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Application of Pyrrole/*N*-Methylpyrrole Composite Polymer to Cathode Active Material of Lithium Secondary Battery

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An electrochemically prepared polypyrrole(PPy)/poly(*N*-methylpyrrole)(PMPy) composite polymer film-(PPy-PMPy) was used as a cathode active material of a rechargeable lithium battery. The charging-discharging behavior of a Li/$LiClO_4$/(PPy-PMPy) battery was studied and compared with those of Li/$LiClO_4$/PPy and Li/$LiClO_4$/PMPy batteries. In order to rationalize the charging-discharging properties of these batteries, anion doping-undoping processes at PPy, PMPy, and PPy-PMPy electrodes were checked using the usual electrochemical techniques, such as cyclic voltammetry and potential step chronoamperometry. A PPy-PMPy film electrode gave an intermediate conductivity as well as an intermediate redox potential just between those of the PPy and PMPy electrodes. Li/$LiClO_4$/(PPy-PMPy) batteries with thin (0.3 $C\,cm^{-2}$-charged) and thick (10 $C\,cm^{-2}$-charged) PPy-PMPy films were found to show different charging-discharging characteristics, depending on their film thickness. The IR spectra obtained for a PPy-PMPy film showed that the composition of PPy and PMPy in the resulting PPy-PMPy film was different according to its film thickness and that the PPy content in the PPy-PMPy film became higher with an increase in its film thickness.

Electrochemical properties of electro-conductive heterocyclic polymers and their derivatives have recently been studied extensively.[1–13,18,19] Greater attention has been paid to the unique applications of these polymers by many workers.[14–19] These polymers are advantageous because of the ease of formation and strong adhesion to various substrates.[9] PPy and its derivatives are expected to be potential candidates for cathode active materials of polymer batteries.[8] Our research group has been working on the electrochemical properties of several kinds of lithium/polymer batteries, where polymers were used exclusively as cathode active materials. Lithium batteries constructed with these polymers have higher capacities per unit weight than conventional secondary batteries.[8] In our previous study,[20] an excellent PPy film suitable as a rechargeable battery material was successfully obtained by electro-oxidative polymerization in the presence of PF_6^- electrolyte anions. By polymerizing pyrrole in the presence of *N*-methylpyrrole, the resulting PPy-PMPy film showed a somewhat different morphology from a PPy film because of the incorporation of PMPy in a PPy film. Recently, copolymerization of pyrrole and *N*-methylpyrrole was attempted; the resulting composite PPy-PMPy film was applied to a Schottky barrier type diode.[18] It had already been noticed that composite PPy-PMPy films gave various conductivities ranging from 10^{-3} to 10^2 $S\,cm^{-1}$ at doped states of usual anions,[1] depending on the composition ratio of pyrrole and *N*-methylpyrrole monomers in the electrolyte solution during polymerization.[7] The conductivity of a PPy-PMPy film gradually decreases with an increase in the PMPy content. This fact may indicate that the polymer layer of a PPy-PMPy film lacks planarity and that the polymer chains are more or less separated because of the bulkiness of the methyl group relative to hydrogen. Hence, the copolymerization of PPy and PMPy is expected to yield a practical means of donating a wide range of conductivities and various patterns of charging-discharging properties of Li/$LiClO_4$/(PPy-PMPy) batteries. It is also noteworthy that a PPy film can be highly stabilized in an ambient condition by copolymerizing with PMPy; the reasons for this are as follows. The degradation of a PPy film is rather substantial in the presence of oxygen or vapor. On the other hand, PMPy shows less reactivity with oxygen and water.[7] Therefore, PPy-PMPy must be more stable than a PPy film in an ambient atmosphere and must also be durable for practical use. As for its electrochemical properties, a PPy-PMPy electrode gives an intermediate redox potential in cyclic voltammograms just between those of PPy and PMPy film electrodes. The main purpose of this study was to examine the possibility of using a PPy-PMPy composite film as the positive electrode of a rechargeable lithium battery. In this connection, we examined the charging-discharging properties of a Li/$LiClO_4$/(PPy-PMPy) battery coupled with the basic electrochemical behavior of anion doping-undoping processes at PPy, PMPy, and PPy-PMPy electrodes.

