Selective Potential Response of a Poly(*N*,*N*-dimethylaniline)/Poly(*o*-chloroaniline) Dual-Layer Coated Electrode to Dissolved Iodide Ions

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Poly(*N*,*N*-dimethylaniline) (PDA) was easily obtained by an anodic oxidation of *N*,*N*-dimethylaniline in acidic media. PDA is a semiconductor having positively charged sites as quaternary ammonium groups in its polymeric backbone. It was possible for a PDA-film coated electrode to incorporate I^- electrostatically; I^- in the film was then oxidized electrochemically. Further, the oxidized products of I^- still remained in the film. Although the electrode responded to dissolved I^- potentiometrically, the response was disturbed by the presence of other redox species. On the other hand, poly(*o*-chloroaniline) (PCA) was also easily prepared by the electro-oxidation of *o*-chloroaniline in acidic solutions. On a PCA-film coated electrode, only the redox wave of I_2/I^- was observed, though PCA, itself, was electroinactive. In other words, the PCA film responded to I^- selectively. The dual-layer (a PDA film incorporated oxidized products of I^- and PCA film) showed a selective Nernstian response to dissolved I^-.

Polyaniline, which is now a familiar conducting polymer, is easily obtained by anodic oxidation of aniline in acidic media. If the anodic oxidation of aniline derivatives, instead of aniline, also gave electroactive conducting polymers, they would have unique properties other than polyaniline. We have already examined the possibility of forming functional polymer films onto Pt electrodes by anodic oxidation.[1] The products of electro-oxidation were classified as follows: (1) deposition of an electroactive polymer film which shows a redox wave of polymer, itself; (2) deposition of an electroactive polymer film which does not show any redox wave of the polymer, itself; (3) formation of soluble products not adhering to an electrode surface; and (4) deposition of an electroinactive polymer film.

The only polymer that belongs to group (2) is poly(*N*,*N*-dimethylaniline) (PDA). PDA can incorporate anionic redox species electrostatically due to its structure, having positively charged sites as quaternary ammonium groups in the polymeric backbone.[2] This means that the PDA-film coated electrodes which incorporate certain oxidized (reduced) products have a potentiometric response to the corresponding dissolved reduced (oxidized) species. For example, a PDA film which incorporates oxidized products of I^- is sure to respond to dissolved I^- potentiometrically. Unfortunately, the response must be disturbed by the presence of other redox species, because PDA is itself conducting.

Only the redox wave of I_2/I^- was obviously observed on some of the polymer films of group (4) described above, although the films were not expected to have any useful functions.[3-5] In other words, those polymer films responded to only I^-, though they were electroinactive. The author would like to employ poly(*o*-chloroaniline) (PCA) here as a representative of group (4).

If a polymer-coated electrode responds to a certain dissolved ion selectively, it would be useful in various fields as a new type of ion sensor. Such a sensor would also have some advantage compared with conventional ion-selective electrodes, particularly regarding miniaturization. There have, however, not been many studies on polymer-coated electrodes used for such sensors. Ohnuki et al. reported that selective film permeation of H^+, Br^-, and Fe^{2+} has been observed in a few polymer-coated electrodes.[6] The electrodes probably act as amperometric sensors for them. On the other hand, a poly(*o*-phenylenediamine)-coated electrode may be applicable to voltammetric pH measurements.[7,8] In studies up to now, the kinds of dissolved ions to be measured (coating polymer materials and so on) have been limited. In this paper the author describes the unique potentiometric sensor of dissolved I^- using the PDA/PCA dual-layer coated electrode.

Experimental

For an electrochemical cell a standard three-electrode system was used for all electrolyses. In measurements of cyclic voltammograms, a platinum wire having a geometry of 1 mm in diameter and 10 mm in length (area=ca. 0.3 cm^2) was employed as the working electrode. In preparing PDA samples for elemental analysis, the electrode substrate used was a platinum plate having a surface area of ca. 8 cm^2. The counter electrode was either a platinum wire or a platinum plate. The reference electrode was a saturated calomel electrode (SCE). The platinum electrodes were treated with 6 M (1 M=1 mol dm^{-3}) HNO_3 and polarized by repeated potential cycling between −0.2 and 1.2 V vs. SCE in 0.1 M H_2SO_4. The electrodes showed the well-known redox waves of platinum. Measurements were carried out with a potentiostat/galvanostat (Model HA-301, Hokuto Denko Co., Ltd.) with a function generator (Model HB-104, Hokuto Denko Co., Ltd.) and an X–Y recorder (Model RW-21, Rikadenki Co., Ltd.).

