Effects of dopant anions and $N$-substituents on the electrochemical behavior of polypyrrole films in propylene carbonate solution

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Abstract

The electrochemical properties of poly($N$-ethylpyrrole) (PEPy) and poly($N$-methylpyrrole) (PMPy) films in propylene carbonate (PC) solution, where ion transport is anion-specific, has been investigated using the cyclic electrochemical quartz crystal microbalance (EQCM) technique and electrochemical impedance techniques. The type of dopant anion ($PF_6^-$ vs. $ClO_4^-$) used for the film preparation and the $N$-substituents (ethyl vs. methyl) have profound effects on the solvent transport behavior, charge capacity, and ionic resistance of the films. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Poly($N$-ethylpyrrole); Poly($N$-methylpyrrole); EQCM; EIS; Anion transport; Solvent transport

1. Introduction

There have been significant efforts to customize or tailor-make the properties of conducting polymers for a desired application such as sensors, energy storage devices, and corrosion inhibitors [1]. The key step in the progress of these applications is to understand the mechanism of mass transport during the redox reaction, which governs the electrochemical properties of conducting polymers. Extensive work has been performed on mass transport in conducting polymers [2,3]. However, it is still far from full understanding because mass transport is rather complex; ion transport is not perm-selective, solvent transport accompanies ion transport, and ion/solvent transports are both time and potential dependant.

The characteristics of conducting polymers strongly depend on their polymerization condition such as the film growth rate, the nature of solvent, and the kind and concentration of dopant anion [4–7]. Another possible way to give variation to polymer properties is to modify the chemical structure of monomer. Diaz et al. [8] prepared the series of poly($N$-alkyl pyrrole) and showed that the nature of substituent affects the various properties such as the redox potential, degree of oxidation, density, and conductivity.

In general, it has been known that ion transport is anion specific in the cases of poly($N$-substituted pyrrole) films in both aqueous and aprotic solutions [9–11]. To our knowledge, however, no systematic study has been reported yet on the effect of $N$-substituents of polypyrrole films on their mass transport behavior.

In the present study, mass transport behavior of poly($N$-ethylpyrrole) (PEPy) and poly($N$-methylpyrrole) (PMPy) films in propylene carbonate (PC) solutions was investigated with the cyclic electrochemical quartz crystal microbalance (the cyclic EQCM) technique [12,13] and the electrochemical impedance spectroscopy (EIS) [14–16]. Two kinds of dopant anion, $PF_6^-$ and $ClO_4^-$ were used in preparing PEPy and PMPy films. First, the solvent transport behavior and the charge capacity of each film were compared using the cyclic EQCM technique both in $PF_6^-$-containing and $ClO_4^-$-containing solutions. Second, to examine the dependence of the mass transport kinetics on dopant anion and $N$-substituent, ionic resistance ($R_D$) was measured using EIS. Finally, the effects of dopant anion and $N$-substituent on the electrochemical properties of films

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were discussed in terms of their morphological difference.

2. Experimental

All the chemicals used in this study are of reagent grade and electrolytes were dried at 80 °C under vacuum before use. A standard three-electrode cell was used for all electrochemical measurement with an Ag/Ag+ (0.01 M AgNO3 in PC) reference electrode and a Pt wire counter electrode. All potentials are quoted against the saturated calomel electrode (SCE). A 6 MHz AT-cut quartz crystal (Inficon, NY) coated with Au, 0.32 cm2 in area, served as the working electrode. The experimental setup for the EQCM, the electrochemical impedance, and the electromechanical impedance measurements was the same as that reported previously [17]. All the films were polymerized galvanostatically at 0.2 mA cm−2 in PC solutions containing 0.1 M monomer and 0.1 M TEAPF6 or TEAClO4. For convenience, the films grown in TEAPF6 solutions are represented as PEPy/PEPy or PMPy/PEPy, whereas the films grown in TEAClO4 solutions are shown as PEPy/ClO4 or PMPy/ClO4. The charge consumed during the polymerization was 300 mC cm−2 for all the films. After polymerization, the films were washed with pure solvent and transferred into an Ar-filled glove box. The cyclic EQCM and the electrochemical impedance experiments were performed in the glove box, and the electromechanical impedance experiment was performed in the atmosphere in a close cell. All the cyclic EQCM data was measured during the second cycle of two consecutive cycles after being held at the positive potential limit unless otherwise noticed. Scan rate was 5 mV s−1 for all the cases. In our previous report [17], we showed that the linear relationship between the mass change and the resonant frequency of an oscillating quartz crystal can be proved by comparing the mass change obtained from the resonant frequency with that obtained from the electromechanical impedance. In every case reported in this study, there was no significant difference between the two mass changes. Consequently, mass change can be obtained from resonant frequency change without consideration of the morphological changes of polymer films. The electromechanical impedance data and the electrochemical impedance data were fitted by using the complex nonlinear least-squares (CNLS) fitting program. The CNLS program used in this work is the LEVM program (Scribner, VA).

