer.

We can regard the increase in the anodic current (the difference between curves **b** and **c** in Fig. 8) as the electrocatalysis of $PAn(OH)_2$ for the oxidation of Fe^{2+}. The increment in the quantity of electricity for the Fe^{2+} oxidation (q_{Fe}) was plotted against the number of potential scannings for film preparation (n) in Fig. 9, where q_{Fe} at $n=0$ corresponds to the anodic charge observed on bare Pt (curve **a** in Fig. 8). For this reaction, q_{Fe} was increased with increasing n. The variation in the anodic peak current with the potential scan rate is shown

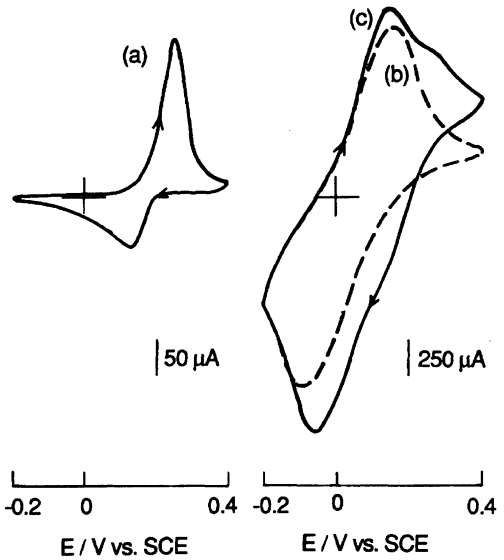

Fig. 8. Cyclic voltammograms for (a) bare Pt in pH 4 buffer solution containing 2×10^{-2} mol dm^{-3} $FeSO_4$, (b) $PAn(OH)_2$-coated Pt in pH 4 buffer solution, (c) $PAn(OH)_2$-coated Pt in pH 4 buffer solution containing 2×10^{-2} mol dm^{-3} $FeSO_4$. Scan rate: 0.005 V s^{-1}, The number of potential scanning for film preparation (n): 2.

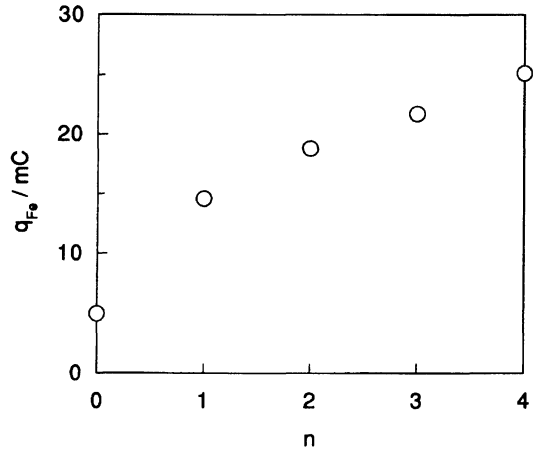

Fig. 9. Variation in q_{Fe} with the number of potential scanning for film preparation (n). q_{Fe}: The quantity of electricity for anodic peak current (-0.2 — $+0.4$ V vs. SCE) obtained from the voltammetry shown in Fig. 8(c).

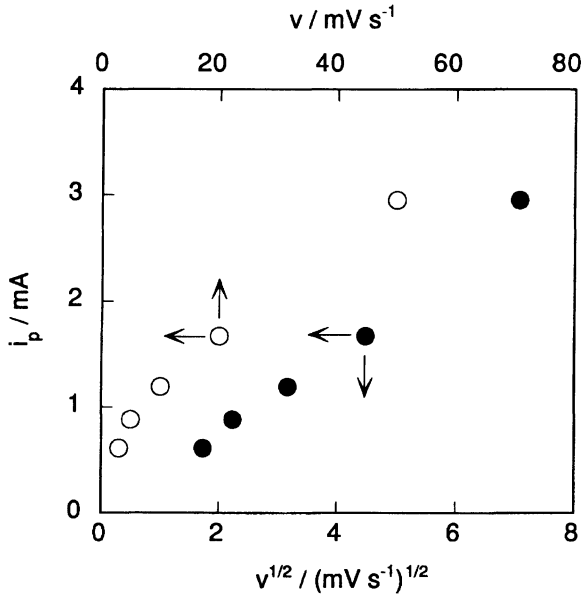

Fig. 10. Relation between the anodic peak current (i_a) and the scan rate (v or $v^{1/2}$) for Fe^{2+} oxidation on $PAn(OH)_2$-coated Pt.

in Fig. 10. The peak current observed on $PAn(OH)_2$ in the $FeSO_4$ solution linearly increased with the square root of the potential scan rate, suggesting that the reaction is controlled by some diffusion process. We have not examined the details in the diffusion process, but speculate that the process in the film is rate-determining, which is somewhat analogous to the processes in poly(*N*,*N*-dimethylaniline), or poly(dimethylamino-1,4-phenylene).[18,19]

Figure 11 shows a voltammetric response for the redox reaction of $[Co(NH_3)_6]Cl_3$ in the pH 7 buffer solution. The reaction is irreversible on a bare Pt electrode, due to the instability of electrochemically reduced $[Co(NH_3)_6]^{2+}$ on Pt.[20] For the $PAn(OH)_2$-coated electrode, however, anodic current was superimposed on the oxidation current of $PAn(OH)_2$ itself. The electrochemically reduced Co(II) species was somewhat stabilized at the $PAn(OH)_2$-coated electrode. Further, the QH_2/Q site of the film is considered to catalyze the oxidation of the Co(II) species. That is, the inhibition of the anodic process from the bare Pt surface was partly reduced at the $PAn(OH)_2$-modified electrode.