Experimental

Reagent grade $LiClO_4$ and propylene carbonate (PC) were used as the electrolyte salt and the solvent, respectively in our experiment. The PC was used after purification by percolating through activated alumina. The minor water in the PC was removed by adding molecular sieves to it and then letting it stand for a few days until use.[15] All the potentials were in reference to the Ag/Ag^+ (0.01 $mol\,dm^{-3}$ $AgNO_3$/PC) electrode. Polymer films were formed by electro-oxidative polymerization at a constant current density of 6.5 $mA\,cm^{-2}$. PPy and PMPy films were formed in 0.2 $mol\,dm^{-3}$ $LiClO_4$/PC containing 0.2 $mol\,dm^{-3}$ pyrrole or *N*-methylpyrrole monomer. A PPy-PMPy composite film was formed in 0.2 $mol\,dm^{-3}$ $LiClO_4$/PC containing 0.1 $mol\,dm^{-3}$ pyrrole and 0.1 $mol\,dm^{-3}$ *N*-methylpyrrole monomers. A platinum plate of 0.25 cm^2 and a platinum wire were used as the deposition of polymers and counter electrodes, respectively. The depos-

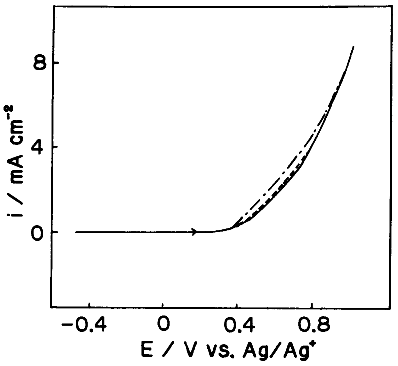

Fig. 1. Current vs. potential curves for Pt electrodes in 0.2 mol dm^{-3} LiClO$_4$/PC containing various monomers (conc.=0.2 mol dm^{-3}) at 50 mV s^{-1}. ——: Pyrrole, ----: pyrrole and *N*-methylpyrrole, -·-·-: *N*-methylpyrrole.

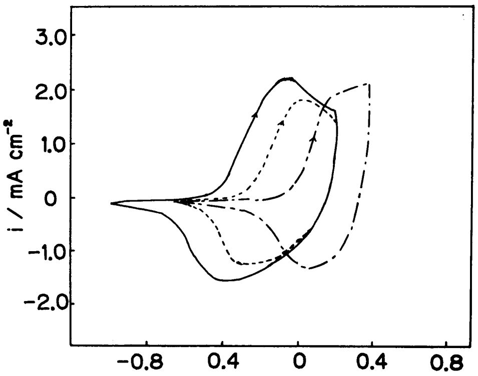

Fig. 2. Cyclic voltammograms of anion doping-undoping process for various polymer electrodes (1.8 C cm^{-2}) in 1.0 mol dm^{-3} LiClO$_4$/PC at 10 mV s^{-1}. ——: Polypyrrole, ----: pyrrole/*N*-methylpyrrole composite polymer, -·-·-: poly(*N*-methylpyrrole).

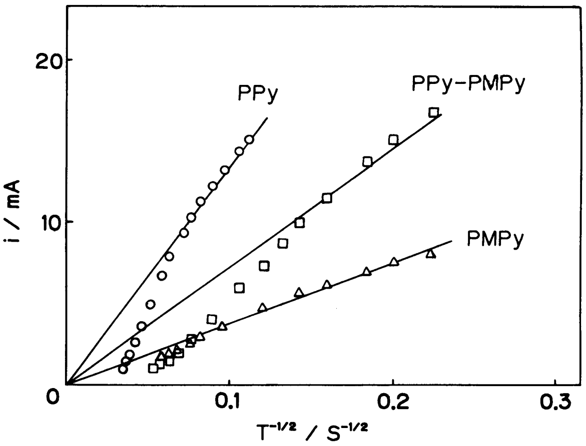

Fig. 3. Typical Cottrell plots for various polymer electrodes formed with 0.3 C cm^{-2}. Potential was stepped from −0.08 V (polypyrrole), 0.0 V (pyrrole/*N*-methylpyrrole composite) and 0.2 V (poly(*N*-methylpyrrole)) to the cathodic direction by 0.8 V.