3. Results and discussion

3.1. Mass transport behavior of PEPy films

There are two methods to correlate the electric response and gravimetric response. The first one is to compare current (I) and mass change rate (G = dM/dt). To be compared with I, G is normalized according to Eq. (1)

\[ G_n = -(zF/W')G, \]

where \( z \) is the charge of an ion, \( F \) is the Faraday constant and \( W' \) is the apparent molar mass of charge compensating species. If the normalized mass change rate (\( G_n \)) is larger than I at any potential, it means that the \( W' \) value used in Eq. (1) is smaller than the actual value. This method is very useful to monitor potential-dependent mass transport as shown in our previous reports [10,17–19]. The second one is to compare charge change (\( \Delta Q \)) and mass change (\( \Delta M \)), in which the average apparent molar mass of charge compensating species (\( W'_{\text{avg}} \)) is obtained by Eq. (2)

\[ W'_{\text{avg}} = -zF(\Delta M/\Delta Q). \]

Both methods were employed in the following section for the cyclic EQCM experiments.

Fig. 1 shows the cyclic voltammograms and \( G_n \) diagrams for PEPy films. In each \( G_n \) diagram, the molar mass of PF6 (\( W_{PF6} \)) or the molar mass of ClO4 (\( W_{ClO4} \)) is regarded as \( W' \). During the redox reaction of a PEPy/PEPy film in LiPF6 (Fig. 1(a)), \( G_n \) is larger than I over the whole potential range. Because the actual \( W' \) is not uniform over the whole potential range, \( W'_{\text{avg}} \) value was obtained. In all experiments, \( W'_{\text{avg}} \) value at the anodic scan is similar to that at the cathodic scan within an experimental error. Thus, \( W'_{\text{avg}} \) at the only cathodic scan was represented in Table 1. For Fig. 1(a), \( W'_{\text{avg}} \) is 215, which is much larger than \( W_{PF6} = 145 \). This indicates that neutral electrolyte or solvent moves in the same direction as PF6 movement. However, \( W'_{\text{avg}} \) is 222 for a PEPy/PEPy film in TEAPF6 (Table 1), which is very similar to that in LiPF6. If there were neutral salt transport, \( W'_{\text{avg}} \) value in TEAPF6 would be much larger than that in LiPF6 due to the larger molar mass of TEAPF6. Therefore, it shows that neutral electrolyte transport is negligible and solvent transport is more probable. Assuming that only anion transport and solvent transport take place, \( W' \) can be expressed as below.

\[ W' = W_a + Y W_s, \]

where \( W_a \) and \( W_s \) are the molar masses of an anion and a solvent, respectively, and \( Y \) is the number of accompanying solvent molecules per anion. As shown in Table 1, the average \( Y (Y_{\text{avg}}) \) values for PEPy/PEPy films in LiPF6/PC and TEAPF6/PC are 0.7 and 0.8, respectively. This means that some PC molecules move in the same direction as PF6 transport.

