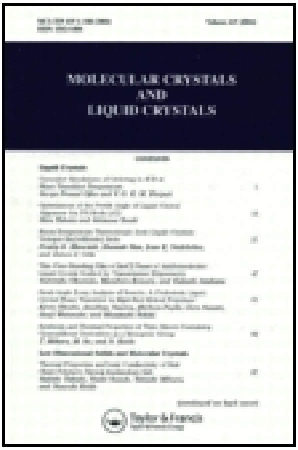

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Anion Movement in Polypyrrole Films Prepared in Lithium Dodecylsulfate Aqueous Solutions

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ANION MOVEMENT IN POLYPYRROLE FILMS PREPARED IN LITHIUM DODECYLSULFATE AQUEOUS SOLUTIONS

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Abstract Electrochemical quartz crystal microbalance (EQCM) was used to study the redox reaction of polypyrrole (PPy) prepared in an aqueous solution containing anionic surfactant. EQCM result confirmed that the small cation in the electrolyte solution rapidly moved into/out of the PPy film during redox reaction at a potentiodynamic condition and also the bulky anion, dodecylsulfate ion (DS^-), additionally took part in redox reaction, especially in positive potential range above -0.2 V. The movement of anion was more clearly seen at potentiostatic condition than in voltammetric measurement, which implies the rate dependency of the anion movement in PPy film.

INTRODUCTION

PPy has been one of the most promising conducting polymers from the industrial point of view due to its chemical/environmental stability and high conductivity. It has been utilized in solid aluminum electrolytic condenser in Japan. The properties of PPy can be varied by using different electrolyte solution in the electrochemical polymerization. Recently, many researchers have focused on the doping mechanism of PPy polymerized in the presence of anionic surfactant.[1~3]

Sodium dodecylsulfate (NaDS) is one of the most extensively studied anionic surfactant due to its high stability and reversibility during redox process in addition to better electrical and mechanical properties. It was reported that when PPy films were prepared and characterized in an aqueous NaDS solution, the small cation, Na^+, rapidly moved through polymer matrix during redox reaction but DS^- was immobilized in the polymer matrix. However, this mechanism is not quite clear because a large decrease in sulfur content upon reduction of PPy in the aqueous lithium dodecylsulfate (LiDS) solution was reported.[4] Therefore, we studied the effect of scan rate on the ion movement during redox process in the aqueous LiDS solution by means of electrochemical quartz crystal microbalance (EQCM).

EXPERIMENTAL

Pyrrole monomer was vacuum-distilled prior to use and electrolytes were used as received without further purification. PPy was electrochemically polymerized onto a working electrode in the aqueous solution containing 0.36 M pyrrole and 0.1 M electrolyte.

EQCM (Elchema Co., EQCN-600) coupled with a potentiostat/galvanostat (EG&G Model 273A) was used to monitor the mass change of the PPy films at redox states. The working electrode was an AT-cut quartz crystal (0.216 cm^2) with a gold layer deposited in key-hole form on both sides. The crystal oscillates in a shear mode at nominal frequency of 10 MHz. The Sauerbrey equation was applied to relate the mass change (Δm) per unit area to the frequency shift (Δf) of a quartz crystal;

$$\Delta f = -C_{\text{m}} \Delta m \tag{1}$$

where the proportionality factor, C_{m}, is 5.2×10^7 Hz g^{-1} cm^2.

Variation of current was measured simultaneously with the change of mass as a function of potential and all potentials were referred to Ag/AgCl (saturated KCl) electrode. Platinum wire was used as a counter electrode.

RESULTS AND DISCUSSION

Mass change of PPy on the quartz crystal during cycling polymerization was shown in Figure 1 along with cyclic voltammograms (CV). Potential was scanned between -0.8 and 0.7 V at a rate of 70 mV/s in the aqueous solution containing 0.36 M pyrrole and 0.1 M LiClO_4 (a) or LiDS (b). The oxidation of monomer starts at 0.5 V on the first anodic sweep but mass increment starts to appear around 0.54 V. Continuous polymerization of PPy is observed down to 0.48 V on the cathodic sweep. Mass gain per cycle increases with scan number, which may be due to the increased surface area or mediator effect of PPy film. But PPy /LiDS film shows faster gain of mass because the anionic dopant, DS$^-$, has larger molecular size than ClO_4^-.

