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Electrochemical Behavior of Polypyrrole Deposited on Nafion-coated Electrodes

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Anodic polymerization of pyrrole at Nafion-coated ITO or Au electrodes gives a polypyrrole-Nafion co-polymer film at the Nafion/electrode substrate interface. Sulfonate groups of Nafion and not the electrolyte anions are involved in the polymerization process. The redox reaction of the resulting polymer film occurs more easily than that of polypyrrole films prepared on the naked electrode substrate.

Polypyrrole films prepared by electrochemical oxidation of pyrrole show electrochemical redox behaviors in both aqueous[1,2] and non-aqueous[3] solutions with involvement of electrolyte anions. The redox behaviors are influenced by the kind of solvent[4] and electrolyte anions.[5,6] Recently, Fan and Bard[7] have reported the preparation of polypyrrole films in ionically conductive matrices of Nafion and the clay, hectorite, in acetonitrile solutions. They suggested that sulfonate groups of Nafion are involved in the polymerization of pyrrole to give a co-polymer, but the structure of the prepared film as well as the redox behaviors of the prepared film itself have not been reported in detail. Here, we would like to report this subject. According to our results, the co-polymer prepared in aqueous solutions exhibits higher activities for the film redox process than polypyrrole alone.

Indium-tin-oxide coated glass (ITO) and Au plates were used as the electrode substrates. Aldrich Nafion 117 (equivalent weight 1100, 5 wt% dissolved in a mixed solution of alcohol and water (9:1)) was applied onto ITO or Au plate in several times to give the total amount of 24 µl. The evaporation of the solvents in air resulted in Nafion films of ca. 2.5 μm thickness. Anodic polymerization of pyrrole was carried out under N_2 atmosphere at 0.3 mA cm^{-2} in an aqueous solution containing 0.1 mol dm^{-3} pyrrole and 0.2 mol dm^{-3} NaCl.

SEM observations revealed that the polypyrrole deposition gave a brown-black polymer film of an uniform thickness in the Nafion layer at the Nafion/electrode substrate interface as shown in Fig. 1. The thickness of the resulting polymer film was of course dependent on the quantity of charges consumed in the anodic polymerization of pyrrole. The deposited polypyrrole was homogenized well with Nafion to give a co-polymer, and no appreciable isolation of these two polymers was seen in the produced polymer films.

It is well known that electrolyte anions are incorporated in polypyrrole films when they are prepared by anodic polymerization of pyrrole.$^{8)}$ This was not the case, however, for the deposition of polypyrrole on the Nafion-coated conductive substrate. The presence of chlorine was confirmed by energy dispersive electron probe X-ray microanalysis for polypyrrole deposited on naked ITO and Au, but the analysis showed that chlorine was absent when polypyrrole was deposited on the Nafion-coated electrodes. This finding together with the finding that polypyrrole was homogenized well with Nafion seem to suggest that sulfonate groups of Nafion were involved in anodic polymerization of pyrrole, as suggested by Fan and Bard.$^{7)}$

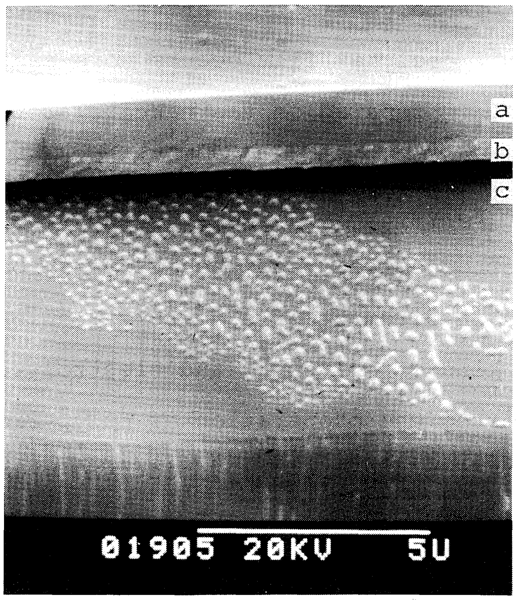

Fig. 1. Cross-sectional view of polypyrrole deposited on Nafion-coated electrode. The quantity of charge used in the film preparation was 90 mC cm^{-2}.

a) Nafion film
b) Polypyrrole-Nafion co-polymer
c) ITO substrate.