On the contrary, during the redox reaction of a PEPy/ClO4 film in LiClO4 (Fig. 1(b)), \( G_n \) is slightly smaller than I over the whole potential range. \( W'_{\text{avg}} \) value is 81, which is smaller than \( W_{ClO4} = 99.5 \). This means that cation, neutral salt, or solvent transport may occur.
Fig. 1. Cyclic voltammograms (I vs. E; •••••) and normalized mass change rate diagrams (Gn vs. E; ———) for (a) PEPy/PF6 in 1 M LiPF6 (W' = WF6), (b) PEPy/ClO4 in 1 M LiClO4 (W' = WClO4), and (c) PEPy/PF6 in 1 M LiClO4/PC (W' = WClO4).

In the opposite direction to ClO4− movement. However, W′avg value for a PEPy/ClO4 film in TEAClO4 is 83, which is not very different from 81. This excludes the possibility of the transport of cation/neutral salt. Thus, smaller W′avg value is due to the solvent transport occurring in the opposite direction to anion transport. The Yavg values for PEPy/ClO4 films are −0.2, which means that some PC molecules move in the opposite direction to ClO4− transport. It is interesting to note that the direction of solvent transport in Fig. 1(a) is opposite to that in Fig. 1(b). In addition, the charge capacity for Fig. 1(a) is larger than Fig. 1(b). ΔQ values during the cathodic scan are 8.4 and 7.0 mC, respectively (Table 1). These differences may be due to the difference in the anion used either at film growth or the cyclic EQCM experiments. To make this point clear, the cyclic EQCM experiment for a PEPy/PF6 film in LiClO4 film in PC (Fig. 1(c)) was performed. The data was obtained after the several redox cycles to make sure the complete anion exchange. The cyclic voltammogram in Fig. 1(c) looks very similar to that in Fig. 1(a) rather than Fig. 1(b). The ΔQ value is 8.5 mC, which is nearly the same as that in Fig. 1(a). Ga is larger than I around peak potentials in Fig. 1(c), which is the behavior observed in Fig. 1(a). These observations support the idea that the nature of anion incorporated during a film preparation governs the charge capacity and solvent transport behavior of PEPy films. Conclusively, PEPy/PF6 films show larger charge capacities than PEPy/ClO4 films, and solvent transport occurs in the same direction to anion transport for PEPy/PF6 films whereas it occurs in the opposite direction to anion transport for PEPy/ClO4 films.

3.2. Mass transport behavior of PMPy films

Fig. 2 shows the cyclic EQCM results of PMPy films. In each Gn diagram, WPF6 or WClO4 is regarded as W′. For a PMPy/PF6 film in LiPF6 (Fig. 2(a)), Ga is slightly smaller than I over the whole potential range. As shown in Table 2, W′avg is 124, which is smaller than WPF6. Similar W′avg is obtained in TEAPF6 (= 116), which implies that the smaller W′avg is due to solvent in the opposite direction to anion transport.

For a PMPy/ClO4 film (Fig. 2(b)), the cyclic voltammogram shows reduced peak currents and the cathodic peak is broadened and shifted to more negative value as compared with that in Fig. 2(a). The counter flux of solvent also occurs in a PMPy/ClO4 film in LiClO4 (Fig. 2(b)) and a PMPy/PF6 film in LiClO4 (Fig. 2(c)). Thus, solvent transport occurs to the opposite direction to anion transport in all the three cases of PMPy films, which is in contrast with the results of PEPy films. ΔQ values of Figs. 2(a)–(c) are 5.8, 5.2, and 5.8 mC, respectively. Note that these values and the differences between them are smaller than those of PEPy films.

