

Dependence of the Electrochemical Behavior of Poly(*N*-Phenylpyrrole) Films on the Type of Anion and Solvent Used in the Electropolymerization

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The mass transport behavior during the redox reaction of poly(*N*-phenylpyrrole) (PPhPy) films in propylene carbonate (PC) and acetonitrile (AN) solutions has been studied using the cyclic electrochemical quartz crystal microbalance (EQCM) technique and the electrochemical impedance technique. It was found that the type of dopant anion and solvent used in the electropolymerization affects the amount and the direction of solvent transport during the redox reaction of a PPhPy film. It was also shown that the charge capacity and ionic resistance of a PPhPy film depends highly on the type of dopant anion and solvent used in the electropolymerization. The PPhPy film grown in a PF_6^- -containing solution shows larger charge capacity and lower ionic resistance than the film grown in a ClO_4^- -containing solution. Moreover, the PPhPy film grown in a PC solution shows similar to or larger charge capacity and lower ionic resistance than the film grown in an AN solution. These dependences on the electropolymerization condition were discussed in connection with the morphology of a film.

Introduction

The morphology of conducting polymer films depends on the electropolymerization conditions such as the type of dopant anion,¹ the nature of solvent,² and the electropolymerization rate.³ Moreover, the morphology affects the charge transport behavior during the redox reaction of conducting polymer films. Osaka et al.^{1a} reported that a polypyrrole (PPy) film prepared in a LiPF_6 -containing propylene carbonate (PC) solution (PPy/ PF_6/PC) shows faster kinetics and larger charge capacity in the ion doping/dedoping process than a film prepared in a LiClO_4 -containing PC solution (PPy/ ClO_4/PC). From the scanning electron microscopy (SEM) study, a PPy/ PF_6/PC film was shown to have rougher or more porous structures than a PPy/ ClO_4/PC film. Ko et al.^{2a} reported that a PPy film prepared in acetonitrile (AN) solution was superior to a film prepared in an aqueous media from the viewpoint of their electrochemical reversibility and electrical conductivity. They suggested that it is due to the fact that the morphology depends on the polarity and nucleophilicity of the solvent used in the electropolymerization. Kanamura et al.^{3a} showed that the diffusion coefficient during the anion dedoping process in polyaniline (PAn) films increases with the decreasing electropolymerization current density. On the basis of the X-ray diffraction study, they insisted that it is because a PAn film prepared at lower current density has the larger irregularity in the arrangement of the molecular chains.

The mass transport of ions and a solvent during the redox reaction of conducting polymers plays a central role in determining their electrochemical properties. Therefore, a great deal of investigation has been performed for the elucidation of the mass transport mechanism.⁴ Despite its complexity, the mass transport mechanism in aqueous solutions has been revealed well recently by our group.⁵ It was shown that cation or anion transport is accompanied by water transport in PPy films and that the ionic conductivity depends on the number of ac-

companying waters per ion and the ion–ion interactions inside the film. Because of its important applications, such as the rechargeable Li battery,⁶ a considerable amount of effort, if not as much as in aqueous solutions, has also been devoted to the mass transport study in nonaqueous solutions.^{6,7} However, a full understanding of its mechanism has not been achieved yet. Furthermore, there has been no systematic report on the effect of electropolymerization condition on the mass transport behaviors of conducting polymers in nonaqueous solutions as well as aqueous solutions.

In this study, the electrochemical behavior depending on the electropolymerization condition is investigated for poly(*N*-phenylpyrrole) (PPhPy) films in propylene carbonate (PC) and acetonitrile (AN) solutions. The electrochemical quartz crystal microbalance (EQCM) technique⁸ is used to monitor ion and solvent transport during the redox reaction, and the electrochemical impedance technique⁹ is used to measure the ionic resistance (R_D) in a film, respectively. First, the effect of dopant anion used in the electropolymerization was studied in PC and AN solutions. We prepared PPhPy films by using two kinds of dopant anion, PF_6^- and ClO_4^- in both solvents. Then, we performed the cyclic EQCM experiments for each film in both PF_6^- -containing and ClO_4^- -containing solutions and compared their charge capacities and solvent transport behaviors. Second, to examine the effect of the solvent used in the electropolymerization, we performed the cyclic EQCM experiments for the case where a PPhPy film prepared in a PC solution is transferred to an AN solution and the case where a film prepared in an AN solution is transferred to a PC solution. Third, to investigate the dependence of the kinetics of mass transport on the electropolymerization condition, R_D was measured for each above case. Finally, the effects of electropolymerization condition on the electrochemical behavior of PPhPy films were discussed in terms of their morphology difference.

Experimental Section

Chemicals. *N*-Phenylpyrrole (PhPy), PC (anhydrous, 99.7%), and AN (anhydrous, 99.8%) were purchased from Aldrich and

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used as received. LiClO₄, (C₂H₅)₄NPF₆ (TEAPF₆), (C₄H₉)₄NPF₆ (TBAPF₆), (C₂H₅)₄NClO₄ (TEAClO₄), and (C₄H₉)₄NClO₄ (TBA-ClO₄) were of reagent grade and dried at 80 °C for several days under vacuum. LiPF₆/PC, LiClO₄/PC, and LiPF₆/AN were of battery grade and were purchased from Mitsubishi Chemicals.

