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

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Poly(2,5-dihydroxyaniline) films, synthesized by electropolymerization of 2,5-dimethoxyaniline followed by hydrolysis of methoxy groups in an acidic solution, gave a characteristic redox response like a hydroquinone/quinone couple in aqueous electrolyte solutions. The film showed electrocatalysis for a simple redox system.

There have been many studies on the synthesis of electroconducting polymers with various functional groups. Among them, much attention has been directed to the application of resulting polymers to electrocatalytic processes. For example, polymers functionalized with ferrocenyl groups were synthesized and their redox properties were investigated.[1-3] Similarly the electrocatalytic behavior of quinoid polymers has been reported.[4] However, those polymers need rather complicated preparation technique. We report here a simple method to prepare polymers with quinoid groups that could act as active redox sites. That is, poly(2,5-dihydroxyaniline) (PAn(OH)$_2$) films were synthesized on a Pt substrate by electropolymerization of 2,5-dimethoxyaniline (DMA) followed by hydrolysis of the methoxy groups in acidic solutions. The resulting polymer film was characterized by electrochemical and spectroscopic methods.

Poly(2,5-dimethoxyaniline) (PAn(OCH$_3$)$_2$) was first deposited on a Pt substrate by anodic polymerization of DMA (0.2 mol dm^{-3}) in mixed water/acetonitrile (H$_2$O/MeCN = 50/50 by volume) containing 0.25 mol dm^{-3} of (C$_2$H$_5$)$_4$NClO$_4$ (TEAP) or HClO$_4$ as a supporting electrolyte. The electrolysis was performed under a constant-potential condition (Potential: +0.65 V vs. SCE., Quantity of electricity passed: 0.15 C cm^{-2}). Pistoia and Rosati,[5] and Storrier et al.[6] have also obtained PAn(OCH$_3$)$_2$ using similar electrolytic methods.

Figure 1(a) shows a cyclic voltammogram of PAn(OCH$_3$)$_2$, prepared in H$_2$O/MeCN containing TEAP, measured in an aqueous HClO$_4$ electrolyte. Sharp redox peaks at about +0.1 V and +0.45 V, which are characteristics for usual polyaniline (PAn)-base films, and a couple of broad redox current peaks were observed at about +0.3 V for the initial potential cycles. The current densities of the former sharp peaks gradually decreased with repeating the cycle, while the latter broad peaks became clear. The results shown in Fig. 1(a) suggest that the redox reaction of PAn(OCH$_3$)$_2$ is essentially the same as that of conventional PAn and the methoxy groups in the film were hydrolyzed during the potential cycling in aqueous HClO$_4$. Then, PAn(OH)$_2$ films were prepared by the electrochemical hydrolysis of PAn(OCH$_3$)$_2$ using potential scan in an aqueous HClO$_4$. In this case, HClO$_4$ in H$_2$O/MeCN was used as the electrolyte for PAn(OCH$_3$)$_2$ preparation. The acidic conditions during the polymerization was favorable to prepare polymers being insoluble in the electrolyte solution. Also the polymerization in the acidic electrolyte made it more easy to hydrolyze the methoxy groups in the resulting polymer film. This was probably because of the inclusion of the acid in the growing film and/or the simultaneous hydrolysis during the polymerization. Figure 1(b) represents a voltammogram for the film that prepared by polymerization of DMA in H_2O/MeCN containing $HClO_4$, followed by the hydrolysis in aqueous $HClO_4$. As the methoxy groups at the surface region of the polymer were thoroughly hydrolyzed, high anodic and cathodic currents based on the redox reaction of hydroxyl groups were observed in the wide potential region. On the other hand, the redox peaks for the PAn-backbone were negligibly small. These results mean that the redox site was changed from the imine group of the PAn-backbone to the hydroxyl group at the benzene ring in $PAn(OH)_2$. Similar voltammetric behavior has been observed for poly(1,5-dihydroxynaphthalene).[7)] The redox behavior of $PAn(OH)_2$ was pH-dependent, but its potential/pH slope was smaller than that observed for a conventional quinone/hydroquinone couple in aqueous electrolytes. The amino/imine group in the PAn-backbone, which can act as some pH buffer in the film, would be responsible for such low pH dependence in the redox process of $PAn(OH)_2$.