ited amount of polymers was controlled by monitoring the charge consumed during electropolymerization. Electrochemical measurements were performed in 1.0 mol dm^{-3} LiClO$_4$/PC in an Ar gas atmosphere. A Li/LiClO$_4$-PC/polymer battery was assembled with a polymer cathode and a Li anode pressed onto a Ni expanded mesh; the cell was placed in a small container purged with Ar gas and tightly sealed. Charging-discharging tests were conducted in 1.0 mol dm^{-3} LiClO$_4$/PC at a constant current density of 0.1 or 0.5 mA cm^{-2}. Apparent diffusion coefficients (D_{app}) of dopants within polymer electrodes were determined by potential step chronoamperometry, where the concentrations of dopants in the films (C_o*) were estimated from the anodization charges in cyclic voltammograms measured at 5 mV s^{-1}. Polymer films formed with different formation charges during electropolymerization, viz., 0.3 and 10 C cm^{-2} were characterized by FT-IR spectroscopy, after undoping anions by short-circuiting the cell for a sufficient time.

Results and Discussion

Figure 1 shows polymerization curves at a Pt electrode in electrolyte solutions containing three different monomers. The onset potentials for the three curves show almost the same values (ca. 0.4 V), at which each film begins to grow. As the anodic potential increases, the corresponding currents increase at the same rates, indicating that the polymerization processes for the three monomers occur at the same rate. However, the current efficiencies of the polymerization of these films may not be identical. On the basis of the above results, we formed these films at constant current densities of 6.5 mA cm^{-2}, since a moderate overpotential (ca. 0.49 V) was maintained throughout the formation of each film in order to avoid any decomposition of the films.

In order to survey the electrochemical responses of PPy, PMPy, and their composite PPy-PMPy films, cyclic voltammetry was employed; results are shown in Fig. 2. The anodic and cathodic current peaks for PPy-PMPy composite film are located just between those for PPy and PMPy films. The results suggest that a Li/LiClO$_4$/(PPy-PMPy) battery possesses intermediate charging and discharging voltages between those of a lithium battery assembled with PPy and PMPy films.

Figure 3 shows typical Cottrell plots for 0.3 C cm^{-2}-charged films (ca. 0.6 μm) obtained by potential step chronoamperometry. A potential was initially applied at the anodic current peaks (cyclic voltammograms in Fig. 2), in order to oxidize (dope) the films so as to make the surface concentration of dopants (C_o*) in the same orders of magnitude (10^{-2} mol dm^{-3}) as indicated later. Then, the potential was stepped to the cathodic direction by 0.8 V in order to allow the films to reduce (undope). At the same time, the reduction currents of these films were monitored against time. Straight lines were obtained when plotting them against $t^{-1/2}$ (so-called Cottrell plots). Deviations of the plots from linear lines could be observed for larger t values, which

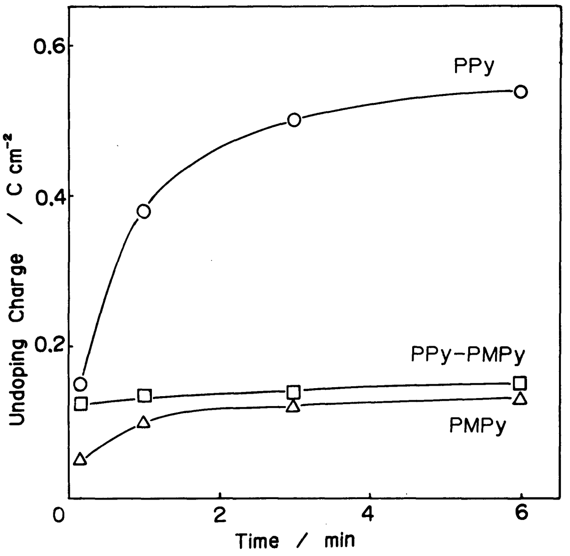

Fig. 4. Time dependence of $\mathrm{ClO_4^-}$ undoped charge for various polymer electrodes at −1.0 V, where these films were formed with 1.8 C cm^{-2}.

