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Selective Nernstian Response of Poly(N,N-dimethylaniline) / Poly(o-chloroaniline) Dual-layer Coated Electrode to Dissolved Iodide Ion

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Poly(N,N-dimethylaniline)(PDA) is a semiconductor having positively charged sites in the polymeric backbone. A PDA coated electrode can capture I^- electrostatically and the I^- in the PDA film can also be oxidized electrochemically. Poly(o-chloroaniline)(PCA) responses to dissolved I^- selectively, though it is quite an insulator. A PDA / PCA dual-layer coated electrode shows selective Nernstian response to dissolved I^-.

If a polymer coated electrode responses to a certain dissolved ion selectively, it would be useful to various fields as a new-type ion sensor. The sensor would also have some advantage as compared with conventional ion-selective electrodes, because it can be prepared in arbitrary shape, in particular for miniaturization. But there are not many studies on the polymer coated electrodes for the sensor like that. Ohnuki et al. reported that selective film permeation of H^+, Br^-, and Fe^{2+} was observed in a few polymer coated electrodes.1) The electrodes are sure to act as an amperometric sensor for them. On the other hand, poly(o-phenylenediamine) coated electrode may be applicable to voltammetric pH measurements.2,3) In the studies up to now, the kinds of dissolved ions to be measured, coating polymer materials and so on have been limited. We would like to show a unique sensor of dissolved I^- using the poly(N,N-dimethylaniline)(PDA) / poly(o-chloroaniline)(PCA) dual-layer coated electrode. PDA can capture redox anion species electrostatically due to its structure with positively charged sites as quaternary ammonium groups in the polymeric backbone.4) PCA responses to only I^-, though it is quite an insulator.5) The PDA / PCA dual-layer coated electrode is expected to be a selective voltammetric sensor of dissolved I^-.

Cyclic voltammogram in a film forming process of PDA onto a Pt electrode is shown in Fig.1 (a). As soon as much oxidative current of N,N-dimethylaniline flowed at around 0.85 V in the first cycle, red powdery product was observed near the surface of the Pt electrode. While potential cycling was repeated, the product went on diffusing from the surface to the bulk. However, after about 180 cycles, deposition of a brown polymer film on the surface was clearly seen. The potential cycling was further continued up to 300 cycles for preparation of the PDA coated electrode. In Fig.1 (a), two anodic peak potentials shift more positively

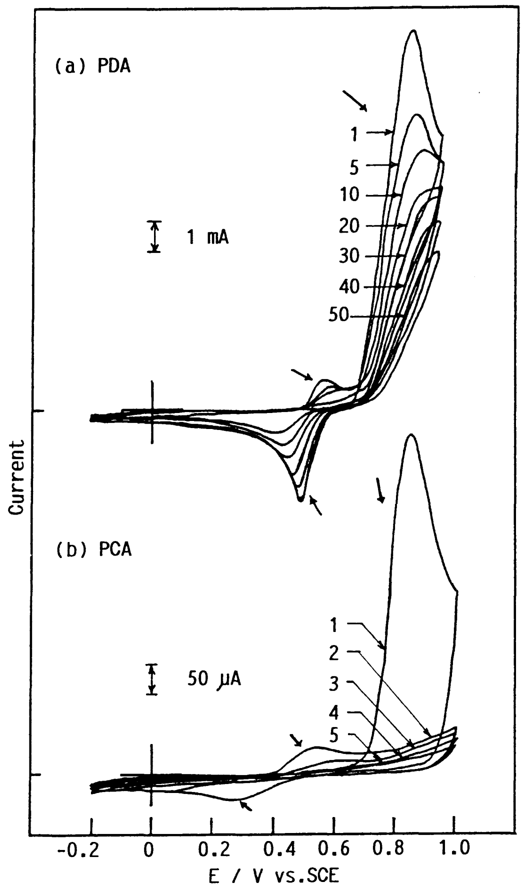

Fig.1. Cyclic voltammograms in the film forming process of PDA (a) and PCA (b). Numbers in figure indicate the number of potential cycle. Sweep rate: 0.1 V s^{-1}, Working electrode: Pt wire (ca.0.3 cm^2), Concentration of the monomer: 0.1 M, Supporting electrolyte: 0.2 M HCl. (1 M = 1 mol dm^{-3})