Electrochemistry and Film Preparation. The experimental apparatus, an electrochemical cell, and electrodes used in this study were the same as those reported previously^{5a} except the reference electrode. Ag/Ag⁺ (0.01 M AgNO₃) in a PC or an AN solution was used as a reference electrode. PPhPy/PF₆ films were electropolymerized galvanostatically at 0.2 mA/cm² in PC or AN solutions containing 0.1 M *N*-phenylpyrrole and 0.1 M TEAPF₆, and PPhPy/ClO₄ films were in PC or AN solutions containing 0.1 M *N*-phenylpyrrole and 0.1 M TEAClO₄. For convenience, PPhPy films electropolymerized in PC solutions are represented as PPhPy/PF₆/PC or PPhPy/ClO₄/PC, whereas PPhPy films electropolymerized in AN solutions are shown as PPhPy/PF₆/AN or PPhPy/ClO₄/AN. The charge consumed during the electropolymerization was 300 mC/cm² for all PPhPy films. From the EQCM experiment during the electropolymerization, it is shown that the amount of an electropolymerized film does not change significantly with the different electropolymerization conditions such as salt and solvent. More detailed discussion is represented in the Supporting Information. After polymerization, the cell and the film were washed with plenty of pure solvent and transferred into an Ar-filled glovebox. The cyclic EQCM and the electrochemical impedance experiments were performed in the glovebox, and the electromechanical impedance experiments were performed in the atmosphere with a closed cell. All the electrolyte concentrations were fixed as 1 M for PC solutions and 0.2 M for AN solutions. All data in the cyclic EQCM experiments were measured during the second cycle of two consecutive cycles after being held at the positive potential limit. The scan rate was 5 mV/s in PC solutions and 10 mV/s in AN solutions. In our previous report,^{5a} 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.¹⁰ In every case reported in this study, there is 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 PPhPy 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).

Results and Discussion

Anion Dependence in Propylene Carbonate Solutions. As shown in our previous reports,⁵ the comparison between current (*I*) and mass change rate ($G = dM/dt$) is very useful in monitoring potential-dependent ion and solvent transport. If ion transport is anion specific, *G* can be normalized as

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

where *F* is 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 indicates that the actual *W'* is larger than the given value.

Figure 1 shows cyclic voltammograms and *G_n* diagrams of cyclic EQCM experiments for PPhPy films in PC solutions. In

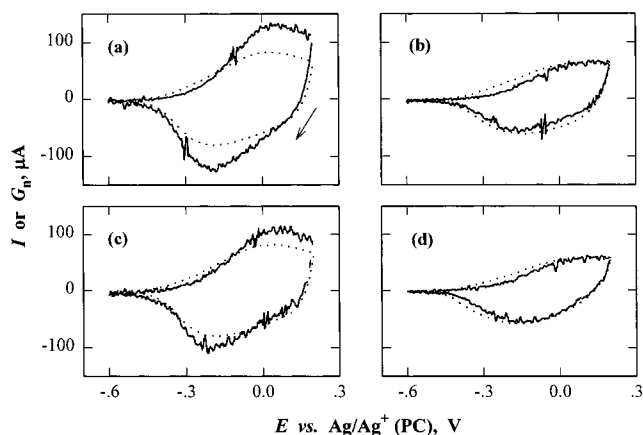


Figure 1. Cyclic voltammogram (*I* vs *E*; ···) and normalized mass change rate diagram (*G_n* vs *E*; —) for (a) a PPhPy/PF₆ film in 1 M LiPF₆/PC ($W' = W_{PF_6^-}$), (b) a PPhPy/ClO₄ film in 1 M LiClO₄/PC ($W' = W_{ClO_4^-}$), (c) a PPhPy/PF₆ film in 1 M LiClO₄/PC ($W' = W_{ClO_4^-}$), and (d) a PPhPy/ClO₄ film in 1 M LiPF₆/PC ($W' = W_{PF_6^-}$) (scan rate = 5 mV/s).

each *G_n* diagram, the molar mass of PF₆⁻ ($W_{PF_6^-}$) or the molar mass of ClO₄⁻ ($W_{ClO_4^-}$) is regarded as *W'*. During the redox reaction of a PPhPy/PF₆/PC film in LiPF₆/PC (Figure 1a), *G_n* is significantly different from *I* over the whole potential range. *G_n* is much larger than *I* around cathodic and anodic peak potentials. If *W'* is obtained by adjusting *G_n* to *I* at 0.1 V during the anodic scan, the fitted *W'* is 230. The value is much larger than $W_{PF_6^-}$ (=145). Because the actual *W'* is not uniform over the whole potential range, we obtained the average apparent molar mass (W'_{avg}) by eq 2.