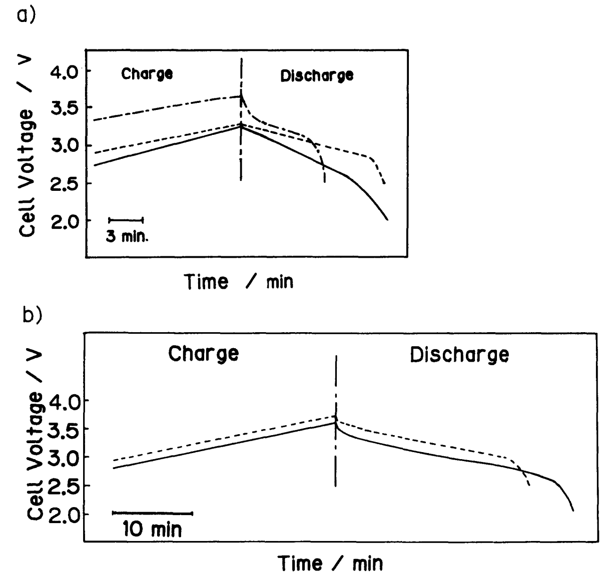

Fig. 5. Charging-discharging curves for Li/polymer batteries at a constant current of a) 0.1 mA cm^{-2} and b) 0.5 mA cm^{-2} in 1.0 mol dm^{-3} LiClO$_4$/PC. These films were polymerized with a) 1.8 C cm^{-2} and b) 10 C cm^{-2}.

——: Polypyrrole, ----: pyrrole/*N*-methylpyrrole composite polymer, —·—·—: poly(*N*-methylpyrrole).

are due to a finite diffusion layer that spread beyond the thickness of the polymer films. The apparent diffusion coefficient of dopants (D_{app}) within these films can be estimated from the slopes of the lines and C_o^* by using the Cottrell equation. The D_{app} values obtained for PPy, PPy-PMPy, and PMPy films are 1.28×10^{-8}, 5.38×10^{-9}, and 3.43×10^{-9} cm^2 s^{-1}, respectively, where the C_o^* values for the oxidized PPy, PPy-PMPy and PMPy films are 8.71×10^{-2}, 7.06×10^{-2}, and 4.52×10^{-2} mol dm^{-3}, respectively. The PPy-PMPy composite film has an intermediate D_{app} value just between PPy and PMPy films. This fact could be expected from the results in Fig. 2 and may have a close relation to the morphology of films having different composition ratios of PPy and PMPy polymers.

Figure 4 shows the undoping charges from polymer electrodes when the electrodes were polarized at −1.0 V. Although the cathodic current peaks in cyclic voltammograms locate more cathodic in the order of PMPy, PPy-PMPy, and PPy films, the dopants in the PPy electrode show the fastest undoping among other electrodes. The PPy-PMPy and PMPy films show a slower undoping process. The undoping behavior of these polymers can be ascribed to the film morphology and the number of effective reaction sites existing within the polymer matrix. The PPy film is considered to show the roughest morphology; also the number of reaction sites available for doping-undoping is much larger than those in PMPy and PPy-PMPy films. On the other hand, the PPy-PMPy and PMPy films show a surface-localized undoping process owing to the lesser degree of the film roughness and porosity. These facts also suggest that PMPy and PPy-PMPy films are more dense than the PPy film, and that the dopants may be confined tightly within the bulk of polymer layers and can hardly undope in spite of the negative potential step.

Figure 5 shows charging-discharging curves of Li/LiClO$_4$/polymer batteries, where the cathode films were formed with two different formation charges, viz., 1.8 C cm^{-2} for Fig. 5a) and 10 C cm^{-2} for Fig. 5b). By using thin PPy-PMPy films (Fig. 5a)), the Li/LiClO$_4$/(PPy-PMPy) battery gives intermediate curves between lithium batteries assembled with PPy or PMPy. The discharging behavior of the Li/LiClO$_4$/(PPy-PMPy) battery became flatter than those of a lithium battery constructed with PPy and PMPy, indicating better discharging characteristics. The coulombic yields for the lithium batteries constructed with PPy and PPy-PMPy films are both excellent and show almost the same values of 100%. In the case of thick films (10 C cm^{-2}), the Li/LiClO$_4$/(PPy-PMPy) battery gives 80% of coulombic yield, whereas 100% was still attained for the Li/LiClO$_4$/PPy battery. The charging-discharging curve for the Li/LiClO$_4$/PMPy battery is not given here since a 10 C cm^{-2}-charged PMPy film could not be obtained because of its high ohmic resistance. That is, under constant-current anodization, the polymerization potential of PMPy constantly increased, even beyond 5.0 V (at which PMPy film begins to decompose). The average discharge voltages for the lithium cells with the PPy and the PMPy films estimated from the figure are 3.0 and 3.2 V, respectively. The charging-discharging behavior for the lithium cells with PPy and PMPy is slightly different, depending on their film thickness. By increasing the thickness, the coulombic yield of the Li/(PPy-PMPy) battery decreases, indicating that the structure of a composite