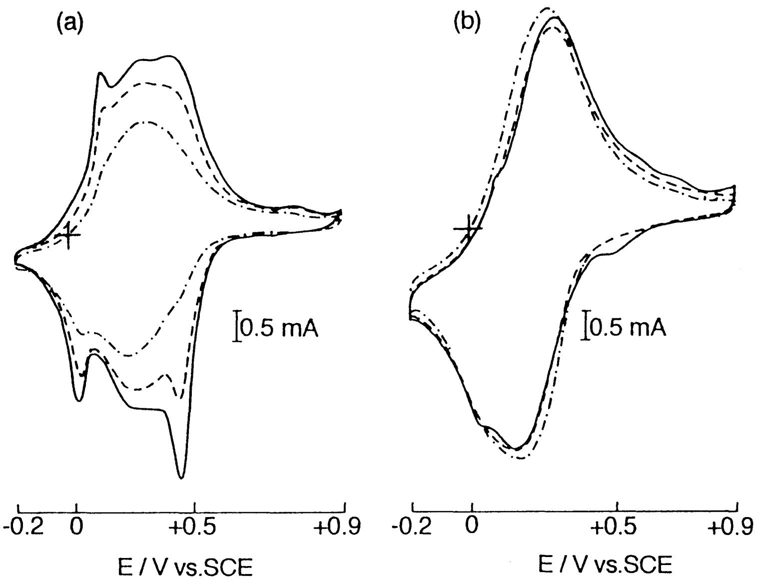

Fig. 1. Cyclic voltammograms of (a) $PAn(OCH_3)_2$ and (b) $PAn(OH)_2$ film electrodes in 0.5 mol dm^{-3} $HClO_4$. Scan rate: 0.02 V s^{-1},
—— : 1 st scan, - - - : 20th scan, —·— : 50th scan.

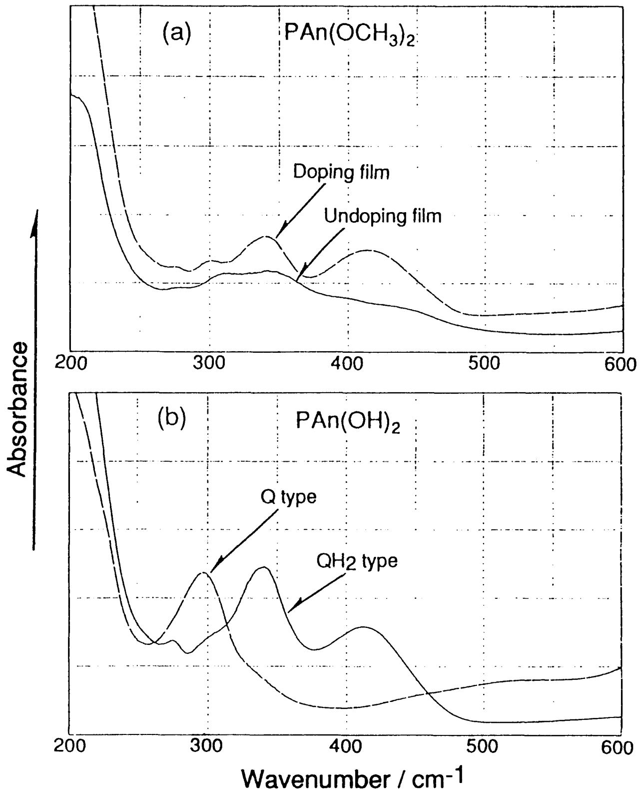

Fig. 2. Absorption spectra of (a) $PAn(OCH_3)_2$ and (b) $PAn(OH)_2$ film electrodes.
- - - : Oxidized, —— : Reduced.

The UV-VIS absorption spectra of $PAn(OH)_2$ and $PAn(OCH_3)_2$ were compared in Fig. 2, where the spectra were measured after the electrochemical oxidation or reduction in aqueous $HClO_4$. The spectra of the $PAn(OCH_3)_2$ films electrochemically oxidized (at +0.125 V) and reduced (-0.20 V) were respectively similar to those of usual PAn.[6,8,9)] 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 for the oxidized PAn(OH)2 (+0.90 V) consisted of that of 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$_3$)$_2$. These results suggest that the reduced PAn(OH)$_2$ has an anion-doped PAn structure. Reflective IR spectra of the PAn(OCH$_3$)$_2$ and PAn(OH)$_2$ films supported above discussion. That is, an absorption band due to the quinoid structure (1650 cm^{-1}) was observed for the oxidized PAn(OH)$_2$, while the bands based on OCH$_3$ groups (1210, 1460, and 3000 cm^{-1}) were found in the PAn(OCH$_3$)$_2$ film. Absorption bands suggesting the ClO$_4^-$ doping (630 and 1090 cm^{-1}) were also detected for PAn(OH)$_2$ and oxidized PAn(OCH$_3$)$_2$.