<table>
<thead>
<tr>
<th>Film</th>
<th>Electrolyte</th>
<th>W′avg</th>
<th>Yavg</th>
<th>ΔQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEPy/PF6</td>
<td>LiPF6</td>
<td>215</td>
<td>0.7</td>
<td>8.4</td>
</tr>
<tr>
<td>PEPy/PF6</td>
<td>TEAPF6</td>
<td>222</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>PEPy/ClO4</td>
<td>LiClO4</td>
<td>81</td>
<td>−0.2</td>
<td>7.0</td>
</tr>
<tr>
<td>PEPy/ClO4</td>
<td>TEClO4</td>
<td>83</td>
<td>−0.2</td>
<td></td>
</tr>
<tr>
<td>PEPy/PF6</td>
<td>LiClO4</td>
<td>154</td>
<td>0.5</td>
<td>8.5</td>
</tr>
</tbody>
</table>

a $W_{avg} = F(ΔM/ΔQ)$ during the cathodic scan (g mol⁻¹).

b $Y_{avg} = (W_{avg} - W)/PF6$, $W_{PF6} = 145$, $W_{ClO4} = 99.5$, and $W_{PC} = 102$. 

Table 2

<table>
<thead>
<tr>
<th>Film</th>
<th>Electrolyte</th>
<th>(W'^{a}_\text{avg} )</th>
<th>(Y'_\text{avg}^{b} )</th>
<th>(\Delta Q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMPy/PF_6</td>
<td>LiPF_6</td>
<td>124</td>
<td>-0.2</td>
<td>5.8</td>
</tr>
<tr>
<td>PMPy/PF_6</td>
<td>TEAPF_6</td>
<td>116</td>
<td>-0.3</td>
<td></td>
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<tr>
<td>PMPy/ClO_4</td>
<td>LiClO_4</td>
<td>82</td>
<td>-0.2</td>
<td>5.2</td>
</tr>
<tr>
<td>PMPy/ClO_4</td>
<td>TEAClO_4</td>
<td>77</td>
<td>-0.2</td>
<td></td>
</tr>
<tr>
<td>PMPy/PF_6</td>
<td>LiClO_4</td>
<td>81</td>
<td>-0.2</td>
<td>5.8</td>
</tr>
</tbody>
</table>

\(^a\) \(W'^{a}_\text{avg} = F(\Delta M/\Delta Q)\) during the cathodic scan (g mol\(^{-1}\)).

\(^b\) \(Y'_\text{avg} = (W'^{a}_\text{avg} - W'_C)/W_{PC}\); \(W_{PC} = 145\); \(W_{ClO_4} = 99.5\); and \(W_{PC} = 102\).
proposed that a PEPy/PF₆ (or a PMPy/PF₆) film has a larger ion channel than a PEPy/ClO₄ (or PMPy/ClO₄) film. However, solvent transport in PMPy films always occurs to the opposite direction to anion transport irrespective of the dopant anion used at the film growth.

In addition, a PMPy film shows smaller charge capacity and larger \( R_D \) than a PEPy film. Thus, it seems that PMPy films have smaller ion channel than PEPy films. The apparent difference between PMPy and PEPy is their \( N \)-substituents, methyl vs. ethyl group. In our previous reports on poly(\( N \)-phenylpyrrole) (PPhPy) [16], solvent transport behavior was very similar to that of PEPy rather than PMPy, but the amount of solvent transport (\( \Delta \alpha_{avg} \)) in PPhPy is somewhat smaller than that in PEPy. These results imply that the channel size of PPhPy is smaller than that of PEPy but larger than that of PMPy. Thus, the size of \( N \)-substituent does not seem to be the only factor to determine the ion channel size. Indeed, Diaz et al. [8,24] explained the influence of phenyl substituent in terms of dipole moment of pyrrole monomer and emphasized the importance of the electronic effect of the unsaturated substituents. Conclusively, the kind of dopant anion and the steric and electronic natures of \( N \)-substituent are important factors to determine the morphology of poly(\( N \)-substituted pyrrole) films and their electrochemical properties.

4. Conclusions

Electrochemical properties of PEPy films such as solvent transport behavior, charge capacity, and the ionic resistance depend on the kind of dopant anion used at the film growth. In case of PMPy films, solvent transport behavior is not affected by the kind of dopant anion. Moreover, PEPy films show larger charge capacity and ionic conductivity than PMPy films. These differences are suggested to be due to the their morphology difference determined at the stage of film growth.

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References