The mass change below 0.5 V is related to the movement of anionic dopant or charging compensating ion and the magnitude also increases with scan number since more PPy was involved in the doping/dedoping process. If the bulky and anionic surfactant (DS$^-$) was immobilized in PPy film during redox reaction, mass on cathodic sweep should increase due to the insertion of the cation but this is not the case. Therefore, the details of ion involvement in the redox process will be discussed.

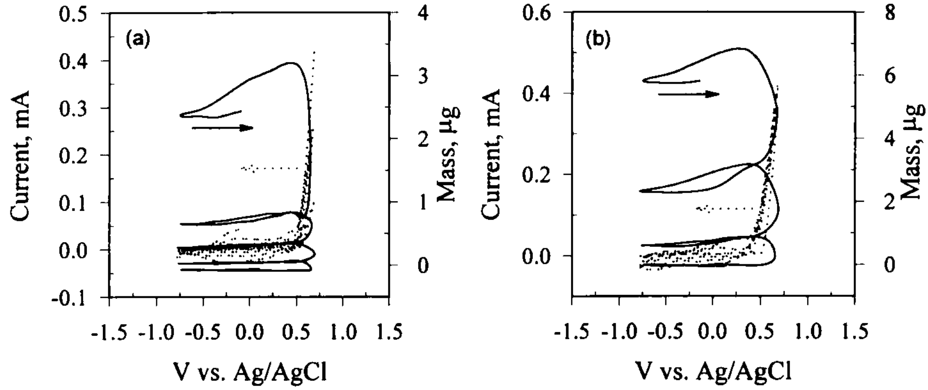

FIGURE 1 Mass change profiles and CV of PPy during polymerization; (a) $PPy/LiClO_4$ and (b) PPy/LiDS.

Figure 2 shows the effect of scan rate on the mass profiles of PPy /LiDS film between -0.8 and 0.5 V. PPy film was galvanostatically prepared at the same condition as the cycling polymerization (20 mC/cm^2, 3 μg). As previously reported[4] both DS$^-$ and cation are involved in the redox reaction and they compete depending on the scan rate. In other words, the fast moving Li^+ plays dominant role between -0.8 and -0.2 V (called region I) but the bulky DS$^-$ does above ~0.3 V (region II). When the potential is swept at a scan rate of 100 mV/s, the total mass change is larger than at a scan rate of 50 mV/s but the mass change in each region does not increase that way. The amount of mass change due to the cation increases while that due to the anion decreases almost by half. This means that the cation moves fast enough to follow the sweep rate but the bulky DS⁻ moves much slowly. Thus Figure 2 clearly shows the scan rate dependency of the anion movement during redox process for PPy/LiDS film.

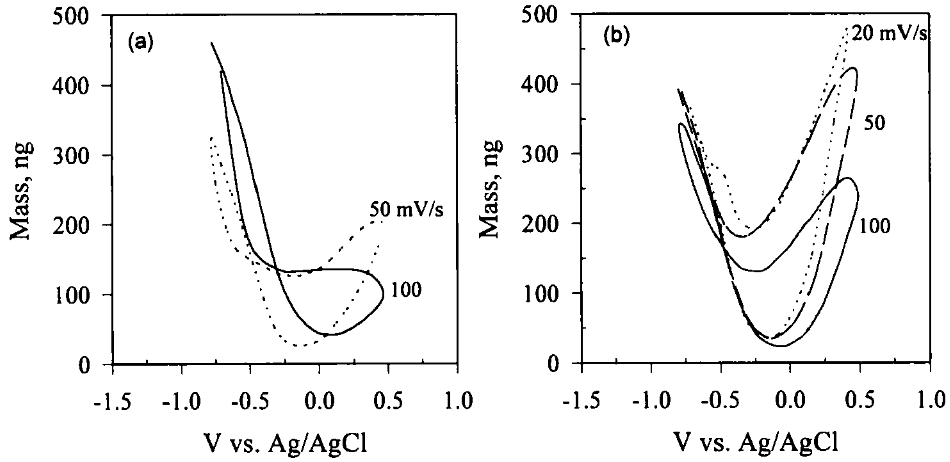

FIGURE 2 Mass change profiles of PPy film prepared at a galvanostatic condition; (a) PPy/LiDS and (b) PPy/NaDS.