$$W'_{avg} = F(\Delta M_t / \Delta Q_t) \quad (2)$$

where ΔM_t and ΔQ_t are a total mass change and a total charge change, respectively, at the anodic or the cathodic scan. In all experiments, the W'_{avg} value at the anodic scan is similar to that at the cathodic scan within an experimental error. Thus, only W'_{avg} at the cathodic scan was obtained. W'_{avg} in Figure 1a is 190, which is also larger than $W_{PF_6^-}$. It means that there is additional mass transport besides PF₆⁻ transport. Two possible explanations can be considered. One is neutral salt transport and the other is solvent transport. To examine the possibility of neutral salt transport, cyclic EQCM experiments were performed in TEAPF₆- and TBAPF₆-containing solutions where the molar masses of electrolytes are much larger than W_{LiPF_6} . *I* and *G_n* in both solutions showed very similar behaviors to those in LiPF₆-containing solution. W'_{avg} and the fitted *W'* in each solution are shown in Table 1. W'_{avg} in LiPF₆-, TEAPF₆-, and TBAPF₆-containing solutions is 186, 192, and 190, respectively. There is no significant difference between the values. It shows that neutral salt transport is evidently negligible. Therefore, solvent transport is more probable. Assuming that only anion and solvent transports occur, *W'* can be represented as follows:

$$W' = W_- + YW_s \quad (3)$$

where *W₋* is the molar mass of an anion, *W_s* is the molar mass of a solvent, and *Y* is the number of accompanying solvents per anion. The amount and direction of solvent transport can be represented by the magnitude and sign of *Y*, respectively. Table 1 shows that the average *Y* (*Y_{avg}*) for PPhPy/PF₆/PC films in PF₆⁻-containing PC solutions ranges over 0.4~0.5. It

TABLE 1: W' and Y Values Obtained in the Cyclic EQCM Experiments for PPhPy Films (Figures 1–3)

film	electrolyte	W'_{avg}^a	Y_{avg}^b	W'^c	Y^c
PPhPy/PF ₆ /PC	1.0 M LiPF ₆ /PC	186	0.4	235	0.9
PPhPy/PF ₆ /PC	1.0 M TEAPF ₆ /PC	192	0.5	230	0.8
PPhPy/PF ₆ /PC	1.0 M TBAPF ₆ /PC	190	0.4	235	0.9
PPhPy/ClO ₄ /PC	1.0 M LiClO ₄ /PC	84	-0.2	103	0.0
PPhPy/ClO ₄ /PC	1.0 M TEAClO ₄ /PC	88	-0.1	102	0.0
PPhPy/PF ₆ /PC	1.0 M LiClO ₄ /PC	111	0.1	130	0.3
PPhPy/ClO ₄ /PC	1.0 M LiPF ₆ /PC	128	-0.2	155	0.1
PPhPy/PF ₆ /AN	0.2 M LiPF ₆ /AN	143	-0.1		
PPhPy/PF ₆ /AN	0.2 M TEAPF ₆ /AN	147	0.1		
PPhPy/PF ₆ /AN	0.2 M TBAPF ₆ /AN	149	0.1		
PPhPy/ClO ₄ /AN	0.2 M LiClO ₄ /AN	92	-0.2		
PPhPy/ClO ₄ /AN	0.2 M TEAClO ₄ /AN	90	-0.2		
PPhPy/PF ₆ /AN	0.2 M LiClO ₄ /AN	111	0.3		
PPhPy/PF ₆ /AN	0.2 M TEAClO ₄ /AN	107	0.2		
PPhPy/ClO ₄ /AN	0.2 M LiPF ₆ /AN	144	-0.0		
PPhPy/ClO ₄ /AN	0.2 M TEAPF ₆ /AN	140	-0.1		
PPhPy/PF ₆ /PC	0.2 M LiPF ₆ /AN	200	1.3		
PPhPy/PF ₆ /AN	1.0 M LiPF ₆ /PC	142	0.0		

^a $W'_{\text{avg}} = F(\Delta M/\Delta Q)$ between 0.2 and -0.6 V vs Ag/Ag⁺ (PC) in PC solutions and between 0.6 and -0.2 V vs Ag/Ag⁺ (AN) in AN solutions, respectively, during the cathodic scan. ^b $Y_{\text{avg}} = (W'_{\text{avg}} - W_-)/W_s$, $W_{\text{PF}_6^-} = 145$, $W_{\text{ClO}_4^-} = 99.5$, $W_s = 41$ for AN or 102 for PC. ^c Fitted at 0.1 V during the anodic scan.

means that there is some amount of PC movement in the same direction as PF₆⁻ movement.

During the redox reaction of a PPhPy/ClO₄/PC film in LiClO₄/PC (Figure 1b), G_n is slightly smaller than I over the whole potential range and W'_{avg} (=84) is smaller than $W_{\text{ClO}_4^-}$ (=99.5) (Table 1). It means that some species move in the direction opposite to ClO₄⁻ movement. In a TEAClO₄-containing solution, W'_{avg} is also similar to that in a LiClO₄-containing solution. It indicates that both cation transport and neutral salt transport are negligible in this system too. Therefore, it is evident that a small amount of PC moves in the direction opposite to ClO₄⁻ movement.

