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Electrogravimetric and Electrochemical Ac Response of Polypyrrole Films

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Abstract : Ion transport of a polypyrrole/chloride (PPy/Cl) film and a polypyrrole/poly(styrenesulfonate) (PPy/PSS) film as a function of applied dc potential was investigated by employing electrogravimetric impedance technique and electrochemical impedance technique. The cation and anion contribution to the whole charge capacitance and the diffusion coefficients of cation and anion in a PPy/PSS film were calculated by fitting the electrogravimetric impedance data with proposed model circuit. The diffusion coefficients of Na^+ in a 1 M $NaClO_4$ solution are over 1 order of magnitude larger than those of ClO_4^-, and ClO_4^- contribution to charge compensation decreases as dc potential lowers. The charge compensation of a PPy/Cl film in a 1 M CsCl solution is carried out largely by Cl^- at 0.2 V vs. Ag/AgCl and by Cs^+ as well as Cl^- at -0.4 V.

Keywords : Polypyrrole, Electrogravimetric Impedance, Electrochemical Impedance, Ion Transport, Diffusion Coefficient

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1. Introduction

Conducting polymer undergoes ion transport, which plays a central role in applications of this material, to preserve the electroneutrality during redox switching. The Electrochemical Quartz Crystal Microbalance (EQCM)[1] has been utilized to investigate ion transport, and some useful informations have been drawn. However, reliable information can't be obtained when this technique is used with transient techniques such as cyclic voltammetry and chronoamperometry, because ion transport mode becomes different as applied potential varies and morphology change (shrinking or swelling) makes additional change in the resonance frequency that alters linearly in proportional to mass change[2, 3].

Another useful technique in this research area is electrochemical impedance technique[4] that can reveal slow diffusion mechanism by measuring over a wide range of frequency and minimize morphological change of polymer by small signal perturbation[5, 6]. The whole ionic conductivity and capacity can be easily obtained with this technique, but information about each ion can't be.

Electrogravimetric impedance technique[7, 8] that takes advantage of the EQCM and electrochemical impedance technique has recently been developed to get separate information of each ion from frequency-resolved mass change. Though this technique will give valuable information if well used, until now the good experimental result hasn't been reported because of instrumental difficulty.

There are two possibilities for the ion transport during redox of a polypyrrole film. One is cation transport, the other is anion transport. It has been noted that anion transport is dominant in a polypyrrole/chloride (PPy/Cl) film and that cation transport is dominant in a ploypyrrole/poly(styrenesulfonate) (PPy/PSS) film. In this study, ion transport of a PPy/Cl film and a PPy/PSS film as a function of applied dc potential was investigated by employing electrogravimetric impedance technique and electrochemical impedance technique. Especially the cation and anion contribution to the whole ionic capacitance and the diffusion coefficient of each ion in a PPy/PSS film were calculated by fitting the electrogravimetric impedance data with proposed model circuit. Ion transport of a PPy/Cl film was studied by comparing the electrogravimetric impedance with the data calculated by assuming permselectivity.

2. Experimental

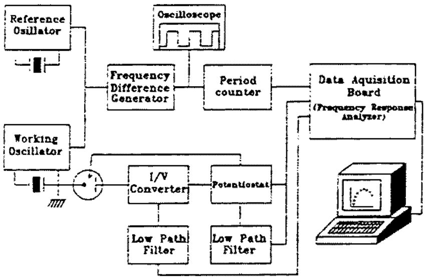
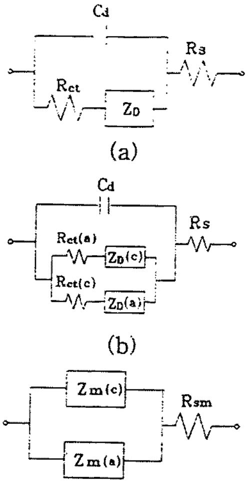


Figure 1. Schematic diagram of the experimental setup for electrogravimetric impedance technique and electrochemical impedance technique.

Pyrrole, sodium poly(styrenesulfonate)(NaPSS), cesium chloride, and sodium perchlorate were purchased from Aldrich and used as received. A standard three-electrode cell was used with a Ag/AgCl reference electrode and a Pt wire counter electrode. Pyrrole was potentiostatically polymerized and the film thickness was estimated assuming that 300 mC/cm^2 corresponds to a 1 μm film[6].