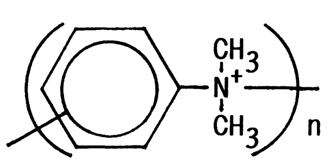

Fig.2. Possible unit structure of PDA.

and the cathodic one more negatively, as the number of cycles increases. This is probably due to iR drop of the growing PDA film. In fact, the conductivity of PDA in dry state was determined to be 6.2×10^{-6} S cm^{-1} by the four point probe method.6) In a coating process of PCA film, Fig.1 (b), anodic peak current for the oxidation of o-chloroaniline diminishes immediately to the first five cycles. This means that the resulting PCA film is quite an insulator.

We have already reported that PDA can capture $[Fe(CN)_6]^{4-}$ because of its structure illustrated in Fig.2.4) Some other multiply-charged anionic redox species can also be incorporated into PDA.7) In order to confirm that PDA can capture dissolved I^-, we carried out the following. After rinsing of the deposited PDA layer with water, the electrode was immersed in 0.1 M KI aqueous solution for ten minutes.8) The electrode was rinsed again and transferred into water for one day. The voltammogram of the electrode which was measured in 0.1 M H_2SO_4 showed the redox wave of I^- distinctly. In this case, the amount of I^- captured into the PDA film was evaluated to be 2.5×10^{-8} mol cm^{-2} by the graphical integration of the voltammogram. It is noticed that the I^- captured is possible to be oxidized electrochemically and the oxidized products, I_2 or partly I_3^-, still remain in the film. The electrode shows the Nernstian response to dissolved I^- as shown in Fig.4. The response was not disturbed by the change of solution pH, as pointed out by Oyama et al.9)

Figure 3 (b) shows the 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 Pt electrode and the PCA coated electrode. Although the PCA film itself is electroinactive (see Fig.3 (a)), the redox wave of the only I_2/I^- is recognized obviously, as can readily be seen from this figure. In addition, the PCA coated electrode gave no redox waves of MnO_2/

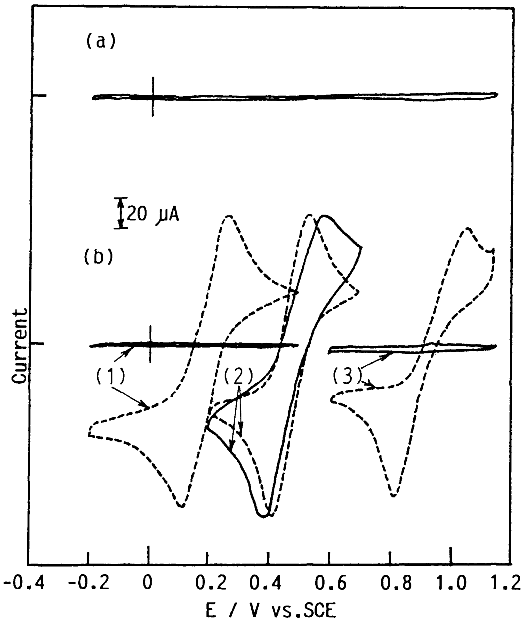

Fig.3. (a) Voltammogram showing the electroactivity of the PCA film in acetate buffer solution (pH 3.5). (b) Voltammograms for the redox of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ (1), I_2/I^- (2), and Br_2/Br^- (3) at both a bare Pt electrode (------) and the PCA coated electrode (———). Concentration of the 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}.

