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Polypyrrole/Polymer Electrolyte Bilayer Composites Prepared by Electrochemical Polymerization of Pyrrole Using Ion-Conducting Polymers as a Solid Electrolyte

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The electrochemical polymerization of pyrrole using ion-conducting polymers as a solid electrolyte produces polypyrrole/polymer electrolyte bilayer composites in situ. The bilayer composites show electrochemical activity, corresponding to doping and undoping reactions, in solid state.

Polymer electrolyte (solvent-free ion-conducting polymers) is a new kind of solid electrolyte.1) Much interest has been focused on fast ion-transport in polymers and further on potential application as solid electrolytes in primary or secondary solid-state-batteries.2) Most of the polymer electrolytes ever studied are solid solutions of salts in polymers, and both cation and anion are mobile in them. Ionic conductivity of highly conductive polymer electrolytes reaches 10^{-5} S cm^{-1} at room temperature.1)

A unique and interesting property of polymer electrolytes, which is not attained by inorganic solid electrolytes such as Na-β-alumina and Ag_4RbI_5, may be the ability to include various kinds of electroactive molecules in them. The combination of this property with their high ionic conductivity will enable us to use polymer electrolytes as media for electrochemical reactions of the electroactive molecules, as we use electrolyte solutions for this purpose. Skotheim has shown3) that use of polymer electrolytes allows both electrochemical synthesis of conducting polymers and investigation of their redox activity in situ under ultra-high vacuum with the assistance of photoelectron spectroscopy techniques. We found first here that electrochemical polymerization of pyrrole using ion-conducting polymers as a solid electrolyte produced polypyrrole/polymer electrolyte bilayer composites in situ. Electronic conductivity of the polypyrrole layer reached 10^1-10^2 S cm^{-1} at room temperature, and the bilayer composites showed electrochemical activity in solid state.

Polymer electrolytes used were network polymers from poly(ethylene oxide) (PEO) triol and 3-methyl-1,3-phenylene diisocyanate, in which several kinds of alkali metal salts were dissolved.4) With respect to the functional groups (-OH and -NCO), stoichiometric amounts of PEO triol (number average mol. wt. = 3000) and the diisocyanate were mixed, cast on glass substrates, and allowed to react under nitrogen atmosphere at 80 °C for 96 h. Unreacted precursors were removed from the network polymers by extraction with acetone. After the complete avaporation of the solvent, network polymer films of about 0.3 mm thickness were obtained. The dissolution of alkali metal salts in the network polymers was performed by an immersion method using salt solutions. The concentration of salt in a network polymer film was determined from the weight change of a dried film before and after the immersion. Preparative method of the polymer electrolytes is described elsewhere.[4)] Polymer electrolyte films of 1.3 cm^2 area were used for polymerization. Pyrrole was incorporated into the polymer electrolytes by adsorption of gaseous monomer or its direct absorption from a microsyringe. A polymer electrolyte film containing pyrrole was sandwiched between two indium-tin oxide coated glass plates under an appropriate pressure, in order to ensure the contacts between electrodes and an electrolyte. Electrochemical polymerization was carried out in galvanostatic conditions. Ionic conductivity of the polymer electrolytes was determined by complex impedance measurements.[5)] Electronic conductivity of polypyrrole was measured by using four-probe technique.

Ionic conductivity of the polymer electrolytes at 30 °C was in the order of 10^{-7}-10^{-5} S cm^{-1}, depending on the kinds of the incorporated salts. The polymer electrolytes containing LiCl and $LiB(Ph)_4$ had the ionic conductivity in the order of 10^{-7} S cm^{-1}, those containing LiBr and LiSCN in the order of 10^{-6} S cm^{-1}, and those containing $LiClO_4$, $LiBF_4$, LiI, KSCN, and NaSCN in the order of 10^{-5} S cm^{-1}. Incorporation of pyrrole in the polymer electrolytes somewhat increased the ionic conductivity due to the plastisizing effect of pyrrole toward these polymer electrolytes.