It is shown that there is some, if not a large amount of, solvent transport during the redox reaction of PPhPy films in PC solutions. However, the solvent transport behavior for a PPhPy/PF₆/PC film in LiPF₆/PC is quite different from that for a PPhPy/ClO₄/PC film in LiClO₄/PC. In addition, peak currents for the former case are larger than those for the latter case. ΔQ_t values during the cathodic scan are 6.5 and 4.9 mC, respectively. It shows that the charge capacity for a PPhPy/PF₆/PC film is larger in LiPF₆/PC than that for a PPhPy/ClO₄/PC film in LiClO₄/PC. These differences seem to be due to the difference in the electropolymerized film or the difference in the electrolyte. To examine the origin of the differences, cyclic EQCM experiments for a PPhPy/PF₆/PC film in LiClO₄/PC (Figure 1c) and a PPhPy/ClO₄/PC film in LiPF₆/PC (Figure 1d) were performed. The data were obtained after several redox cycles to ensure complete anion exchange. The cyclic voltammogram in Figure 1c is very similar to that in Figure 1a, whereas it is quite different from that in Figure 1b. This means that a cyclic voltammogram depends on the electropolymerized film rather than on the electrolyte. For the same reason, the cyclic voltammogram in Figure 1d is similar to that in Figure 1b, not that Figure 1a. Moreover, G_n is larger than I around peak potentials in Figure 1c, which is the behavior observed in Figure 1a. On the other hand, G_n is slightly smaller than I over the whole potential range in Figure 1d, which is also the case in Figure 1b.

In brief, PPhPy/PF₆/PC films show larger charge capacities than PPhPy/ClO₄/PC films irrespective of the anion of an

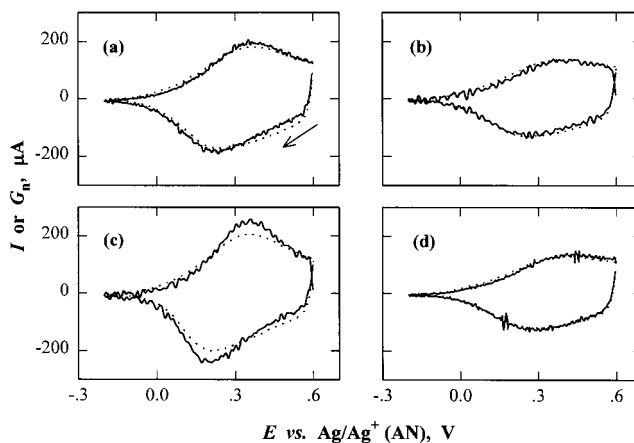


Figure 2. Cyclic voltammogram (I vs E ; \cdots) and normalized mass change rate diagram (G_n vs E ; $-$) for (a) a PPhPy/PF₆ film in 0.2 M LiPF₆/AN ($W' = W_{\text{PF}_6^-}$), (b) a PPhPy/ClO₄ film in 0.2 M LiClO₄/AN ($W' = W_{\text{ClO}_4^-}$), (c) a PPhPy/PF₆ film in 0.2 M LiClO₄/AN ($W' = W_{\text{ClO}_4^-}$), and (d) a PPhPy/ClO₄ film in 0.2 M LiPF₆/AN ($W' = W_{\text{PF}_6^-}$) (scan rate = 10 mV/s).

electrolyte solution. Moreover, for PPhPy/PF₆/PC films, solvent transport occurs in the same direction as anion transport. On the contrary, for PPhPy/ClO₄/PC films, it occurs in the direction opposite to anion transport. These results indicate that the nature of anion incorporated during a film preparation determines the charge capacity and solvent transport behavior of PPhPy films in PC solutions.

Anion Dependence in Acetonitrile Solutions. Figure 2 shows the results of cyclic EQCM experiments for PPhPy films in AN solutions. In each G_n diagram, $W_{\text{PF}_6^-}$ or $W_{\text{ClO}_4^-}$ is regarded as W' . For a PPhPy/PF₆/AN film in LiPF₆/AN (Figure 2a), G_n is very similar to I over the whole potential range. Only an average value is shown in Table 1 because the actual W' value does not change markedly with the applied potential. W'_{avg} for Figure 2a is 143, which is nearly equal to $W_{\text{PF}_6^-}$. For TEAPF₆ or TBAPF₆ solution, W'_{avg} is not significantly different from $W_{\text{PF}_6^-}$, as shown in Table 1. These results indicate that neutral salt or solvent transport is negligible, and only PF₆⁻ transport occurs during the redox reaction of PPhPy/PF₆/AN films in PF₆⁻-containing AN solutions.

For a PPhPy/ClO₄/AN film in LiClO₄/AN (Figure 2b), G_n is slightly smaller than I over most of the potential range. In this case, W'_{avg} (=92) is slightly smaller than $W_{\text{ClO}_4^-}$. W'_{avg} obtained in TEAClO₄ solution is similar to that in LiClO₄ solution. It proves the absence of cation or neutral salt transport. This supports the idea that some AN molecules move in the opposite direction of ClO₄⁻ movement. In addition, peak currents are lower than those for a PPhPy/PF₆/AN film in LiPF₆/AN (Figure 2a). It shows that the charge capacity is larger for Figure 2a than for Figure 2b, which is similar to the behavior in PC solution (parts a and b of Figure 1).

