

# Ion and solvent transport during the redox reaction of polypyrrole and poly(*N*-substituted pyrrole) films in aprotic solutions

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## Abstract

Polypyrrole (PPy), poly(*N*-methyl pyrrole) (PMPy) and poly(*N*-phenyl pyrrole) (PPhPy) films in acetonitrile (AN) and propylene carbonate (PC) have been compared focusing on their different ion and solvent transport behaviors. During the redox reaction of PPy films, cation, anion, and solvent take part in mass transport. Whereas during the redox reaction of PMPy and PPhPy films, anion and solvent transport are dominant but cation transport is negligible. In addition, solvent transport occurs in the same direction with cation transport for PPy films. On the other hand, solvent transport occurs in the opposite direction to anion transport for PMPy films, and it changes its amount and direction with the kind of the dopant anion and the solvent used at electropolymerization for PPhPy films.

**Key words :** Polypyrrole, Poly(*N*-methylpyrrole), Poly(*N*-phenylpyrrole), EQCM

## 1. Introduction

The electrochemical characteristics of polypyrrole (PPy) and its derivatives have been studied extensively by many groups.<sup>1)</sup> Diaz *et al.* prepared the series of poly(*N*-substituted pyrrole) by electropolymerization and examine the effects of nature of substituent on the electrochemical properties such as the redox potential, degree of oxidation, density, and conductivity.<sup>2,3)</sup> They stated that the steric effect is a critical factor when the substituent is saturated and electronic effect becomes important when the substituent is unsaturated. To our knowledge, however, no systematic comparison about the mass transport behaviors of polypyrrole and its derivatives has been reported yet. Recently, we revealed that PPy and poly(*N*-methyl pyrrole) (PMPy) films show different ion and solvent transport behaviors in acetonitrile solution (AN) solutions.<sup>4)</sup> In case of PPy films, cation as well as anion takes part in ion transport during the redox reaction, and the break-in process in the first cathodic scan is observed. In case of PMPy films, on the other hand, anion transport is dominant, and no break-in process is observed. Moreover, solvent transport takes place in the same direction with cation transport in PPy films, whereas it occurs in the opposite direction to anion transport PMPy films.

In this study, for the purpose of extending the previous result, the ion and solvent transport behaviors of PPy and PMPy, and poly(*N*-phenyl pyrrole) (PPhPy) films in AN and PC solutions are investigated with the cyclic electrochemical quartz crystal microbalance (EQCM) technique.<sup>5,6)</sup> In addition, the effect of anion and solvent used at PPhPy film synthesis on the solvent transport is discussed.

## 2. Experimental

Pyrrole, *N*-methylpyrrole, *N*-phenylpyrrole, acetonitrile (anhydrous, 99.8%), and propylene carbonate (PC) (anhydrous, 99.7%) are purchased from Aldrich and used as received. All the electrolytes used in this study are of reagent grade and dried at 80°C under vacuum before use.

A standard three-electrode cell was used for all electrochemical measurement with Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub> in AN or PC) reference electrode and Pt wire counter electrode. All potentials are quoted against the saturated calomel electrode (SCE). The experimental setup for an EQCM experiment was the same as that reported previously.<sup>7)</sup> All the films were polymerized galvanostatically at 0.2 mA/cm<sup>2</sup> in AN or PC solutions containing 0.1 M monomer and 0.1 M TEAClO<sub>4</sub> or TEAPF<sub>6</sub>. The electrolyte used in polymerization contained TEA<sup>+</sup> as cation commonly, and the anion and solvent were chosen as same as the ones that will be used in the cyclic EQCM experiments. The charge consumed during the polymerization was 300 mC/cm<sup>2</sup> for all the films. After polymerization, the films were washed with pure solvent and transferred into an Ar-filled glove box. All cyclic EQCM experiments were performed in the glove box. All data were measured during the second cycle of two consecutive cycles after being held at the positive potential limits. Scan rate was 10 mV/sec for all experiments.

## 3. Result and Discussion

As pointed out in our previous report,<sup>7)</sup> it is convenient to compare current (*I*) and normalized mass change rate (*G<sub>n</sub>*) to examine the mass transport behaviors that depend on the applied potential. *G<sub>n</sub>* is obtained from the mass change rate

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( $G=dM/dt$ ) according to Eq. (1)

$$G_n = -(zF/W')G \quad (1)$$

where  $z$  is the charge of ion,  $F$  is Faraday constant,  $W'$  is the apparent molar mass of charge compensating species. If  $G_n$  is larger than  $I$  at a certain potential, it means that the real  $W'$  value is larger than the given  $W'$  and vice versa.