Figure 1 shows schematic view of the electrochemical polymerization of pyrrole (Py) using polymer electrolytes. The polymerization was carried out under various conditions. When the dissolved salts were LiI, LiSCN, NaSCN, and KSCN, no polymerization occurred. In the case of LiCl and $LiB(Ph)_4$, the polymerization occurred, but its rate seemed to be slow. The polymer electrolytes containing $LiClO_4$, $LiBF_4$, and LiBr were effective for the polymerization. The salt concentration (1-15 wt%) and pyrrole concentration (10-35 wt%) had little effect on the polymerization and conductivity of resulting polypyrrole. Consumed monomer and salt in the cource of polymerization (< 2×10^{-1} C) were much smaller than the incorporated amounts of them, even if we assumed that the coulombic efficiency of polymerization was unity and that all of the monomer unit of polypyrrole were doped with anion. Current density for the electolysis was changed (7.5-75 μA cm^{-2}). However, it had little effect on the conductivity of resulting polypyrrole. Under these conditions, if appropriate salts were selected, the potential difference between both electrodes was 1.8-2.5 V and

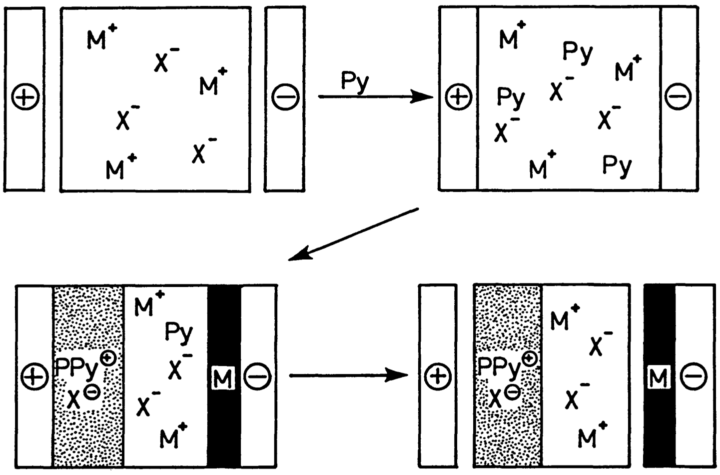

Fig. 1. Schematic view for electrochemical polymerization of pyrrole using ion-conducting polymers as a solid electrolyte.

tended to increase with proceeding the polymerization. When the electrodes were removed from the polymer electrolytes after polymerization, polypyrrole grew on the surface of polymer electrolytes in contact with anode, as shown in Fig. 1. As the results, polypyrrole/polymer electrolyte bilayer composites were obtained. Judging from deeply colored feature of the polypyrrole layers, the as-grown polypyrrole proved to be doped with anion. The bilayer structure was confirmed by observing cross-sectional view of the composites by means of a microscopic examination. Homogeneity of the surface polypyrrole was much affected by the contact of polymer electrolytes with electrodes.

Electronic conductivity of polypyrrole was measured on the surface of the bilayer composites after evaporating unreacted pyrrole under reduced pressure. Since sheet resistance of the polypyrrole layer was lower than that of the polymer electrolytes by a factor of 10^{-4} or lower, the conductivity of polypyrrole was calculated from the sheet resistance. Figure 2 shows change in the conductivity of polypyrrole with the quantity of electricity. σ was calculated from the sheet resistance and thickness of the polypyrrole layer. Since exact polypyrrole thickness was hard to estimate from a microscopic examination, especially in a thin film case, it was calculated from the quantity of electricity, assuming that the coulombic efficiency was 0.5, one anion was doped per four repeat units of polypyrrole, and the density of doped polypyrrole was 1.5, irrespective of kinds of the dopants. The σ values thus obtained were almost independent of the quantity of electricity and in the order of 10^{1}-10^{2} S cm^{-1} at room temperature. These values were comparable to those of polypyrrole synthesized electrochemically by using electrolyte solutions.6) σ_{app} was calculated from the sheet resistance, assuming that the polypyrrole layer had the same thickness as the bilayer composites. The inconsistency of σ_{app} with σ also supported the bilayer structure of the composites, and the increase in σ_{app} with the quantity of electricity corresponded to the increase in thickness of the polypyrrole layer.