The voltammetric behavior and the absorption spectra of the PAn(OCH$_3$)$_2$ and PAn(OH)$_2$ films lead to redox mechanisms shown in Fig. 3. The electrochemical oxidation of the PAn(OCH$_3$)$_2$ prepared from H$_2$O/MeCN containing TEAP is accompanied by anion-doping, which would correspond to the first anodic peak in the voltammogram. Further oxidation (the second anodic peak) of PAn(OCH$_3$)$_2$ leads to undoping of proton and anion (Fig. 3a). These processes are essentially the same as those for conventional PAn.$^{8-10)}$ In acidic solutions, another process could occur during the redox cycle. The methoxy groups at the benzene rings are hydrolyzed to yield hydroxyl groups. The resulting polymer has a 2,5-dihydroxy anilinium structure doped with anion. For the completely hydrolyzed polymer, PAn(OH)$_2$, the anodic oxidation process consists of the oxidation of hydroquinone units to yield benzoquinone (Fig. 3b). From the spectrum data, PAn(OH)$_2$ is considered to be doped with anion, even in its reduced form. The redox mechanisms shown in Fig. 3 are somewhat different from those proposed by Storrier et al.,$^{6)}$ in which the degree of hydrolysis for the methoxy groups

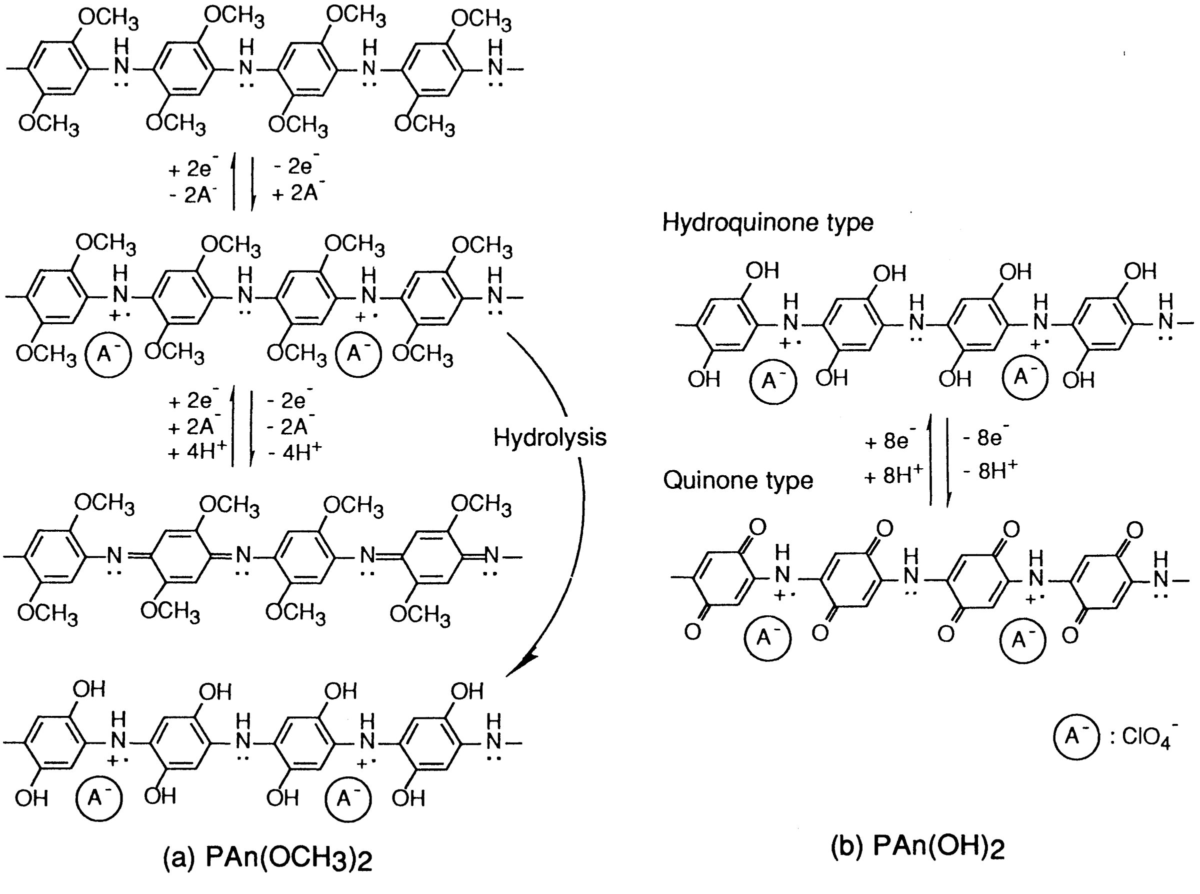

Fig. 3. The electrochemical redox processes of (a) PAn(OCH$_3$)$_2$ and (b) PAn(OH)$_2$ films.

would be rather low. The large and broad voltammetric peaks, shown in Fig. 1b, for this redox process suggest that the density of the quinone/hydroquinone redox site introduced in the polymer was very high and that the reaction rate would be lower than that for conventional benzoquinone/hydroquinone couple in solution phase.