The experimental setup for the electrochemical impedance and electrogravimetric impedance is shown in Fig. 1. A 6 MHz AT-cut quartz crystal (Inficon, electrode area = 0.32 cm^2) with a sensitivity of approximately 4.0 ng/Hz was used for electrogravimetric study. The frequency was calculated by measuring the time-interval of the difference between the resonance frequency of working crystal and that of reference crystal. Electrochemical impedance data and electrogravimetric impedance data were simultaneously obtained, and also the 12 frequency data in 4 kinds of frequency range (40 kHz - 400 Hz, 400 Hz - 4 Hz, 4 Hz - 40 mHz, 400 mHz - 4 mHz) were at once obtained by using fast Fourier transform (FFT) method[9] with computer programmed sum of 12 sine signals which have 20 mV amplitudes, random phase angles, and 6 data per each decade.

Impedance data were analyzed by using the complex nonlinear least squares (CNLS) fitting to a model. The CNLS program used in this work was the LEVM program.



(a)

(b)

(c)

Figure 2. (a) Modified Randle's equivalent circuit, (b) equivalent circuit dividing diffusion process into cation and anion diffusion process and (c) equivalent circuit of electrogravimetric impedance considering only $R_D(a)$, $R_D(c)$ and R_s of (b): R_s, electrolyte resistance; R_{ct}, charge transfer resistance; C_{dl}, double layer capacitance; Z_D, diffusion impedance; *c*, cation; *a*, anion.

3. Impedance Model Circuit

Fig. 2. shows (a) a modified Randle's equivalent circuit, (b) an equivalent circuit considering the contribution of each ion and (c) an equivalent circuit of electrogravimetric impedance. The mathematical form [10] of diffusion process is given by

$$Z_D = R_D \coth((jwl^2/D)^{1/2})/(jwl^2/D)^{1/2} \qquad (1)$$

where R_D is the ionic resistance of the film, j is $\sqrt{-1}$, w is an angular frequency, l is the film thickness, D is the diffusion coefficient of ion, and D is given by

$$D = l^2/R_D C_D \qquad (2)$$

where C_D is the charge capacitance of the film.

The electrochemical capacitance($\Delta Q/\Delta E$) and the electrogravimetric transmittance ($\Delta m/\Delta E$) have relation as follows

$$\left(\frac{\Delta m_i}{\Delta E}\right) = -\frac{M_i}{n_i F}\left(\frac{\Delta Q_i}{\Delta E}\right) \qquad (3)$$

where M_i is the molar mass of ionic species, n_i is the number of electric charge, F is the faradaic constant, and negative sign is used to make the electrogravimetric transmittance to have positive value in case that mass increases by anion insertion during oxidation. Also, R_m, C_m and $R_m C_m$ of electrogravimetric impedance are given by

$$R_m(i) = -\frac{n_i F}{M_i} R_D(i) \qquad (4)$$

$$C_m(i) = -\frac{M_i}{n_i F} C_D(i) \qquad (5)$$

$$R_m(i)\,C_m(i) = R_D(i)\,C_D(i) \qquad (6)$$

If there are no solvent and neutral salt transport, the equivalent circuit of Fiq. 2c. is taken for electrogravimetric impedance. The electrogravimetric transmittance plots in some cases are shown in Fig. 3. where only $Z_m(a)$ and $Z_m(c)$ are considered in equivalent circuit of Fig. 2c. The shapes of these plots have large variation as a function of C_m and $R_m C_m$

that contain information about diffusion process of each ion. Thus if we can determine the values of $R_m(a)$, $C_m(a)$, $R_m(c)$, and $C_m(c)$, the contribution and diffusion coefficient of each ion can be obtained.

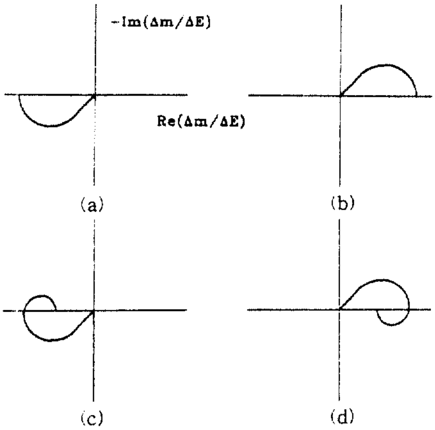


Figure. 3. Complex plane plots of predicted electrogravimetric transmittance by using equivalent circuit of Fig. 2b. in case that only diffusion process is present: ; (a) $|C_m(c)| \neq 0$, $|C_m(a)| = 0$ (b) $|C_m(c)| = 0$, $|C_m(a)| \neq 0$; (c) $|C_m(a)| < |C_m(c)|$, $R_m(a)C_m(a) > R_m(c)C_m(c)$; (d) $|C_m(a)| > |C_m(c)|$, $R_m(a)C_m(a) < R_m(c)C_m(c)$

