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Electroactivity Change of Electropolymerized Polypyrrole/ Polystyrenesulfonate Composite Film in Some Organic Electrolytes

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Electroactivity of polypyrrole/polystyrenesulfonate composite film obtained from an aqueous solution was examined in various organic electrolytes. The composite film worked like electroinactive film in electrolyte using propylene carbonate or some solvents except in the case of DMF or DMSO electrolytes, however, the film changed from electroinactive to electroactive even in propylene carbonate and some organic electrolytes after an electrochemical potential application to the film while in DMF or DMSO electrolytes.

In recent years, electropolymerized conducting polymers show promise for various kinds of applications, such as battery cathodes, electrocatalysts, etc.[1)] Most electropolymerized conducting polymers are p-type materials which are oxidized or reduced through the insertion or removal of anion to compensate the film charges. Shimidzu *et al.* have indicated that the p-type polymer film with fixing polyanion works as an n-type polymer in appearance because cation penetrated from the electrolyte compensates the electroneutrality of the film.[2)] When using this composite material as a cathode, the lithium secondary battery does not need a large volume electrolyte solution due to the fact that there is no change of electrolyte concentration during charging and discharging.[3)]

Since metal salts of polyanion are usually able to dissolve only in aqueous electrolyte, not in organic ones, the polypyrrole composite film with polystyrenesulfonate (PPy/PSS) could be formed only from an aqueous solution containing pyrrole and poly(sodium 4-styrenesulfonate) by electro-oxidation onto a Pt substrate. For the purpose of applying the film to a lithium battery cathode, we have to use organic electrolytes with a process to exchange the electrolyte and remove the water solvated in the film. The composite film showed good electroactivity in an aqueous electrolyte containing $LiClO_4$ as shown in Fig. 1a; however in the propylene carbonate (PC) electrolyte, the composite film became electro-inactive as shown in Fig. 1b.

On the contrary, in the organic electrolyte of 1.0 mol dm^{-3} $LiClO_4$ / dimethylfolmamide (DMF) electrolyte, the film showed high electroactivity after applying 2.0 V vs. Li/Li^+ potential to the film. When the 2.0 V was applied, cathodic current was observed initially, and it disappeared in a few seconds as shown in Fig. 2a. Figure 2b shows the cyclic voltammograms after 2.0 V application, where high-reversibly faradaic waves appear at around *ca.* 3.0 V vs. Li/Li^+. The reversible currents are attributed to the redox reactions of polypyrrole with ion doping-undoping in the composite film.

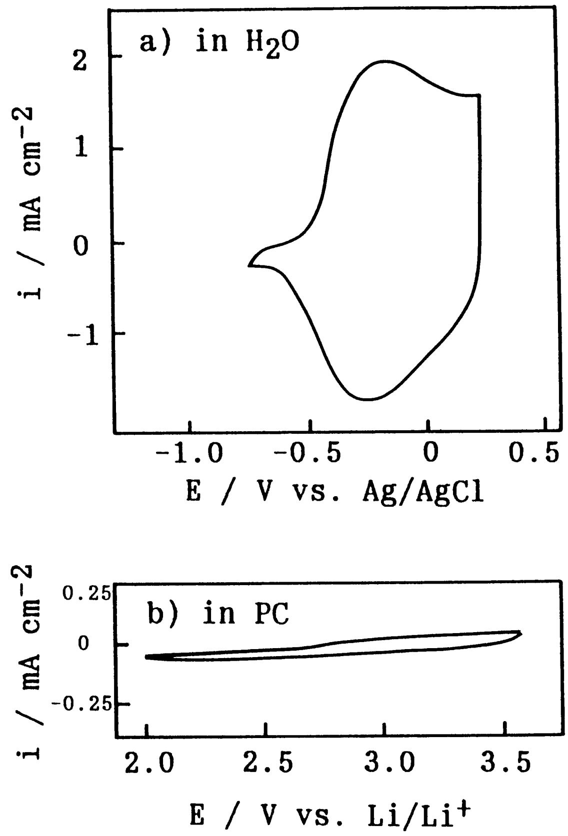

Fig. 1. Cyclic voltammograms of PPy/PSS composite films at 20 mV s^{-1}. Electrolytes were a) H_2O and b) PC containing 1.0 mol dm^{-3} $LiClO_4$. The films were prepared from 0.25 mol dm^{-3} pyrrole and 0.5 mol dm^{-3} SO_3^- unit of PSS-Na / H_2O at 0.75 V vs. Ag/AgCl with 0.5 C cm^{-2}.