N,*N*-dimethylaniline and *o*-chloroaniline (Tokyo Kasei Co., Ltd.) were used after distilling under reduced pressure. Other chemicals were of reagent grade and used as received. All of the aqueous solutions were prepared with doubly distilled deionized water.

In order to examine whether dissolved I^- permeates through a PDA film, a technique using a rotating disk electrode (RDE) was employed. Measurements were carried out using an RDE-measuring system (Model HR-103A, Hokuto Denko Co., Ltd.). A platinum disk of 5.0 mm diameter (area=ca. 0.196 cm^2) was used as the working electrode. Prior to use, it was polished and then polarized by repeated potential cycling between −0.2 and 1.2 V vs. SCE in 0.1 M H_2SO_4. A platinum plate (area=ca. 8 cm^2) was used as the counter electrode and an SCE was also used as the reference electrode.

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with a Perkin–Elmer 240-C. Those of chlorine and iodine were carried out by the following method. The PDA samples were subjected to perfect combustion; the gases produced were absorbed in water and the amounts of chlorine and iodine in the aqueous solution determined by ion chromatography (Dionex 2000-I). Procedures for the preparation of the polymer-film coated electrodes are described in more detail in the Results and Discussion sections. All experiments were carried out at room temperature.

Results and Discussion

Preparation of PDA-Film and PCA-Film Coated Electrodes. PDA and PCA films were formed onto platinum electrodes using the same type electrolysis methods as were described in a previous paper,[1] except that the electrolytic solutions were 1.0 M HCl containing 0.5 M respective monomers. Cyclic voltammograms of the film-forming process of PDA onto a platinum electrode are shown in Fig. 1 (a). During the first positive sweep monomeric *N*,*N*-dimethylaniline was oxidized, exhibiting a distinct irreversible current peak at about 0.85 V. As soon as this peak current flowed, red powdery products were observed near the electrode surface. The products continued to diffuse from the surface to the bulk, while potential cycling was repeated. After about 100 cycles, however, deposition of a brown film on the electrode surface was clearly seen. The potential cycling was further continued for up to 300 cycles in preparation of the PDA-film coated electrode.

Redox peaks at ca. 0.55 V were observed until about the fiftieth cycle. The peaks corresponded to the *N*,*N*,*N'*,*N'*-tetramethylbenzidine/the quinone diimine redox pair.[9–11] In Fig. 1 (a), the two anodic peak potentials shift more positively, and cathodic one more negatively, as the number of cycles increases. This is probably due to an *iR* drop of the growing PDA film. In fact, the conductivity of PDA in the dry state was determined to be 6.2×10^{-6} S cm^{-1} by the four-point probe method.[3]

Figure 1 (b) shows cyclic voltammograms for a coating process of the PCA film onto a platinum electrode. The anodic peak current for the oxidation of *o*-chloroaniline diminishes immediately during the first five cycles. This means that the resulting PCA film is electroinactive and quite an insulator.

The morphologies of the PCA films and the PDA films on platinum electrodes were observed using a scanning electron microscope (SEM). The PCA film