Fig. 1 shows the cyclic voltammograms and  $G_n$  diagrams of a PPy film in 1 M LiClO<sub>4</sub>/PC. When the molar mass of ClO<sub>4</sub><sup>-</sup> ( $W_{ClO_4^-}$ ) is taken as  $W'$  (Fig. 1a),  $G_n$  is slightly smaller than  $I$  at the initial part of the cathodic scan. It means that anion transport contributes dominantly to ion transport in highly oxidized state of a film but there also exists transport of other species in the opposite direction to anion transport. The additional species might be cation and/or solvent, however, the identity can not be determined evidently at present state. In Fig. 1b, when the molar mass of Li<sup>+</sup> and 5 PC (=517) is taken as  $W'$ ,  $G_n$  and  $I$  show a similar behavior at the potential region below the cathodic peak potential. It indicates that cation transport is accompanied by the substantial amount of solvent transport when a PPy film is in its lightly oxidized state. The average apparent molar mass ( $W'_a$ ) can be obtained according to Eq. (2).

$$W'_a = F (\Delta M / \Delta Q) \quad (2)$$

where  $\Delta M$  and  $\Delta Q$  are mass change and the charge change over a given potential range, respectively.  $W'_a$  over lightly oxidized state of a film is 440, which equals to the molar mass of Li<sup>+</sup> and about 4.3 PC molecules. In our previous study,<sup>9</sup> we showed that Li<sup>+</sup> is accompanied by about 2.7 AN molecules during the redox reaction of a PPy film in LiClO<sub>4</sub>/AN. Thus, the number of accompanying solvent molecules per Li<sup>+</sup> is larger in case of PC solution than AN solution. This seems to be due to the different natures of PC and AN. Consequently, cation, anion, and solvent take part in mass transport during the redox reaction of a PPy film in ClO<sub>4</sub><sup>-</sup>-containing PC solutions as well as AN solutions.

Fig. 2 shows the results of the cyclic EQCM experiments of a PMPy film in 0.2 M TEAPF<sub>6</sub>/AN (Fig. 2a) and in 0.5 M TEAPF<sub>6</sub>/PC (Fig. 2b). In contrast with PPy films, PMPy films show anion-dominant mass transport behaviors. As seen in Fig. 2a and Fig. 2b,  $G_n$  is smaller than  $I$  over the whole potential range when  $W_{PF_6^-}$  is taken as  $W'$ .  $W'_a$  is 129

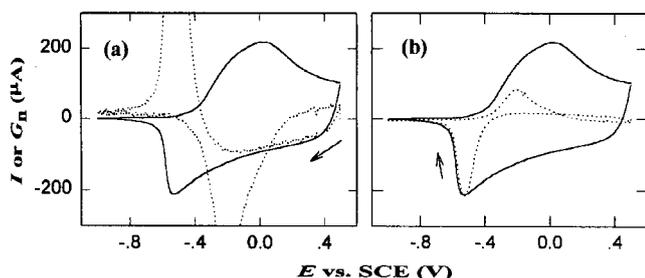


Fig. 1. Cyclic voltammogram ( $I$  vs.  $E$ ; —) and normalized mass change rate diagram ( $G_n$  vs.  $E$ ; ···) for PPy/ClO<sub>4</sub> film in 1 M LiClO<sub>4</sub>/PC (a) when  $W_{ClO_4^-}$  is taken as  $W'$ , (b) when  $W_{Li^+}$  and 5 PC is taken as  $W'$ .

and 116 for Fig. 2a and Fig. 2b respectively, which are smaller than  $W_{PF_6^-}$  (=145). It means that some species move in the opposite direction to anion movement. We observed similar behaviors during the redox reactions of PMPy films in ClO<sub>4</sub><sup>-</sup>-containing AN solutions, and showed that the counter flux of solvent is responsible for the smaller  $W'_a$  than  $W_{ClO_4^-}$ .<sup>9</sup> Similarly, it seems that the solvent transport in opposite direction to anion transport takes place in case of PF<sub>6</sub><sup>-</sup>-containing AN and PC solutions.