The same experiment was done to investigate the effect of cation on the mass profiles. PPy was galvanostatically prepared in a NaDS solution at the same condition (20 mC/cm^2, 3 μg). PPy/NaDS film shows similar behavior to that of PPy/LiDS but the different things are observed: the mass change in region I is almost independent of the scan rate and the mass change in region II is much larger than PPy/LiDS system. Na^+ is hydrated with 3 H_2O molecules in the aqueous solution but Li^+ is with 5 H_2O molecules. Thus it is expected that the mobility of Na^+ is much faster than that of Li^+ and the movement of Na^+ may not be affected by the scan rates used.

Figure 3 shows mass profiles of PPy films as a function of time at a fixed potential, called potentiostatic conditions where the scan rate dependency of ion movement is neglected. The mass profiles were obtained at -0.8 V, 0.5 V and then ~0.0 V. The mass of PPy/LiDS at -0.8 V rapidly decreases at initial stage, especially ca. 0.35 min and then the mass decrement slows down. When the reduced PPy is reoxidized at 0.5 V the mass gradually increases with time due to the redoping of DS⁻. The gradual increase at the initial stage may be related to more resistance to the diffusion of DS⁻, which resulted from the film shrinkage upon reduction. The film shrinkage upon reduction was confirmed by Rhee's Auger electron spectroscopy (AES) result.[5] The reason that mass increment at 0.5 V is more than the mass reduction at -0.8 V may reflect its different oxidation state from the polymerized film. The mass gain at 0.0 V is very small compared with the other two conditions.

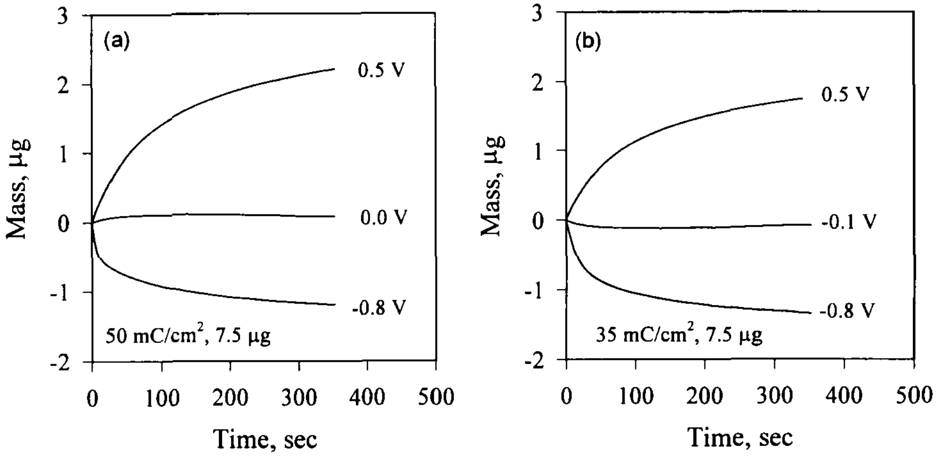

FIGURE 3 Mass change profiles of PPy at a potentiostatic condition; (a) PPy/LiDS and (b) PPy/NaDS.

CONCLUSIONS

PPy/LiDS film showed that both the cation and the bulky anion participated in redox reaction and the movement of the anion is highly dependent on scan rate due to its bulkiness. PPy/NaDS film also showed scan rate dependency of the anion movement but Na^+ movement is almost independent of scan rate due to its high mobility compared with Li^+. The insertion rate of DS^- is slower than the release rate of DS^- at potentiostatic measurement, which is related to the film shrinkage during reduction process. Also, the anion movement was dominant at potentiostatic condition rather than at potentiodynamic condition since DS^- has enough time to move through polymer matrix irrespective of its bulkiness.

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