Such a phenomenon is observed not only with the PPy/PSS composite film but also with small anion-doped polypyrrole film such as PPy/ClO_4^-, which is prepared from an aqueous solution containing pyrrole monomer and $LiClO_4$. In order to investigate the effect of such electrolyte solvents on the electroactivity of the PPy/PSS film, the electrochemical behavior of the PPy/PSS film obtained from an aqueous solution was examined in various organic electrolytes. Sulfolane (SL) (acceptor number AN=19.3), dimethylsulfoxide (DMSO) (donor number DN=29.8) and dimethylacetoamide (DMA) having physical properties similar to those of DMF (AN=16.0), were selected as electrolyte solvents. In the electrolytes using DMA and SL, the composite film showed electroinactivity, but in the DMSO electrolyte the film showed a particular phenomenon which is exhibited in Fig. 3a. The faradaic currents due to the reversible redox reaction of polypyrrole gradually grew with potential cycling and reached a stable state as shown in the figure. In Fig. 3a, low cathodic current at the lower potential region under 2.5 V vs. Li/Li^+ decreases with cycling and finally disappears. At the same time the reversible redox currents of polypyrrole, at the potential of around 3.0 V, reach a stable state. In the cyclic voltammograms obtained in the DMF electrolyte a similar phenomenon occuring in the DMSO electrolyte was observed when the potential was cycled between 2.75 V and 3.55 V vs. Li/Li^+. Figure 3b shows a current-potential curve of Pt electrode in the DMSO electrolyte containing a small amount of H_2O, where the potential is scanned to a negative direction. In Fig. 3b, the cathodic current is observed in the potential range under 2.5 V vs. Li/Li^+ and usually the current does not appear in the DMSO electrolyte. Therefore the cathodic current observed under 2.5 V in Fig. 3a is assigned to the reduction of H_2O in the film. When considering the growth of polypyrrole electroactivity with the disappearing cathodic current, electroactivity of polypyrrole in the organic electrolytes may be enhanced by removing the solvated H_2O in the film where the active site is surrounded by an H_2O molecule. From these results, it is suggested that the DMSO electrolyte has an intermediate performance against PPy/PSS film between PC and DMF electrolytes.