The present PAn(OH)$_2$ film showed electrocatalytic activities for some redox reactions of metal complexes. Figure 4 shows a voltammetric response for the redox reaction of Co(NH$_3$)$_6$Cl$_3$. The reaction was irreversible on a bare Pt electrode in pH 7 buffer solution (Curve a). This is due to the instability of Co(NH$_3$)$_6^{2+}$ on Pt.[11)] For the PAn(OH)$_2$-covered electrode, however, anodic current was observed superimposed on the oxidation current of PAn(OH)$_2$ itself. The quinone /hydroquinone site of the film is considered to catalyze the oxidation of the Co(II) species, which is probably an aqua complex of Co^{2+}. Such mediation of the anodic reaction means that the inhibition of the anodic process from the bare Pt surface was partly reduced at the PAn(OH)$_2$-modified electrode. The rate of the current increase depended on the concentration of the complex and the film thickness. Details of the electrocatalytic properties of the PAn(OH)$_2$ film are now under investigation.

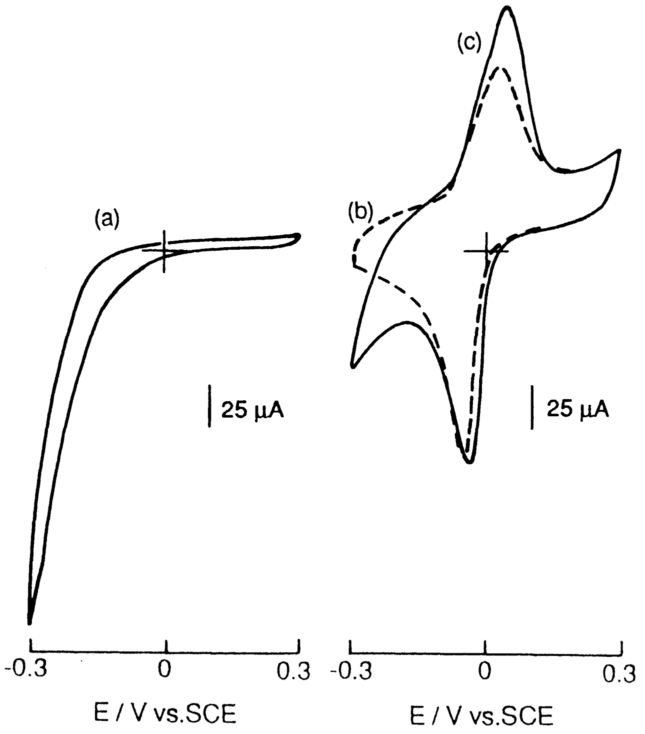

Fig. 4. Cyclic voltammograms for (a) Pt electrode in Co(NH$_3$)$_6$Cl$_3$(1×10^{-2} mol dm^{-3})/pH 7 buffer, (b) PAn(OH)$_2$ film in pH 7 buffer, and (c) PAn(OH)$_2$ film in Co(NH$_3$)$_6$Cl$_3$ (1×10^{-2} mol dm^{-3}) /pH 7 buffer, Scan rate: 0.01 V s^{-1}.

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References

1) M. V. Rosenthal, T. Skotheim, and J. Warren, *J. Chem. Soc., Chem. Commun.*, **1985**, 342.
2) J. G. Evans, H. S. Munro, and D. Parker, *Synthetic Metals*, **16**, 123 (1986).
3) C. P. Horwitz and G. C. Dailey, *Chem. Mater.*, **2**, 343 (1990).
4) M. Fukui, A. Kitani, C. Degrand, and L. L. Miller, *J. Am. Chem. Soc.*, **104**, 28 (1982).
5) G. Pistoia and R. Rosati, *Electrochim. Acta*, **39**, 333 (1994).
6) G. D. Storrier, S. B. Colbran, and D. B. Hibbert, *Synthetic Metals*, **62**, 179 (1994).
7) L. Wang, E. Kobatake, Y. Ikariyama, and M. Aizawa, *Denki Kagaku*, **60**, 1050 (1992).
8) Y. Li, B. Yan, J. Yang, Y. Cao, and R. Qian, *Synthetic Metals*, **25**, 79 (1988).
9) T. Hirai, S. Kuwabata, and H. Yoneyama, *J. Chem. Soc., Faraday Trans. I*, **85**, 969 (1989).
10) M. Leclerc, *J. Electroanal. Chem.*, **296**, 93 (1990).
11) I. M. Kolthoff and S. E. Khalafalla, *Inorg. Chem.*, **2**, 133 (1963).

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