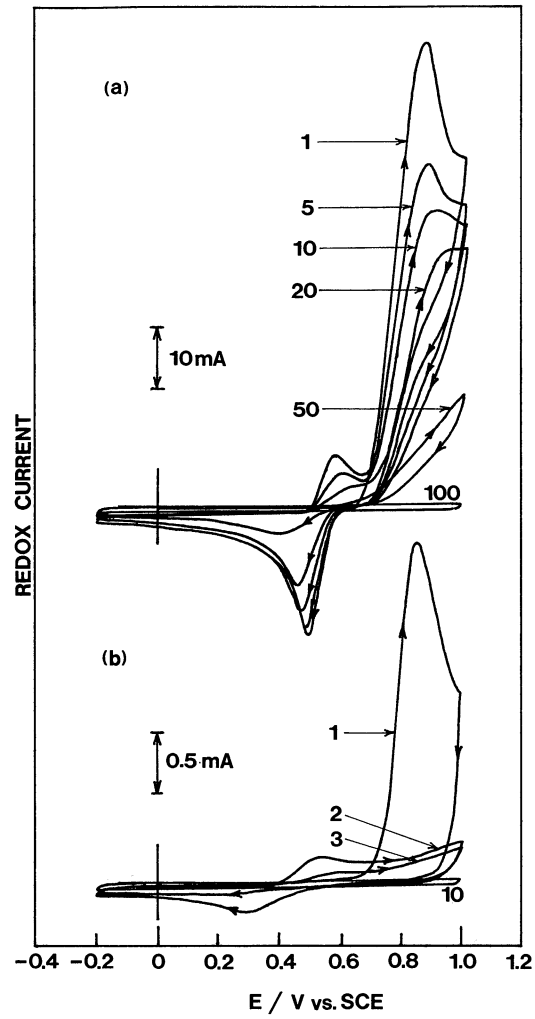

Fig. 1. (a) Cyclic voltammograms in the film forming process of poly(*N*,*N*-dimethylaniline) (PDA). Sweep rate: 50 mV s^{-1}, Solution: 0.5 M *N*,*N*-dimethylaniline+1.0 M HCl, Electrode area: 0.307 cm^2. (b) Cyclic voltammograms in the film forming process of poly(*o*-chloroaniline) (PCA). Sweep rate: 50 mV s^{-1}, Solution: 0.5 M *o*-chloroaniline+1.0 M HCl, Electrode area: 0.311 cm^2. Numbers in the figure indicate the number of potential cycles.

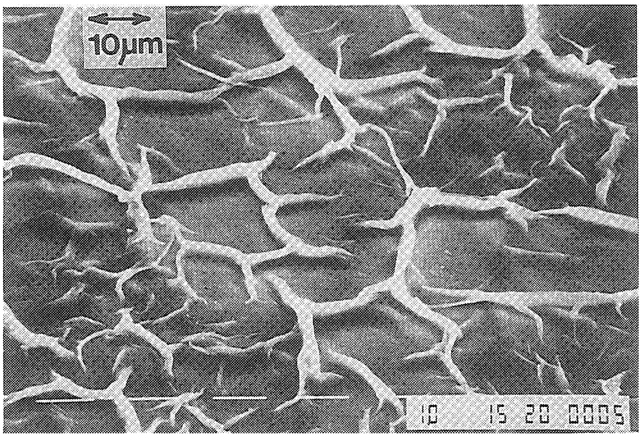

Fig. 2. Scanning electron microphotograph of the surface of the PDA film.

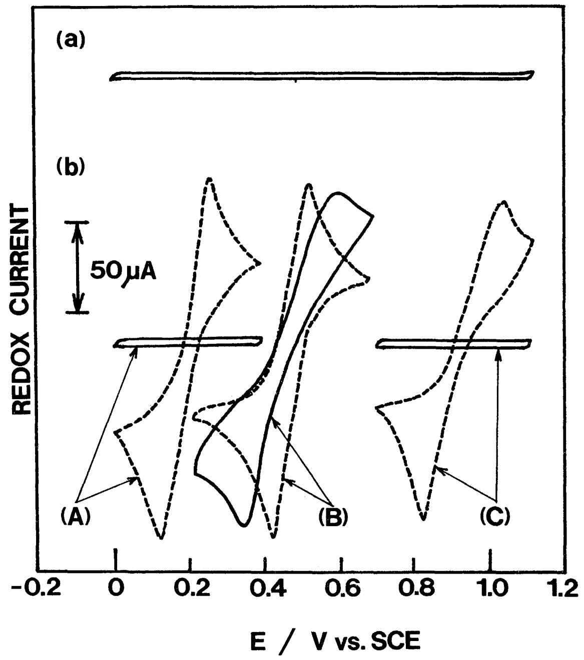

Fig. 3. (a) Voltammogram showing the electroactivity of the PCA film itself in an acetate buffer solution (pH 3.5). Sweep rate: 20 mV s^{-1}. (b) Voltammograms for the redox reactions of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ (A), I_2/I^- (B), and Br_2/Br^- (C) at both a bare platinum electrode (broken line) and the PCA-film coated electrode (solid line). Concentration of the species: $[Fe(CN)_6{}^{4-}]=4$ mM, $[I^-]=[Br^-]=2$ mM, Supporting electrolyte: acetate buffer solution (pH 3.5), Sweep rate: 20 mV s^{-1}.

had a featureless smooth surface. Figure 2 shows a typical morphology of the PDA films. In contrast to the PCA film, it is interesting to clearly observe defined fibrils on a compact microspheroid underlayer of the polymer. The fibril diameter (ca. 3 μm) is greater than that found in polyaniline (ca. 1 μm).[12] In addition, the dry film thickness of PCA and PDA was determined to be ca. 6 μm and 15 μm, respectively, from observations of the cross-sectional morphologies of the films.