Fig. 3 shows the results of the cyclic EQCM experiment of a PPhPy film in 0.2 M TEAPF<sub>6</sub>/AN (Fig. 3a) and in 1 M TEAPF<sub>6</sub>/PC (Fig. 3b). PPhPy films as well as PMPy films show anion-dominant mass transport behaviors. However, their solvent transport behaviors are very different from those of PMPy films. In Fig. 3a,  $G_n$  is very similar to  $I$  over the whole potential range when  $W_{PF_6^-}$  is taken as  $W'$ .  $W'_a$  is 147, which is nearly equal to  $W_{PF_6^-}$ . It means that the mass transport is accomplished by only anion and no solvent transport occurs. In Fig. 3b,  $G_n$  is much larger than  $I$  near the peak potentials when  $W_{PF_6^-}$  is taken as  $W'$ .  $W'_a$  is 192, which is much larger than  $W_{PF_6^-}$ . It indicates that some species move together with PF<sub>6</sub><sup>-</sup> during the redox reaction of a PPhPy film in TEAPF<sub>6</sub>/PC. There are two possibilities for the larger  $W'_a$  than  $W_{PF_6^-}$ . One is neutral electrolyte transport and the other is solvent transport. In order to reveal the presence of neutral electrolyte transport, we performed the cyclic EQCM experiment of a PPhPy film in 1 M TBAPF<sub>6</sub>/PC. If there was neutral electrolyte transport, increased  $W'_a$  would be obtained because of larger molar mass of TBAPF<sub>6</sub> than TEAPF<sub>6</sub>. However, very similar  $W'_a$  values were obtained in both cases. It means that neutral

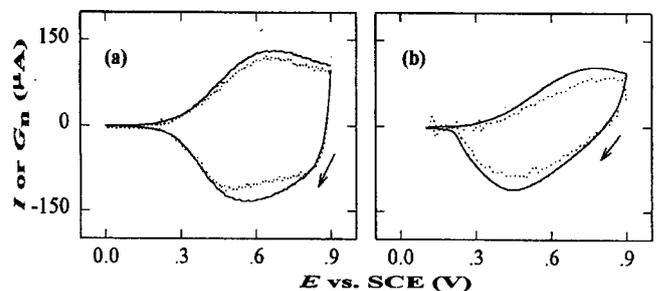


Fig. 2. Cyclic voltammogram ( $I$  vs.  $E$ ; —) and normalized mass change rate diagram ( $G_n$  vs.  $E$ ; ···) for PMPy/PF<sub>6</sub> film in (a) 0.2 M TEAPF<sub>6</sub>/AN, and (b) 0.5 M TEAPF<sub>6</sub>/PC ( $W' = W_{PF_6^-}$ ).

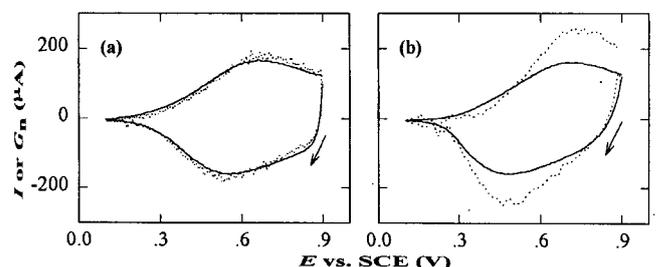


Fig. 3. Cyclic voltammogram ( $I$  vs.  $E$ ; —) and normalized mass change rate diagram ( $G_n$  vs.  $E$ ; ···) for PPhPy/PF<sub>6</sub> film in (a) 0.2 M TEAPF<sub>6</sub>/AN, and (b) 1 M TEAPF<sub>6</sub>/PC ( $W' = W_{PF_6^-}$ ).

electrolyte transport is negligible and solvent transport is more probable. Therefore, it can be said that one  $\text{PF}_6^-$  is accompanied by about 0.5 PC molecule during the redox reaction of PPhPy films in  $\text{PF}_6^-$ -containing PC solutions. Unlike PPhPy films grown in  $\text{PF}_6^-$ -containing solution, PPhPy films grown in  $\text{ClO}_4^-$ -containing shows similar solvent transport behaviors to PMPy films in both AN and PC solutions. From these results we can notice that the kind of anion and solvent used in a film synthesis plays an important role in determining mass transport behavior of the film. We are performing further experiments to reveal the dependence of mass transport on the electropolymerization conditions.

#### 4. Conclusion

It has been revealed that PPy, PMPy, and PPhPy films show different ion and solvent transport behaviors by using the cyclic EQCM technique. Cation, anion, and solvent take part in mass transport during the redox reaction of PPy films. Moreover, solvent transport occurs in the same direction with cation transport. Whereas anion and solvent transports are dominant but cation transport is negligible during the redox reaction of PMPy and PPhPy films.

Solvent transport occurs in the opposite direction to anion transport for a PMPy film. For a PPhPy film, it changes its amount and direction with the kind of the dopant anion and the solvent used at the film synthesis.

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