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Dependence of Film Thickness on Electrochemical Kinetics of Polypyrrole and on Lithium/Polypyrrole Battery

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The charging-discharging behavior of lithium/$LiClO_4$/polypyrrole battery was found to show a different dependence on film thickness of polypyrrole cathode prepared at various film formation potentials. In order to rationalize these battery properties, cyclic voltammetry was employed for the polypyrrole films prepared at different potentials as a function of film thickness.

Numerous researches on electrochemically prepared polypyrrole have been done after the pioneering investigations by Diaz and coworkers.1-3) Studies on polypyrrole are now directed to a wide range of applications, for example, electrochromic devices,4) lithium-polypyrrole battery,5-9) and ion switching devices,10) and so on. In our research group, we have mainly been working on the properties of Li-polypyrrole batteries.7,8) It was already found that electrochemically prepared polypyrrole films show various morphologies and anion doping-undoping process, which particularly depends on their formation factors such as potentials,7) and electrolyte anions.3,7) A Li/$LiClO_4$/polypyrrole battery will also give various charging-discharging properties depending on the polypyrrole film thickness. However, film thickness dependence of the doping-undoping reaction of polypyrrole electrode has not been reported except some works.11) In order to increase the charge capacity of a polymer battery, the doping charge of polypyrrole must be increased. This goal can be reached by increasing the film thickness of polypyrrole cathode. By considering above, the film thickness dependence of the electrochemical kinetics of polypyrrole must be checked up in advance. In this letter, we report how the doping charges and electrochemical kinetics vary as a function of polypyrrole film thickness and the formation potentials. We also examine several Li/polypyrrole batteries for their charging-discharging behavior.

Propylene carbonate(PC) was used as the solvent after purification.7) Water in the PC was removed with molecular sieves. Polypyrrole films were formed by electro-oxidative polymerization at 0.32V or 0.84V vs. Ag/Ag^+ in 0.2

mol dm^{-3} $LiClO_4$/PC containing 0.2 mol dm^{-3} pyrrole monomer. A platinum plate and wire were used as a substrate for the polypyrrole deposition and counter electrodes, respectively. Film thickness was controlled by monitoring charges during the polymerization. Cyclic voltammograms were obtained in 1.0 mol dm^{-3} $LiClO_4$/PC in the Ar gas atmosphere. The ΔEp (separation potential of the anodic and cathodic current peaks) and the doping charges (oxidation charges) were estimated from the cyclic voltammograms measured at the scan rate of 5 mV s^{-1}. A Li/$LiClO_4$-PC/polypyrrole battery was assembled with a polypyrrole/Pt cathode and a Li/Ni-mesh anode. Charging-discharging tests were conducted in 1.0 mol dm^{-3} $LiClO_4$/PC at constant current densities.

Figure 1 shows the correlation of ΔE_p and doping charge against the film thickness both of which are obtained from the cyclic voltammograms with films of various thickness at two different potentials. The polypyrrole electrodes formed at the several potentials between 0.32 V and 0.84 V give just intermediate electrochemical responses in the cyclic voltammograms for the 0.32 V and the 0.84 V prepared polypyrrole films depending on the film formation potential. For simplification, only the results for the polypyrrole electrodes prepared at 0.32 V and 0.84 V are shown as typical examples of lower and higher potential preparations. The thicknesses of polypyrrole are represented in terms of the charges consumed during the film preparation. The ΔE_p values may reflect the reversibility (smoothness) of anion doping-undoping reaction. The values of ΔE_p are nearly the same for thin polypyrrole films (0.5 C cm^{-2}), irrespective of the formation potential. In the case of polypyrrole formed at a lower potential (0.32 V), ΔE_p increases substantially. The results indicate that the anion diffusion across the polypyrrole becomes slower as the polypyrrole thickness increases. On the other hand, a polypyrrole film formed at higher potential(0.84 V) does not show so remarkable increase of ΔE_p value for given films of various thickness. The polypyrrole film formed at 0.84 V maintains smooth doping-undoing process even for thick film. This

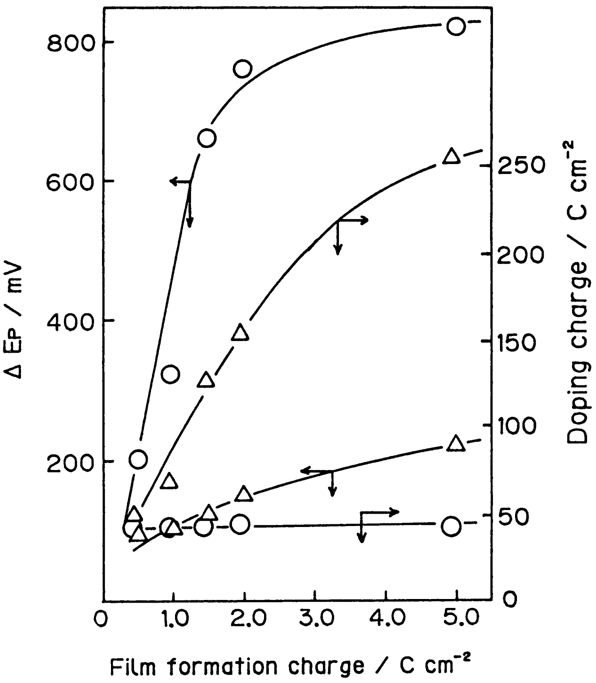

Fig.1. Film thickness dependence of peak separation potentials (ΔE_p) and doping charges for polypyrrole film electrodes. These values were estimated from the cyclic voltammograms at a scan rate of 5 mV s^{-1}. The polypyrrole films were formed at 0.32V(–○–) and 0.84V(–△–).