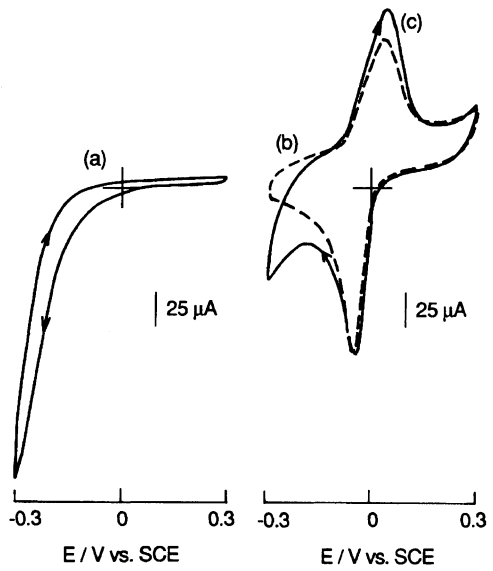

Fig. 11. Cyclic voltammograms for (a) bare Pt in pH 7 buffer solution containing 1×10^{-2} mol dm^{-3} $[Co(NH_3)_6]Cl_3$, (b) $PAn(OH)_2$-coated Pt in pH 7 buffer solution, (c) $PAn(OH)_2$-coated Pt in pH 7 buffer solution containing 1×10^{-2} mol dm^{-3} $[Co(NH_3)_6]Cl_3$. Scan rate: 0.01 V s^{-1}, The number of potential scanning for film preparation (n): 1.

The integrated anodic current, or the quantity of electricity (q_{Co}), is a measure of the electrocatalytic activity of $PAn(OH)_2$ for the oxidation of $[Co(NH_3)_6]^{2+}$. In Fig. 12, q_{Co} is shown as a function of n in the film preparation. The catalytic activity was increased with increasing the film thickness, although it tended to saturate for thicker films. As the reduced $[Co(NH_3)_6]^{2+}$ is unstable on bare Pt, the catalytic reaction would occur in the surface (polymer/electrolyte interface) region. Therefore, distribution of QH_2/Q sites with higher density in the surface region would be responsible for the activity saturation shown in Fig. 12.

Conclusion

Poly(2, 5- dihydroxyaniline) (poly[imino(2, 5- dihydroxy- 1, 4- phenylene)]; $PAn(OH)_2$) films were synthesized by anodic oxidation of 2,5-dimethoxyaniline (DMA) followed by electrochemical hydrolysis of methoxyl groups in an acidic solution. The resulting polymers have structures of hydroxyl-substituted polyaniline (PAn) doped with anions (in the reduced state) and those like poly(aminoquinone), or poly[imino(2,

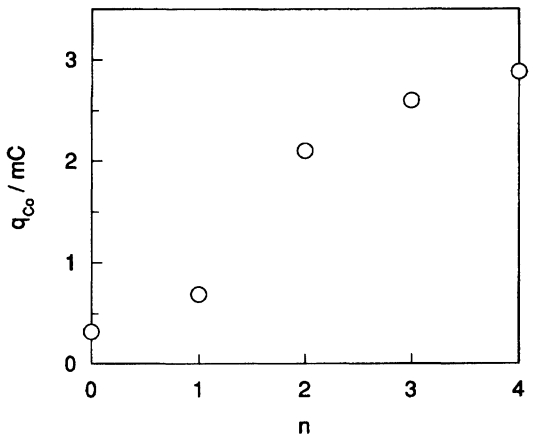

Fig. 12. Variation in q_{Co} with the number of potential scanning for film preparation (n). q_{Co}: The quantity of electricity for anodic peak current (−0.3 — +0.3 V vs. SCE) obtained from the voltammetry shown in Fig. 11(c).

5-dioxo-2,5-dihydro-1,4-phenylene)], (in the oxidized state). Thus, redox responses characteristic of a hydroquinone/quinone couple were observed for the polymer coated electrodes in aqueous electrolyte solutions. The PAn(OH)$_2$-modified electrode showed electrocatalytic activities for such simple redox systems as the oxidation reactions of $[Fe(CN)_6]^{4-}$, Fe^{2+}, and $[Co(NH_3)_6]^{2+}$. The activity of the electrocatalysis was qualitatively discussed by drawing on cyclic voltammetry results. The mode of electromediation of the QH_2/Q sites was dependent on the sort of redox system. Differences in the redox potentials between the QH_2/Q site and the metal complexes, and the ionic structure of the complexes would relate to such differences in the mode of the electromediation. Detailed discussion will need quantitative analyses of the catalytic activities for this type of polymer-coated electrodes.

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