The cyclic voltammogram for a PPhPy/PF₆/AN film in LiClO₄/AN (Figure 2c) is similar to that for a PPhPy/PF₆/AN film in LiPF₆/AN (Figure 2a). Moreover, G_n is larger than I around peak potentials. W'_{avg} (=111) is larger than $W_{\text{ClO}_4^-}$, which means that there is some solvent transport in the same direction as ClO₄⁻ movement. On the other hand, the cyclic voltammogram and G_n diagram for a PPhPy/ClO₄/AN film in LiPF₆/AN (Figure 2d) is similar to those of a PPhPy/ClO₄/AN film in LiClO₄/AN (Figure 2b). These results mean that, in AN solution as well as in PC solution, the nature of the anion used in a film preparation plays an important role in determining the electrochemical properties of the film.

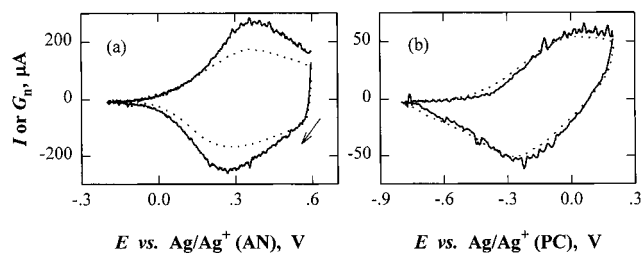


Figure 3. Cyclic voltammogram (I vs E ; \cdots) and normalized mass change rate diagram (G_n vs E ; $-$) for (a) a PPhPy/PF₆/PC film in 0.2 M LiPF₆/AN ($W' = W_{PF_6^-}$, scan rate = 10 mV/s) and (b) a PPhPy/PF₆/AN film in 1 M LiPF₆/PC ($W' = W_{PF_6^-}$, scan rate = 5 mV/s)

Solvent Dependence. As shown in the previous two sections, solvent transport behaviors in PC solutions are different from those in AN solutions. For example, solvent transport occurs considerably with anion transport for a PPhPy/PF₆/PC film in LiPF₆/PC (Figure 1a), but it is negligible for a PPhPy/PF₆/AN film in LiPF₆/AN (Figure 2a). To examine the origin of the difference, we performed the cyclic EQCM experiments by using a different solvent from that used in electropolymerization. The cyclic voltammogram for a PPhPy/PF₆ film electropolymerized in a PC solution was obtained in LiPF₆/AN (Figure 3a), and that for a PPhPy/PF₆/AN film was in LiPF₆/PC (Figure 3b). $W_{PF_6^-}$ is regarded as W' in each G_n diagram. The data were obtained after the films reached their steady states. For Figure 3a, fully developed current response is obtained within a couple of cycles and the cyclic voltammogram is very similar to that of Figure 2a. On the other hand, for Figure 3b, the peak current grows gradually with successive cycles and reaches constant values after about 50 cycles. The cyclic voltammogram shows smaller peak currents and larger peak separation than that in Figure 1a. These show that the charge capacity of a PPhPy/PF₆/PC film is not affected significantly by the nature of solvent used in the following redox reaction, whereas that of a PPhPy/PF₆/AN film is considerably decreased when the film is transferred to a PC solution.

In addition, G_n is much larger than I over the whole potential range in Figure 3a. This behavior is not similar to that observed in Figure 2a, but resembles that seen in Figure 1a. W'_{avg} is 200, which is much larger than $W_{PF_6^-}$. It seems to be due to the accompanying solvent transport, as in Figure 1a. On the other hand, G_n is very similar to I over the whole range in Figure 3b. W'_{avg} is 141, which is very similar to $W_{PF_6^-}$. It means that there is only anion transport as in Figure 2a. These results indicate that the solvent transport behavior is determined mainly by the kind of the solvent used in a film preparation rather than the one used in the following redox reaction. Thus, we can notice that the nature of solvent used in a film preparation is also an important factor that affects the electrochemical properties of the film.

Anion and Solvent Dependence of Ionic Resistance. Figure 4 shows electrochemical impedance plots for the PPhPy films used in Figure 1 (Figure 4a) and Figure 2 (Figure 4b). Electrochemical impedance plots are composed of two parts. One is the finite diffusion region at low frequency, and the other is the semi-infinite diffusion region at high frequency.^{11,12a} Except for a PPhPy/ClO₄/PC film in LiPF₆/PC, both regions are observed within the measured frequency range (0.04~272 Hz). R_D values shown in Table 2 are obtained by fitting electrochemical impedance data with the modified Randle's equivalent circuit.^{11,12} Figure 5 shows the modified Randle's equivalent circuit for the electrochemical system where only one kind of ion takes part in ion transport, which is much slower than electron transport.¹² The mathematical form of the imped-