behavior may be associated with the morphology of polypyrrole film formed at different rates of film growth. In fact, the inspection by SEM micrographs have already revealed that the polypyrrole film prepared at higher anodic potential showed rougher morphology than that prepared at lower potential.6-8) When polymerized at the lower potential, the doping charge does not show any remarkable dependence of the film thickness, indicating that the number of anions doped at a certain duration of time is almost the same irrespective of the film thickness. However, the polypyrrole film prepared at 0.84 V show steady increase of the amount of doping charges with increasing the film thickness. Since the doping charges were estimated from the voltammetry at 5 mV s^{-1}, the anions diffused slower than the time scale of the measurement are not detected as the oxidation (doping) current. Therefore, the amount of doping charges can be a measure of the degree of the diffusion rate of anions within the film. Polypyrrole film becomes more dense when polymerized at lower potentials, and therefore the diffusion process of anions in the bulk of polymer layer may become slower than the oxidation process at the polypyrrole film electrode.

Figure 2 shows typical charging-discharging curves for Li batteries assembled with various thicknesses of polypyrrole cathode prepared at the different formation potentials of 0.32 V and 0.84 V. The current densities for the charging-discharging process are varied for each thickness of polypyrrole electrode as indicated in the caption of Fig.2. As is evident from the results, the Li batteries with the polypyrrole films formed at 0.84 V show better charging-discharging characteristics than those with the polypyrrole films formed at 0.32 V. In the latter case, cell voltages during the charging process saturates at ca. 4.5 V for thicker polypyrrole films, which may represent the upper limit of charging voltage. The saturation of the cell voltage is often observed during charging process for the batteries of low capacities at a very high current densities. The fact may be related to the degradation (oxidative decomposition) of poly-

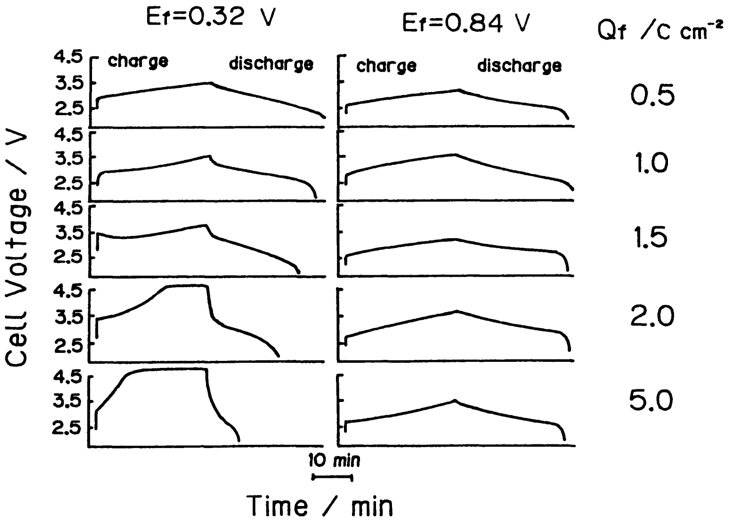

Fig.2. Charging-discharging curves for Li/$LiClO_4$/polypyrrole batteries assembled with various thicknesses of polypyrrole cathodes at constant current densities of 0.05, 0.10, 0.15, 0.20, and 0.50 mA cm^{-2} for 0.5, 1.0, 1.5, 2.0, and 5.0 C cm^{-2} of polypyrrole films, respectively. The film formation charges (Q_f) and potentials(E_f) are indicated in the figure.

pyrrole film due to high anodization potentials.[5,6] The discharging capacity and the coulombic yield for the batteries (E_f=0.32 V) decreases drastically with an increase of polypyrrole thickness. In contrast, the batteries(E_f=0.84 V) give excellent charging-discharging curves for every range of polypyrrole film thickness. The coulombic yields for batteries (Ef=0.84 V) are maintained at ca. 100% and are not affected by varying the film thickness of polypyrrole.

Obviously different tendencies for these batteries can reasonably be interpreted on the basis of the results in Fig.1. By forming polypyrrole at a sufficiently high anodic potential, even a very thick polypyrrole film shows smooth doping-undoping and high doping capacity. Whereas, the Li batteries assembled with the polypyrrole films prepared at lower potentials did not give capacity increase by thickening the polypyrrole films. Therefore, the capacity of Li/polypyrrole battery can be increased by thickening the polypyrrole film only when the film was prepared at high anodic potential.

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