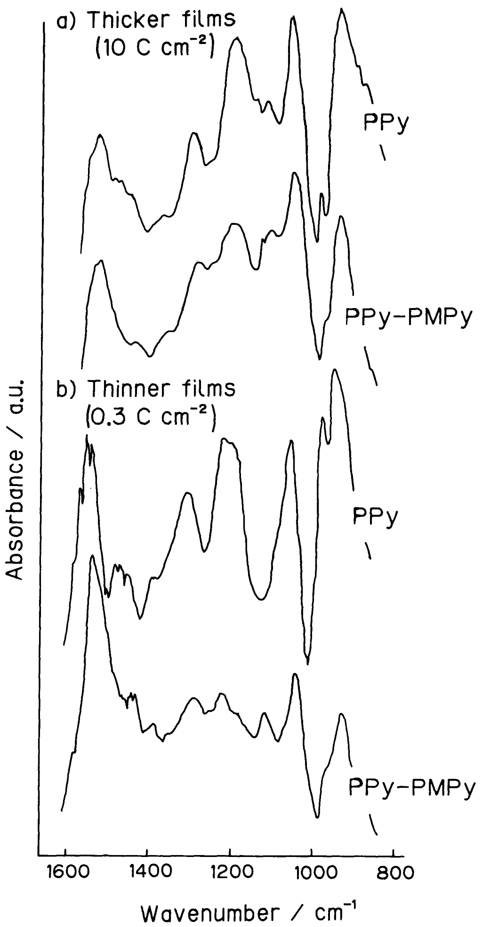

Fig. 6. Infrared spectra of a) thick and b) thin polymer films formed by passing a) 10 C cm^{-2} and b) 0.3 C cm^{-2} at the constant current density of 6.5 mA cm^{-2}.

film is dependent upon the film thickness.

Figure 6 shows the FT-IR spectra of PPy, and PPy-PMPy films of different formation charges. These charts show similar bands due to the pyrrole moiety (1300 cm^{-1}: C-N stretching; 1180, 1045 cm^{-1}: C-H deformation vibration; 965 cm^{-1}: N-H deformation vibration).[21] The IR spectrum of the PPy-PMPy (10 C cm^{-2}) film shown in Fig. 6a) is essentially the same as that of PPy film (10 C cm^{-2}). It is supposed that the PPy-PMPy film has almost the same structure as a PPy film and that the PMPy content is negligibly small in a thick PPy-PMPy film. The peaks due to ClO_4^- anions (1060~1140 cm^{-1}) shown in the two charts for thick films are slightly different. The fact indicates that the number of dopants remaining in the polymer films is different. In a thick PPy-PMPy film, greater amounts of dopants are still confined in the polymer chain than in the PPy film, although dopants have been undoped by short-circuiting the cells for the same duration of time. As for the thin films shown in the lower part of Fig. 6, the PPy-PMPy film shows less similarity to the PPy film than those shown in the thicker films. In the chart of the PPy-PMPy film, several splited peaks can be observed in the region of the C-H or N-H deformation vibration (1000~1300 cm^{-1}). The PMPy content in a PPy-PMPy film of this thickness may be larger than that in a thick PPy-PMPy film.

By comparing the IR charts shown in Figs. 6a) and 6b), the structures of the PPy-PMPy composite films show a strong dependency upon their thickness. It is also deduced from the IR results that each peak in the thick films is broadened because of the poor crystallinity of the polymer layer. Hence, a composite film contains more PMPy at the beginning of film formation. However, as the film grows thicker, the PPy content gradually becomes dominant in the composite film because of an easier growth of a PPy film on thicker polymer films (as is suggested in cyclic voltammograms shown in Fig. 2).

The composition ratio of PPy and PMPy in the PPy-PMPy film offering an optimal charging-discharging curves should await further investigation.

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