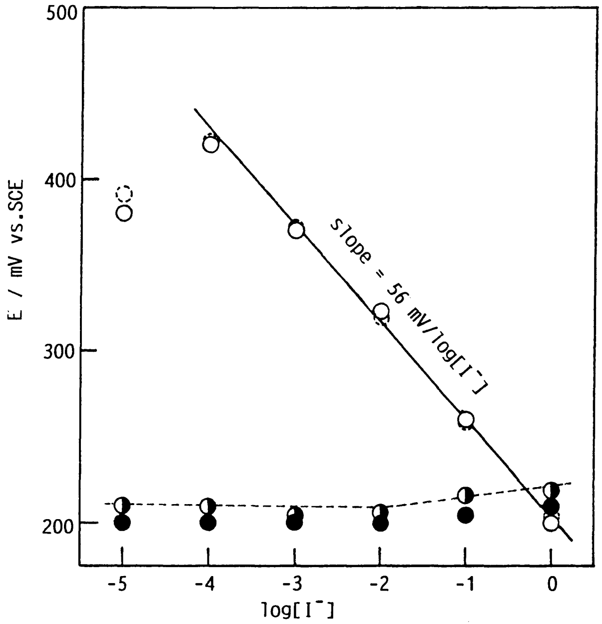

Fig.4. Potential response of a bare Pt electrode (●), the PDA coated electrode (◑,◌), and the PDA / PCA dual-layer coated electrode (○) with changes in log$[I^-]$ from -5 to 0. Each solution contained 10 mM $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ except for ◌. The response time of the PDA / PCA dual-layer coated electrode is less than five seconds.

Mn^{2+}, Tl^{3+}/Tl^+, Fe^{3+}/Fe^{2+}, p-quinone/hydroquinone, and o-quinone/catechol, though we did not draw them in Fig.3 (b). It is noteworthy that the voltammogram of Br^- whose size is smaller than I^- is hardly observed. If the redox reaction of I_2/I^- took place on the Pt substrate not on the PCA film, in other words, I^- permeated through the PCA film, the redox wave of Br_2/Br^- could also be observed. Perhaps some interactions between the film and I^- such as the formation of the charge transfer complex may make the film conducting and further experiments will be needed to know the mechanism of the charge transfer. Anyway the PCA coated electrode responses only to dissolved I^-. However, this electrode does not show the Nernstian response to dissolved I^- without the presence of dissolved I_2, because the PCA film cannot capture I^- and its oxidized products.

A PDA / PCA dual-layer coated electrode for voltammetric I^- sensing was made by means of the following. The PDA coated electrode prepared under the condition like Fig.1 (a) was immersed in aqueous 0.1 M KI solution for ten minutes. After adequate rinsing of the electrode with water, the coating of the PCA film on it was next performed under the condition of Fig.1 (b). This electrode was held at 0.7 V vs. SCE for five minutes in 0.1 M H_2SO_4 to make I^- captured its oxidized products. Figure 4 shows potential response of a bare Pt electrode, the PDA coated electrode, and the PDA / PCA dual-layer coated electrode to dissolved I^-. The PDA coated electrode itself without the PCA coating has the Nernstian response (—◌—) but the response is disturbed by the presence of a $[Fe(CN)_6]^{3-}$/ $[Fe(CN)_6]^{4-}$ couple (---◑---). As expected, the PDA / PCA dual-layer coated electrode shows the selective Nernstian response (—○—). Iodine species incorporated into the film seem to be I_2 and a little I_3^-, judging from the slope value in Fig.4. This response is not influenced by the presence of other redox couples such as Br_2/Br^-, Fe^{3+}/Fe^{2+}, and p-quinone/hydroquinone and the change of solution pH, though we did not illustrate them in Fig.4. In $[I^-]<10^{-5}$ M, this electrode does not give the potential response anymore. However, we believe that the limitation would be improved by changing the amount of I^- captured in the PDA film, the thickness of each film and so on. Further, if we found out polymer films having the selective response to a certain ion, the ion-selective sensor consisting of PDA / the polymer dual-layer coated electrodes could be prepared in the same way.

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