Redox Reactions of Dissolved Species on the PCA-Film Coated Electrode. Figure 3 (b) shows voltammograms for the redox reactions of Br_2/Br^-, I_2/I^-, and $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ at both a naked platinum electrode and the PCA-film coated electrode. Although the PCA film is itself electroinactive (see Fig. 3 (a)), the redox wave of only the I_2/I^- is evident. In addition, the PCA-film coated electrode gave no redox waves for Fe^{3+}/Fe^{2+}, *o*-quinone/catechol, *p*-quinone/hydroquinone, MnO_2/Mn^{2+}, and Tl^{3+}/Tl^+.

Insulator-film coated electrodes do not respond to dissolved species unless the films are permeable. The PCA film is probably permeable to dissolved I^- since it is an insulator.[3] In order to confirm this, the RDE voltammograms for the oxidation of dissolved I^- were measured with both the PCA-film coated disk electrode

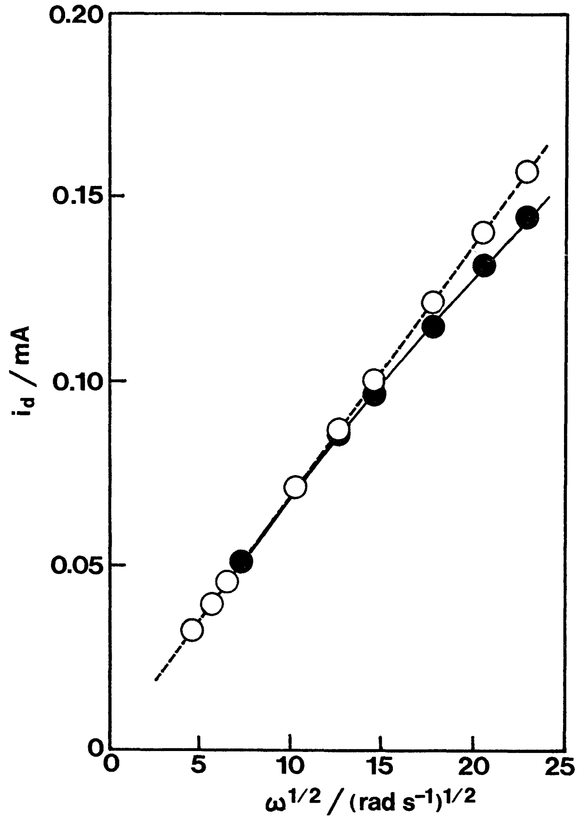

Fig. 4. Plots of the limiting anodic current (i_d) versus the square root of the rotation rate ($\omega^{1/2}$) for the electro-oxidation of dissolved I^- on the PCA-film coated platinum disk electrode (solid line) and a bare platinum disk electrode (broken line). Solution: 0.1 M H_2SO_4 containing 10 mM KI.

and a naked platinum disk electrode. The PCA-film coated electrode was prepared by the same type electrolysis described in Fig. 1 (b). The limiting anodic current (i_d) vs. the square root of the rotation rate ($\omega^{1/2}$) plots obtained are shown in Fig. 4. Deviations of i_d for a PCA-film coated electrode from a linear Levich line obtained with a naked platinum electrode gradually increase with the rotation rate, in particular when $\omega^{1/2}>44.7$ (rpm)$^{1/2}$. This is evidence that the PCA film is permeable to dissolved I^-.[13] Therefore, in the selective response of the PCA-film coated electrode, the charge transfer is caused by the following mechanism. Dissolved I^- permeates through the film selectively and is then electro-oxidized on the platinum substrate.

Redox Reactions of Dissolved Species on the PDA-Film Coated Electrode. Most organic conduting polymers, such as polyaniline, have a redox activity; nonconducting polymers do not show such activity. Practically, a PCA film which has no redox activity is nonconducting and electroinative to dissolved species, except for I^- which can permeate the film. The PDA film also produces no redox waves originating from redox reactions of the film, itself (Fig. 5 (a)).[1] However, a marked difference of PDA film is that the film, itself, is