Cyclic voltammograms of polypyrrole deposited on Nafion-coated Au (PPy-Nafion/Au) electrodes in an aqueous solution containing 0.2 mol dm^{-3} NaCl was shown in Fig. 2 together with those of polypyrrole deposited on naked Au (PPy/Au) electrodes. It is seen that well-defined anodic and cathodic waves appeared at the PPy-Nafion/Au electrode, while broad peaks appeared at the PPy/Au electrode, as have been reported by many investigators.[4,9]

The broadness of the cyclic voltammogram of PPy/Au is due to a slow diffusion of electrolyte anions in the polymer film,[4] and the redox potential of the anion doping and undoping process is not precisely determined from the voltammograms of PPy/Au electrodes. The redox potential for the film redox reaction, however, can be more easily determined for PPy-Nafion/Au electrodes. Since the anodic and cathodic peak potentials are -0.345 V and -0.405 V vs. SCE, respectively, -0.375 V vs. SCE is derived as this redox potential.

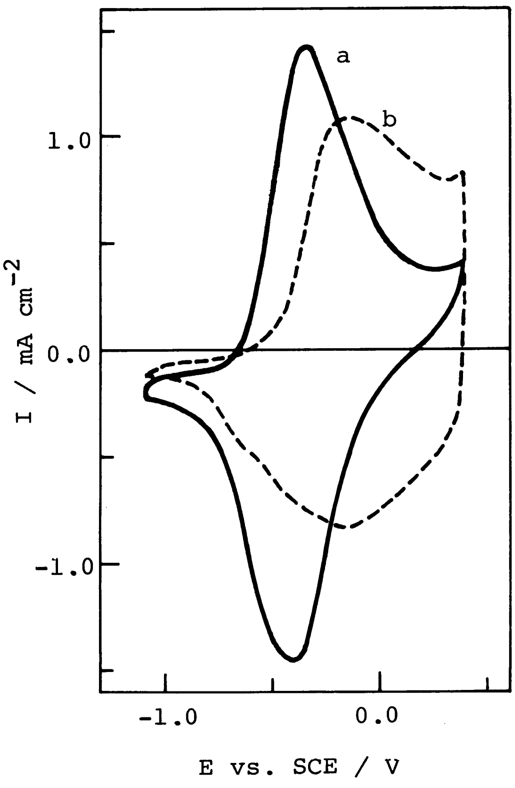

Fig. 2. Cyclic voltammograms of (a) PPy-Nafion/Au and (b) PPy/Au electrodes in 0.2 mol dm^{-3} NaCl aqueous solution. Scan rate: 100 mV s^{-1}. The quantity of charge used in the film preparation was 90 mC cm^{-2}.

The gain of the sharpness of the voltammogram at the PPy-Nafion/Au electrodes seems to suggest that the nature of the redox process is quite different from that at PPy/Au electrode. Since sulfonate groups of Nafion must be involved in the polypyrrole deposition at the Nafion-coated electrode as described above, and these groups cannot be eliminated during the course of reduction of the resulting co-polymer films, another reaction must take place to keep electrical neutrality on the reaction of the co-polymer. We propose that electrolyte cations (Na^+) are inserted into co-polymer film when the film reduction occurs, and that the inserted cations are dissolved out on reoxidation of the film. The involvement of chloride anions seems unlikely, because they were absent in PPy-Nafion/Au electrodes. The appearance of well-defined voltammetric waves at the PPy-Nafion/Au electrodes must be due to a larger mobility of cations in the Nafion film.10) Apparent diffusion coefficient of electrolyte ions which are involved in the film redox process was determined by chronocoulometry with application of a potential pulse of -1.1 V and +0.45 V vs. SCE. The determined apparent diffusion constant was 5.5×10^{-8} cm^2 s^{-1} for PPy-Nafion/Au electrodes while that of PPy/Au was 3.4×10^{-10} cm^2 s^{-1}, the latter being agreement with the reported value.4) The observed difference in the apparent diffusion constant seems to fit well in explaining higher activity of PPy-Nafion/Au electrode for the redox reaction of the polymer film itself.

References

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