Similar enlargement of redox

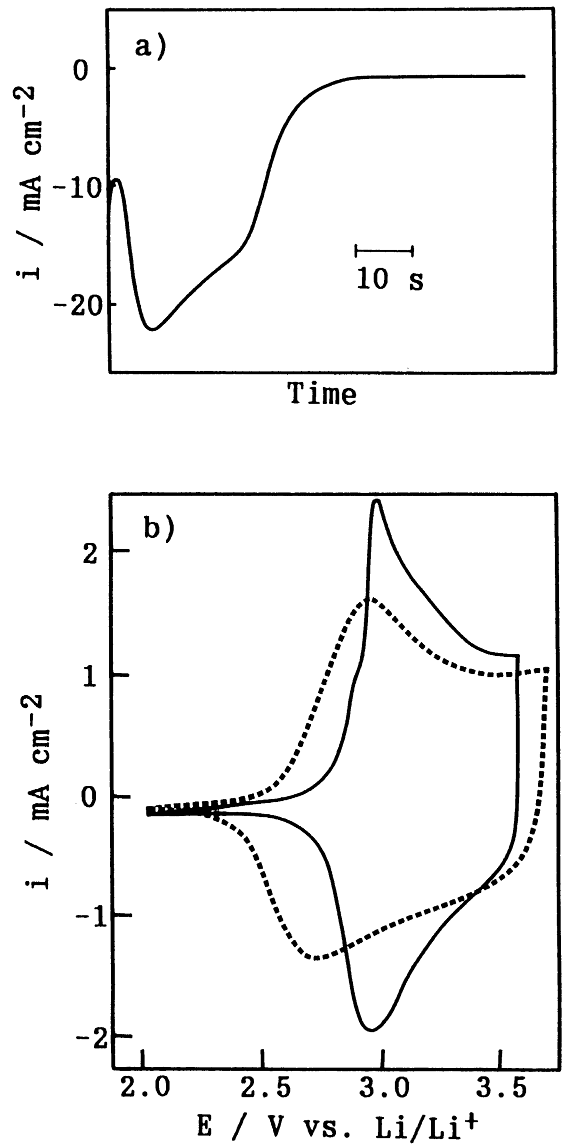

Fig. 2. a) Cathodic current change on PPy/PSS film while applying 2.0 V vs. Li/Li^+ in DMF electrolyte.

b) Cyclic voltammograms of PPy/PSS film at 20 mV s^{-1} in organic electrolyte containing 1.0 mol dm^{-3} $LiClO_4$. The solid and dotted lines are obtained in DMF and PC electrolytes, respectively. The composite films were formed at 0.55 V vs. Ag/AgCl with 0.5 C cm^{-2} from 0.1 mol dm^{-3} SO_3^- unit of PSS-Na polymerization solution.

currents in the cyclic voltammetry of polymer coated electrode, where redox active species is involved, was reported by Anson *et al.*[4] In such a case, the enhanced electroactivity of the thin film coated electrode was caused by increasing electroactive species penetrated. However in the case of polypyrrole, the electroactive species were located on the electrode substrate and only the environment of the electroactive sites could be altered.

In conclusion, the electroactivity of the PPy/PSS films deposited by aqueous solutions is electroinactive in PC electrolyte as-deposited state. After reducing H_2O, while applying cathodic potential in suitable organic electrolytes, the film shows good electroactivity. Such an electrochemical method of exchanging solvent in the film may be useful in the organic solution for the use of electropolymerized film obtained from an aqueous solution.

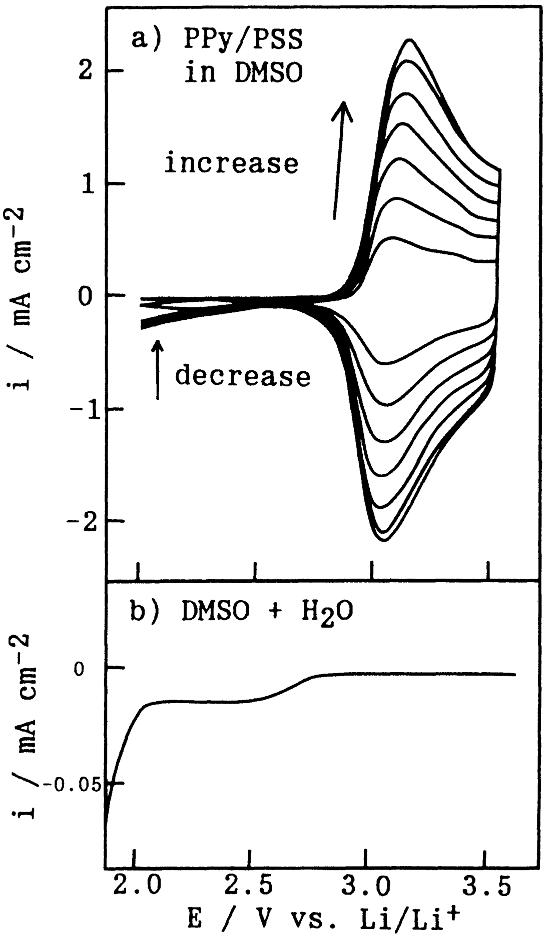

Fig. 3. a) Cyclic voltammograms of PPy/PSS composite film at 20 mV s^{-1} in DMSO electrolyte containing 1.0 mol dm^{-3} $LiClO_4$. The composite films were formed at 0.55 V vs. Ag/AgCl with 0.5 C cm^{-2} from 0.1 mol dm^{-3} SO_3^- unit of PSS-Na polymerization solution.
b) Current vs. potential curve of Pt at 10 mV s^{-1} in DMSO electrolyte with an addition of 1 v/o water.

References
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