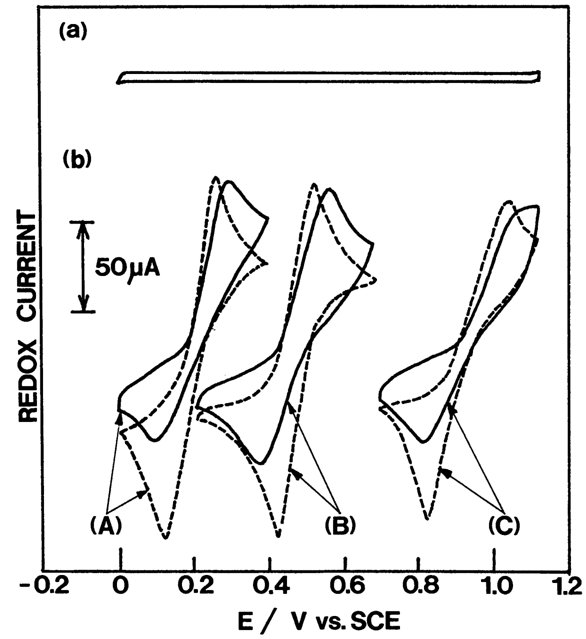

Fig. 5. (a) Voltammogram showing the electroactivity of the PDA film itself in the acetate buffer solution (pH 3.5). Sweep rate: 20 mV s^{-1}. (b) Voltammograms for the redox reactions of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ (A), I_2/I^- (B), and Br_2/Br^- (C) at both a bare platinum electrode (broken line) and the PDA-film coated electrode (solid line). Concentration of the species: $[Fe(CN)_6^{4-}]=4$ mM, $[I^-]=[Br^-]=2$ mM, Supporting electrolyte: acetate buffer solution (pH 3.5), Sweep rate: 20 mV s^{-1}.

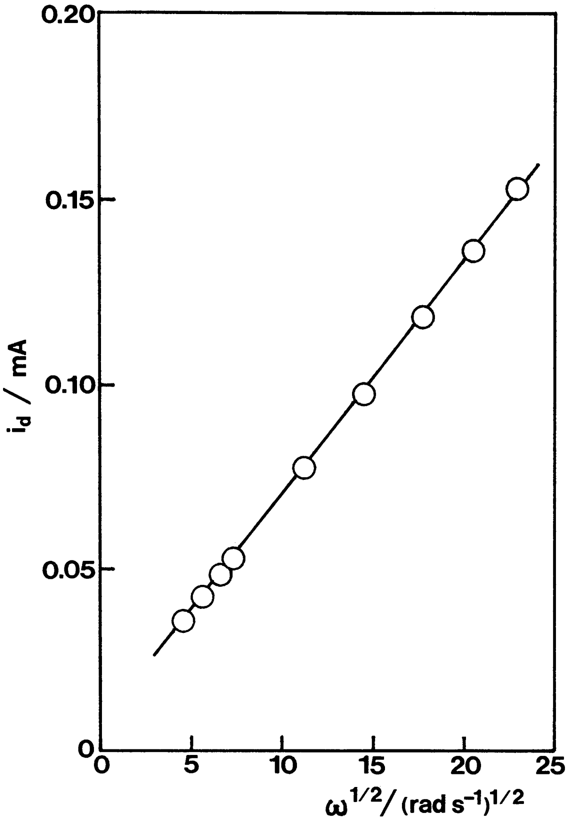

Fig. 6. Levich plots ($\omega^{1/2}$—i_d plots) for the electro-oxidation of dissolved I^- on the PDA-film coated platinum disk electrode. Solution: 0.1 M H_2SO_4 containing 10 mM KI.

electrically conducting.[3] Therefore, a PDA-film coated electrodes is expected to be active towards the electrode reactions of dissolved species. Figure 5 (b) shows voltammograms for the redox reactions of Br_2/Br^-, I_2/I^-, and $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ at both a naked platinum electrode and the PDA-film coated electrode. Although the reversibility of the redox reactions is somewhat poor, compared with that of naked platinum, the PDA film does respond to redox couples. Another characteristics of the PDA film is that the cathodic current of the redox couples is always suppressed with this electrode. A similar behavior was also observed with MnO_2/Mn^{2+}, Tl^3/Tl^+, Fe^{3+}/Fe^{2+}, *p*-quinone/hydroquinone, and *o*-quinone/catechol. Judging from the conductivity, the PDA film is a typical semiconductor. Suppression of the cathodic current may be correlated, at least in part, to a rectification effect of a *p*-type semiconductor. A polyaniline-film coated electrode is active to dissolved redox species only in the limited potential range where polyaniline, itself, is electroactive.[14] The PDA-film coated electrode has no such limitation. The oxidation peaks of Br^-, Mn^{2+}, and Tl^+ were clearly observed with the PDA-film coated electrode, while the polyaniline-film coated electrode was found to be inactive to these species. A nonconducting polyaniline film, which exhibits no redox wave of polymer, itself, shows a limited response towards the redox reactions of dissolved species.[6] The electrochemical response for such a case was observed only for relatively small ions which can permeate through the film. On the other hand, the PDA-film coated electrode was found to be electroactive to all dissolved species studied, regardless of their size and redox potentials.