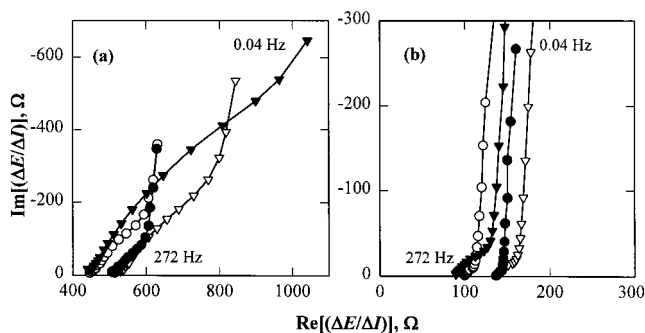


Figure 4. Electrochemical impedance ($\Delta E/\Delta I$) plots in (a) PC solutions and (b) AN solutions (a PPhPy/PF₆ film in LiPF₆ (O), a PPhPy/ClO₄ film in LiClO₄ (∇), a PPhPy/ClO₄ film in LiPF₆ (●), and a PPhPy/PF₆ film in LiClO₄ (▼)).

TABLE 2: Ionic Resistance (R_D) Obtained in the Electrochemical Impedance Experiments (Figure 4)

film	electrolyte	R_D^a (Ω)
PPhPy/PF ₆ /PC	1.0 M LiPF ₆ /PC	554
PPhPy/PF ₆ /PC	1.0 M TEAPF ₆ /PC	471
PPhPy/PF ₆ /PC	1.0 M TBAPF ₆ /PC	659
PPhPy/ClO ₄ /PC	1.0 M LiClO ₄ /PC	960
PPhPy/PF ₆ /PC	1.0 M LiClO ₄ /PC	342
PPhPy/ClO ₄ /PC	1.0 M LiPF ₆ /PC	>2000
PPhPy/PF ₆ /AN	0.2 M LiPF ₆ /AN	44
PPhPy/PF ₆ /AN	0.2 M TEAPF ₆ /AN	64
PPhPy/ClO ₄ /AN	0.2 M LiClO ₄ /AN	85
PPhPy/PF ₆ /AN	0.2 M LiClO ₄ /AN	25
PPhPy/ClO ₄ /AN	0.2 M LiPF ₆ /AN	160
PPhPy/ClO ₄ /AN	0.2 M TEAPF ₆ /AN	195
PPhPy/PF ₆ /PC	0.2 M LiPF ₆ /AN	21
PPhPy/ClO ₄ /PC	0.2 M LiClO ₄ /AN	24
PPhPy/PF ₆ /AN	1.0 M LiPF ₆ /PC	>4000
PPhPy/ClO ₄ /AN	1.0 M LiClO ₄ /PC	>4000

^a Obtained at -0.1 V vs Ag/Ag⁺ (PC) in PC solutions or 0.3 V vs Ag/Ag⁺ (AN) in AN solutions.

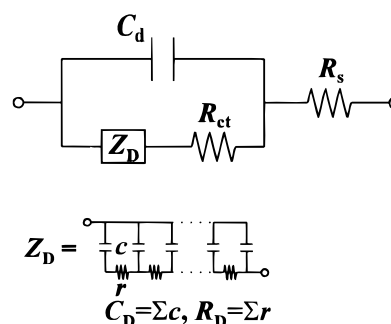


Figure 5. Modified Randle's equivalent circuit: R_s , solution resistance; R_{ct} , charge-transfer resistance; C_d , double layer capacitance; Z_D , impedance related to ion transport; R_D , ionic resistance in a film; C_D , redox capacitance in a film.

ance Z_D is given by

$$Z_D = R_D \frac{\coth \sqrt{j\omega R_D C_D}}{\sqrt{j\omega R_D C_D}} \quad (4)$$

where C_D is the redox capacitance in a film, j is $\sqrt{-1}$, and ω is an angular frequency. In both parts a and b of Figure 4, R_D increases in the following series:

$$R_D(\text{PF}_6, \text{ClO}_4) < R_D(\text{PF}_6, \text{PF}_6) < R_D(\text{ClO}_4, \text{ClO}_4) < R_D(\text{ClO}_4, \text{PF}_6) \quad (5)$$

where $R_D(\text{PF}_6, \text{ClO}_4)$ represents R_D of ClO_4^- for a PPhPy/PF₆/PC (or AN) film in a PC (or AN) solution. As seen in the series, the R_D of ClO_4^- is smaller than that of PF_6^- for the same film ($R_D(\text{PF}_6, \text{ClO}_4) < R_D(\text{PF}_6, \text{PF}_6)$ and $R_D(\text{ClO}_4, \text{ClO}_4) < R_D(\text{ClO}_4, \text{PF}_6)$). This can be ascribed to the smaller ionic size of ClO_4^- compared to that of PF_6^- . Although the difference in their crystallographic ionic radius is not very large,¹³ its effect on R_D can be very significant within the film because the environment in the interior film is very different from that in the electrolyte solution. In addition, it is noteworthy that R_D of the same anion in a PPhPy/PF₆/PC (or AN) film is smaller than that in a PPhPy/ClO₄/PC (or AN) film ($R_D(\text{PF}_6, \text{PF}_6) < R_D(\text{ClO}_4, \text{PF}_6)$ and $R_D(\text{PF}_6, \text{ClO}_4) < R_D(\text{ClO}_4, \text{ClO}_4)$). It indicates that R_D is governed by the kind of the film, namely, that the nature of anion used in the electropolymerization has a profound effect on R_D in the film. R_D values obtained for the PPhPy films in Figure 3 are shown in Table 2, and R_D values of ClO_4^- are also included. By combining them with the previous data, the following series is obtained for the same anion:

$$R_D(\text{PC}, \text{AN}) < R_D(\text{AN}, \text{AN}) < R_D(\text{PC}, \text{PC}) < R_D(\text{AN}, \text{PC}) \quad (6)$$

where $R_D(\text{PC}, \text{AN})$ represents the R_D of PF_6^- (or ClO_4^-) for the PPhPy/PF₆ (or ClO_4)/PC film in an AN solution. This shows that, in the same solvent, a PPhPy/PC film has a lower R_D than a PPhPy/AN ($R_D(\text{PC}, \text{AN}) < R_D(\text{AN}, \text{AN})$ and $R_D(\text{PC}, \text{PC}) < R_D(\text{AN}, \text{PC})$). It means that the nature of the solvent used in the electropolymerization also affect R_D profoundly.

Morphology of a Film. From the preceding experimental results, it is evident that the electrochemical properties of PPhPy films such as the charge capacity, the solvent transport behavior, and the ionic resistance depend on the kind of anion and solvent used in the electropolymerization. It is probable that the dependence on the electropolymerization condition is due to the difference in the morphology of a film or the chemical bond characteristics of a polymer chain. In the early studies,^{1a,3a} it was shown that the infrared spectra of PPy and PAN films were not affected significantly by the kind of dopant anion nor by the electropolymerization current density. It seems that the different chemical bond is not related to the dependence. Thus, the morphological difference between PPhPy films seems to be responsible for the dependence on electropolymerization conditions in this study. Many reports on the comparison of the morphology of conducting polymers are based on the SEM observations. However, we need to be more prudent in making use of SEM results because it is unsure whether the structure on the microscopic level offered by SEM can be correlated to that on the nanoscopic level, where the interaction between a polymer chain and charge compensating species should be treated.

Some researchers¹⁴ introduced the term "ion channel size" or "pore size" to explain their observations on the ion transport behaviors in PAN and poly(*N*-methylpyrrole) (PMPy) films. They observed that a large anion is hindered from penetrating into the film that is prepared with a small dopant anion, whereas a small anion is free to move through the film prepared with a large dopant anion. They proposed that it is because the ion channel size in a film is proportional to the size of dopant anion used in the film preparation. Although their assumption has not been proven directly yet, it seems to be quite probable and applicable to our case as well. When we assume that a PPhPy/PF₆ or PPhPy/PC film has a larger ion channel size than a PPhPy/ClO₄ or a PPhPy/AN film, their different electrochemical properties can be explained. Because ion movement is expected

to be less hindered in the film with large ion channel size, the relatively low R_D will be obtained for a PPhPy/PF₆ or a PPhPy/PC film and the enhanced kinetics in charge transport will increase the charge capacity of the films. In addition, solvent molecules can move along with anions more readily when the ion channel size is large enough, which explains why larger Y values are obtained for a PPhPy/PF₆ or PPhPy/PC film rather than a PPhPy/ClO₄ or PPhPy/AN film.

The hypothesis of the ion channel size assumes that the ion channel size formed at the stage of electropolymerization is maintained during the following redox cycles. It is known that the morphology of conducting polymer films may be changed during the redox reaction.¹⁵ Furthermore, the exchange of electrolyte may result in the structural change into a new conformation adequate to the electrolyte applied.¹⁶ In this study, however, the redox reaction or changing anion or solvent between PF_6^- and ClO_4^- or PC and AN does not seem to cause the dramatic conformational change. It can be inferred from this fact that W'_{avg} and R_D values are maintained at least within the experimental time scale. Consequently, the morphology difference of PPhPy films can be confirmed indirectly from the electrochemical properties of the films. Additionally, the morphology at the stage of the electropolymerization is found to affect markedly the electrochemical characteristics of a PPhPy film.

Conclusions

We revealed that the electrochemical properties of PPhPy films are greatly affected by their electropolymerization condition. The amount and direction of solvent transport depend on the type of anion and solvent used in the electropolymerization. Therefore, to obtain the conducting polymer films of desired properties, the type of dopant anion and solvent used at this stage of the film preparation should be considered seriously.