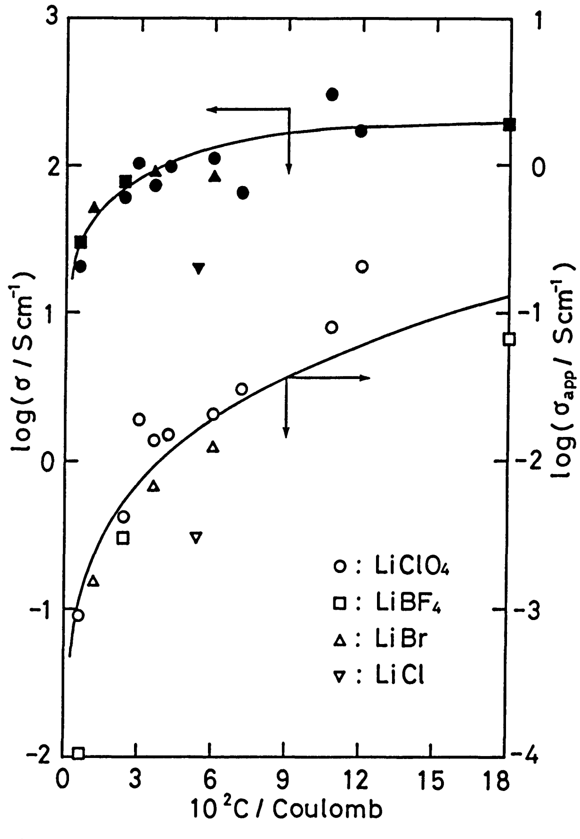

Fig. 2. Change in electronic conductivity of polypyrrole with quantity of electricity used in polymerization.

Electrochemical activity of the bilayer composites was investigated by measuring cyclic voltammograms of solid cell systems with an Ag electrode as a quasi-reference electrode. Pyrrole was polymerized in a three electrode cell by sweeping the potential of a working electrode (Pt) between 0 and 1.5 V vs. Ag, repeatedly. Polypyrrole grew on the surface of a polymer electrolyte film in contact with the working electrode. After removing unreacted monomer from the composites, these composites were subjected to cyclic voltammetry. The cyclic voltammogram of a typical polypyrrole/polymer electrolyte (PEO-LiClO$_4$) composite at 200 mV s^{-1} showed an anodic shoulder at ca. 0.6 V and a cathodic peak at ca. 0.2 V vs. Ag, which corresponded to doping and undoping processes of polypyrrole in the bilayer composite, respectively.

Figure 3 shows change in electronic spectra of the polypyrrole/polymer electrolyte (PEO-LiClO$_4$) bilayer composite film, corresponding to the redox reactions (doped $\rightleftarrows$ undoped state), in solid state. The spectra of heavily doped, lightly doped, and undoped states corresponded to the color of blue, dark brown, and yellow green, respectively. The spectral change was well coincided with that of polypyrrole synthesized and measured in an electrolyte solution.7)

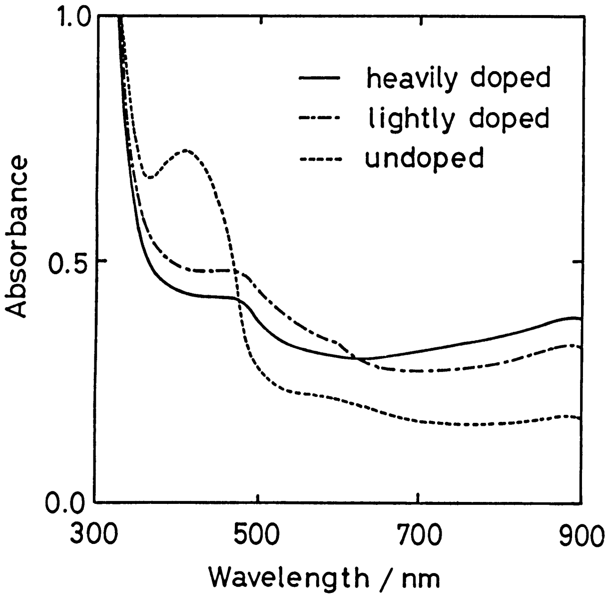

Fig. 3. Change in electronic spectra of polypyrrole/polymer electrolyte bilayer composite film corresponding to redox reactions in solid state.

In conclusion, we have demonstrated that the electrochemical polymerization of pyrrole using the ion-conducting polymers as a solid electrolyte produces polypyrrole/polymer electrolyte bilayer composites in situ. The bilayer composites not only have improved mechanical property, similar to previously reported polypyrrole composites,8) but also have electrochemical activity in solid state. The latter property might open a route to apply these bilayer composites to solid electrochemical devices.

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