In order to examine whether the PDA film is permeable to dissolved species in the redox reactions or not, the RDE technique was employed. An iodide ion was used here as being representative of dissolved species. A PDA-film coated disk electrode was prepared by the same type electrolysis process as shown in Fig. 1 (a). By using this electrode, voltammograms for the oxidation of dissolved I^- were measured at different rotation rates from 200 to 5000 rpm. A Levich plot obtained from the voltammograms is shown in Fig. 6. The limiting anodic current is proportional to the square root of the rotation rate, as can readily be seen in Fig. 6. If dissolved species permeate through polymer films and then electro-oxidized on the electrode substrate, Levich plots do not give a straight line.[13] The proportionality shown in Fig. 6 means that such a permeation does not occur; in other words, it is not on the electrode substrate, but on the PDA film that the electro-oxidation of I^- takes place.

A polyaniline-film coated electrode is useful only within a limited pH range.[15] For example, the redox wave of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ is not observed in neutral or alkaline solutions (pH>4). As long as the redox reaction of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple is concerned, the PDA-film coated electrode gave a constant electrochemical response over the entire pH range studied (pH 1—13).

Incorporation of Anionic Redox Species into the PDA Films on Platinum Electrodes. The mechanism of electropolymerization of *N*,*N*-dimethylanilne has yet not been clarified. Various coupling patterns, such as para–para coupling[9] and ortho–para coupling,[11] have been reported. In any case, the resulting PDA films have structures with positively charged sites as quaternary ammonium groups in their polymeric backbones (Fig. 7).

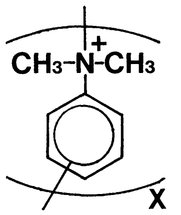

Fig. 7. Possible molecular structure of PDA.

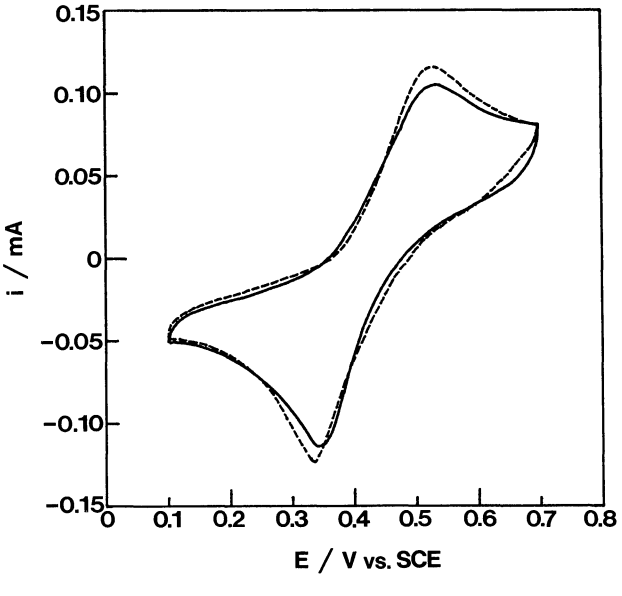

Fig. 8. Redox wave of the I^- incorporated into the PDA film. The broken line indicates the redox wave before the water immersion of one day (see text).

PDA film can incorporate $[Fe(CN)_6]^{4-}$ due to its structure (Fig. 7).[2] Several other multiply-charged anionic redox species can also be incorporated into the PDA film.[16] In order to confirm that the PDA film can incorporate dissolved I^-, the following was carried out. A PDA-film coated electrode was prepared by the same electrolysis method as shown in Fig. 1 (a). After rinsing the deposited PDA layer with water the electrode was immersed in 0.1 M KI aqueous solution for ten minutes.[17] The electrode was rinsed again and then transferred into water for one day. A cyclic voltammogram of the electrode measured in 0.1 M H_2SO_4 is shown in Fig. 8. The redox wave of the I^- incorporated in the film is evident, though the redox charge decreases slightly with water immersion. In this case, the amount of the I^- incorporated in the film was roughly evaluated to be 2.5×10^{-8} mol cm^{-2} by a graphical integration of the voltammogram.