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Supporting Information Available: Details of the EQCM experiment during the electropolymerization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) Osaka, T.; Naoi, K.; Sakai, H.; Ogano, S. *J. Electrochem. Soc.* **1987**, *134*, 285. (b) Osaka, T.; Naoi, K.; Ogano, S. *J. Electrochem. Soc.* **1987**, *135*, 1071. (c) Zotti, G.; Cattarin, S.; Comisso, N. *J. Electroanal. Chem.* **1988**, *239*, 387.
- (2) (a) Ko, J. M.; Rhee, H. W.; Park, S.-M.; Kim, C. Y. *J. Electrochem. Soc.* **1990**, *137*, 905. (b) Yonezawa, S.; Kanamura, K.; Takehara, Z. *J. Electrochem. Soc.* **1995**, *142*, 3309. (c) Osaka, T.; Ogano, S.; Naoi, K.; Oyama, N. *J. Electrochem. Soc.* **1989**, *136*, 306.
- (3) (a) Kanamura, K.; Kawai, Y.; Yonezawa, S.; Takehara, Z. *J. Phys. Chem.* **1994**, *98*, 2174. (b) Osaka, T.; Naoi, K.; Ogano, S. *J. Electrochem. Soc.* **1987**, *134*, 2096. (c) Sabatani, E.; Ticianelli, E.; Redondo, A.; Rubinstein, I.; Rishpon, J.; Gottesfeld, S. *Synth. Met.* **1993**, *55–57*, 1293.
- (4) (a) Diaz, A. F.; Bargon, J. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 2, p 81. (b) Inzelt, G. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1994; Vol. 18, p 89. (c) Lyons, M. E. G. In *Electroactive Polymer Electrochemistry*; Lyons, M. E. G., Ed.; Plenum: New York, 1994; Part 1, p 1.
- (5) (a) Yang, H.; Kwak, J. *J. Phys. Chem. B* **1997**, *101*, 774. (b) Yang, H.; Kwak, J. *J. Phys. Chem. B* **1997**, *101*, 4656. (c) Yang, H.; Kwak, J. *J. Phys. Chem. B* **1998**, *102*, 1982.

- (6) (a) Momma, T.; Nishimura, K.; Osaka, T.; Kondo, N.; Nakamura, S. *J. Electrochem. Soc.* **1994**, *141*, 2326. (b) Nověák, P.; Müller, K.; Santhanam, K. S. V.; Haas, O. *Chem. Rev.* **1997**, *97*, 207.
- (7) (a) Daifuku, H.; Kawagoe, T.; Yamamoto, N.; Ohsaka, T.; Oyama, N. *J. Electroanal. Chem.* **1989**, *274*, 313. (b) Daifuku, H.; Kawagoe, T.; Matsunaga, T.; Yamamoto, N.; Ohsaka, T.; Oyama, N. *Synth. Met.* **1991**, *41–43*, 2897. (c) Desilvestro, J.; Scheifele, W.; Hass, O. *J. Electrochem. Soc.* **1992**, *139*, 2727. (d) Hillman, A. R.; Swann, M. J.; Bruckenstein, S. *J. Electroanal. Chem.* **1990**, *291*, 147. (e) Schiavon, G.; Zotti, G.; Comisso, N.; Berlin, A.; Pagani, G. *J. Phys. Chem.* **1992**, *102*, 1982.
- (8) (a) Buttry, D. A.; Ward, M. D. *Chem. Rev.* **1992**, *92*, 1355. (b) Buttry, D. A. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1991; Vol. 17, p 1.
- (9) (a) Southampton Electrochemistry Group. *Instrumental Methods in Electrochemistry*; Horwood: New York, 1993; Chapter 8. (b) Macdonald, J. R. *Impedance Spectroscopy*; Wiley: New York, 1987. (c) Musiani, M. *Electrochim. Acta* **1990**, *35*, 1665.
- (10) (a) Martin, S. J.; Granstaff, V. E.; Frye, G. C. *Anal. Chem.* **1991**, *63*, 2272. (b) Yang, M.; Thompson, M. *Anal. Chem.* **1993**, *65*, 1158. (c) Noël, M. A. M.; Topart, P. A. *Anal. Chem.* **1994**, *66*, 484.
- (11) Duffitt, G. L.; Pickup, P. G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1417.
- (12) (a) Albery, W. J.; Elliott, C. M.; Mount, A. R. *J. Electroanal. Chem.* **1990**, *288*, 15. (b) Rubinstein, I.; Sabatati, E.; Rishpon, J. *J. Electrochem. Soc.* **1987**, *134*, 3078.
- (13) Ue, M. *J. Electrochem. Soc.* **1994**, *141*, 3336.
- (14) (a) Kalaji, M.; Nyholm, L.; Peter, L. M. *J. Electrochem. Soc.* **1991**, *313*, 271. (b) Ouyang, J.; Li, Y. *J. Appl. Polym. Sci.* **1996**, *59*, 1827.
- (15) (a) Topart, P. A.; Noël, M. A. M. *Anal. Chem.* **1994**, *66*, 2926. (b) Pei, Q.; Inganäs, O. *J. Phys. Chem.* **1992**, *96*, 10507. (c) Pei, Q.; Inganäs, O. *J. Phys. Chem.* **1993**, *97*, 6034.
- (16) Pruneanu, S.; Csahók, E.; Kertész, V.; Inzelt, G. *Electrochim. Acta.* **1998**, *16–17*, 2305.