The amounts of Cl^- and I^- ions incorporated into the PDA films were determined by elemental analysis of PDA. Three PDA samples were prepared for this purpose. The first sample (Sample 1) was an original PDA film which was prepared by the electro-oxidation of 1.0 M HCl containing 0.5 M *N*,*N*-dimethylaniline under continuous potential cycling in the range from −0.2 to 1.0 V on the SCE scale. The second sample (Sample 2) was basically the same as Sample 1, but was immersed in a 1 mM KI aqueous solution for one day. The third sample (Sample 3) was also the same as Sample 1, but was immersed in a 1 mM I_2 aqueous solution for one day. All of the samples were scratched off from the electrode substrate and washed with water sufficiently. They were dried in vacuo at 50 °C for 12 h and subjected to elemental analysis. The obtained results are summarized in Table 1. Although the data lack precise consistency, it is undoubted that the PDA film has anion exchangeability. The original PDA film (Sample 1), which was analysed just after preparation in a 1.0 M HCl solution, contained Cl^- ions with an atomic ratio of roughly 0.6 with respect to the nitrogen content. Hand and Nelson have reported that the electro-oxidation of *N*,*N*-dimethylaniline gives such secondary amines as *N*-(*p*-dimethylaminobenzyl)-*N*-methylaniline, as well as *N*,*N*-dimethylanilines.[18] The atomic ratio

Table 1. Elemental Composition of PDA

Sample	Treatment	Elemental composition				
		C	H	N	Cl	I
1	As prepared in HCl[a]	8	10.79	1.07	0.61	
2	1 was immersed in a KI solution[a]	8	10.34	1.06	0.02	0.58
3	1 was immersed in an I_2 solution[a]	8	12.62	1.04	0.43	0.20

a) For details, see text.

being less than unity is probably due to the presence of tertiary amino groups in the polymeric backbone. The data from Sample 2 is evidence regarding the anion exchangeability of the PDA film. The Cl^- ions in the PDA film are almost replaced by I^- ions after immersing the film in a KI aqueous solution, although only a few Cl^- ions still remain. It is noteworthy that not only I^-, but also I_2, which is electroneutral, is incorporated into the PDA film (see the data of Sample 3).

Selective Potential Response of a PDA/PCA Dual-Layer Coated Electrode to Dissolved Iodide Ions. As described previously, dissolved I^- can be incorporated in a PDA-film coated electrode and then electro-oxidized to generate oxidized products of I^-. If these products still remain in the electrode, the electrode will show a potentiometric response to dissolved I^-. Further, if the electrode responds to only I^- by coating the PDA layer with a PCA layer, it is applicable to potentiometric sensing of dissolved I^-.

The PDA/PCA dual-layer coated electrode for potentiometric sensing of I^- was prepared by means of the following. Initially, a PDA-film coated electrode was prepared under the same electrolytic condition as shown in Fig. 1 (a). After adequate rinsing of the electrode with water, the electrode was immersed in an aqueous 0.1 M KI solution for ten minutes. Coating of the PCA film on the electrode was next performed under the same conditions as shown in Fig. 1 (b). The PDA/PCA dual-layer coated electrode obtained was finally held at 0.7 V vs. SCE for five minutes in 0.1 M H_2SO_4 to change the incorporated I^- into its oxidized products. Figure 9 (a) shows the potential response of a bare platinum electrode, a PDA-film coated, and a PDA/PCA dual-layer coated electrode to dissolved I^-. Both the PDA-film coated electrode and the PDA/PCA dual-layer coated electrode have a Nernstian response to I^-, with the slope of -56 mV/log$[I^-]$. This potential response is evidence that the oxidized products of I^- still remain in the PDA layer. The products seem to be I_2 and a little I_3^-, judging from the slope.

Figure 9 (b) shows the effect of interfering substances on the potential response. The interfering substance in this case is the redox pair of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$. The PDA/PCA dual-layer coated electrode obviously has the potential response, while the PDA-film coated electrode itself without the PCA-layer coating has no such response. The response of the PDA/PCA dual-layer

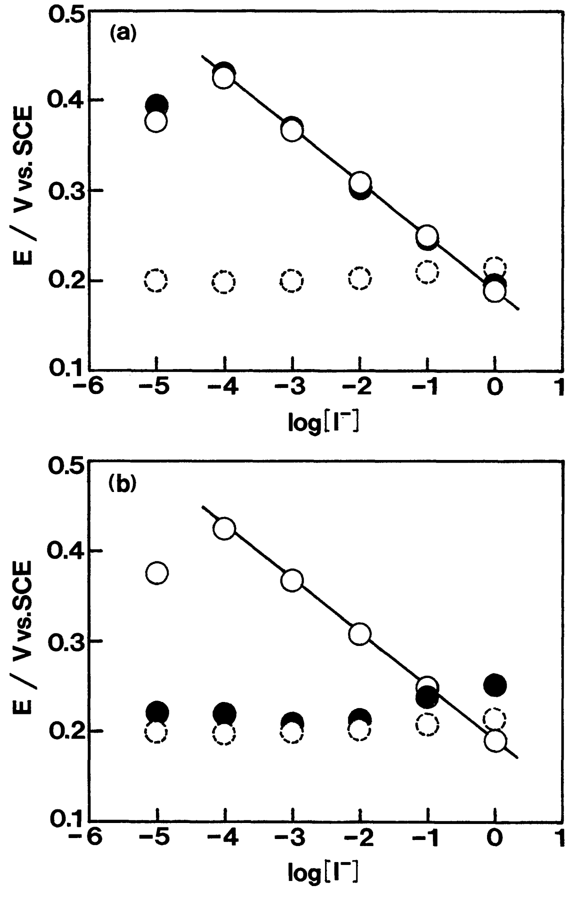

Fig. 9. (a) Potential response of a bare platinum electrode (◌), the PDA-film coated electrode (●), and the PDA/PCA dual-layer coated electrode (O) with changes in log$[I^-]$ from -5 to 0. Solution: acetate buffer solutions containing KI (pH 3.5). The response time of the PDA-film coated electrode and the PDA/PCA dual-layer coated electrode were less than ten seconds. (b) Effect of interfering substance on the potential response of (a). The interfering substance was the redox pair of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$. Solution: acetate buffer solutions containing not only KI but also 10 mM $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$.

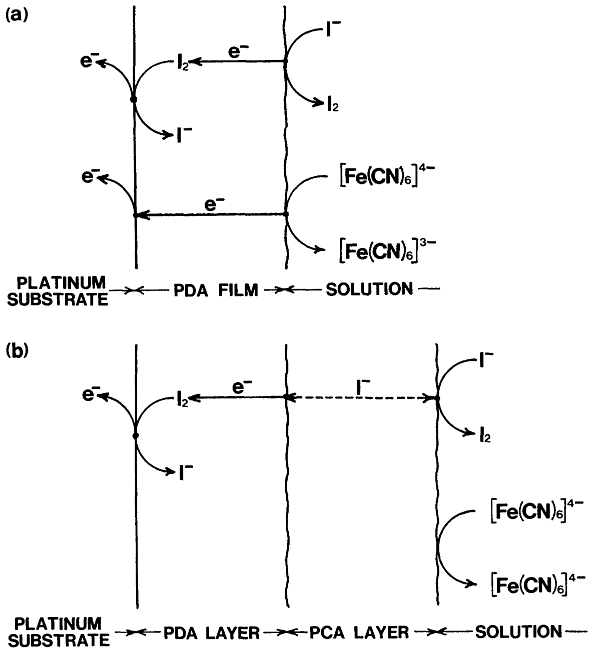

Fig. 10. Schematic depiction of the response mechanisms of dissolved I^- on the PDA-film coated electrode (a) and the PDA/PCA dual-layer coated electrode (b).

coated electrode was not disturbed by the presence of Fe^{3+}/Fe^{2+}, *p*-quinone/hydroquinone, and $Fe(edta)^-$/$Fe(edta)^{2-}$ and by a change of the solution pH, although they are not illustrated in Fig. 9 (b).

Figure 10 is a schematic depiction explaining how a PDA-film coated electrode and a PDA/PCA dual-layer coated electrode respond to dissolved I^-. In the case of the PDA-film coated electrode, the charge transfer between the oxidized products of I^- in the film and dissolved I^- can occur spontaneously. The oxidized product is regarded as being I_2 in this case. Consequently, the electrode has a Nernstian response to dissolved I^-. The reason why the electrode, itself, does not have a selective potential response is that the PDA film is electrically conducting, as is the electrode substrate. Charge transfer between other redox couples, such as $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$, takes place on the electrode as well, and the response of I^- is disturbed (Fig. 10 (a)). This disturbance can be repressed by a coating with a PCA layer. The PCA layer blocks the permeation of other dissolved species than I^-. As a result, the PDA/PCA dual-layer coated electrode shows a selective potential response to dissolved I^- (Fig. 10 (b)). For $[I^-]<10^{-5}$ M, it does not give a response anymore. However, this limitation might be improved by changing the amount of oxidized products of I^- in the PDA layer, the thickness of the respective layers, and so on.

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