4. Results and Discussion

Fig. 4. shows the amperometric and gravimetric responses of a PPy/PSS film where the dopant is immobile, during the first two times of CV sweep in a 1 M $NaClO_4$ solution. An initial large cathodic amperometric peak and large mass increase are observed. This phenomenon has been known as the "break-in " process, which happens when the packed film swells by sudden ion (and solvent) insertion[11]. The total charge of the first cathodic sweep is 15.4 mC corresponding to 3.67 μg mass change if only Na^+ insertion contributes to mass increase. The large mass change (25 μg) in gravimetric response implies

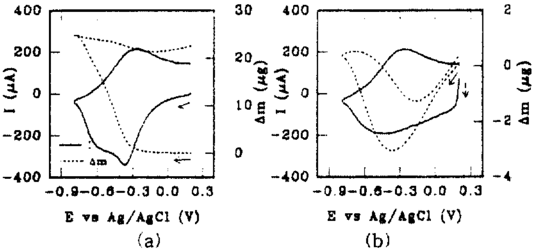


Figure 4. Amperometric and gravimetric response (scan rate = 10 mV/sec; a, the first scan; b, the second scan) of a PPy/PSS film, polymerized (Q = 102.5 mC/cm^2) in a 0.1 M NaPSS solution containing 0.1 M pyrrole, in a 1 M $NaClO_4$ solution. The full line (—) and the dashed line (···) indicate the amperometric response and the gravimetric response, respectively.

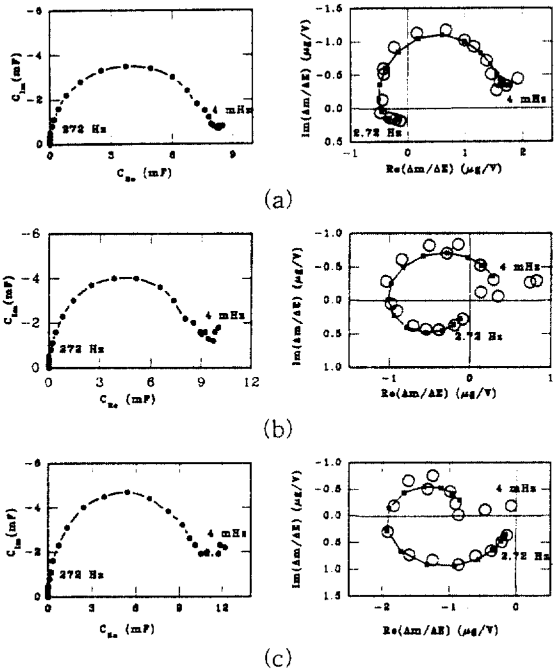
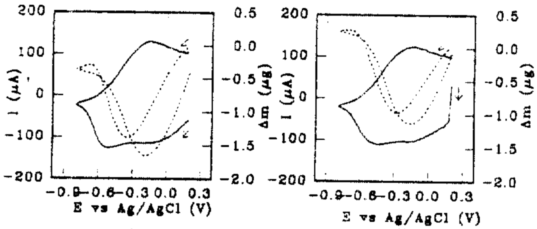


Figure 5. Complex plane plots of capacitance and electrogravimetric transmittance at (a) 0.1 V, (b) -0.1 V and (c) -0.3 V for a PPy/PSS film in a 1 M $NaClO_4$ solution. These data were obtained after two times of CV sweep (Fig. 4.). Experimental plots (∘) and fitted plots (•) are presented together for electrogravimetric plot.



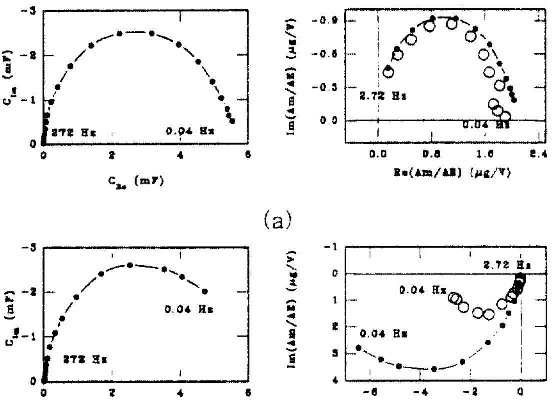
(a) (b)

Figure 6. Amperometric and gravimetric response (scan rate = 10 mV/sec; a, the first scan; b, the second scan) of a PPy/Cl film, polymerized (Q = 128 mC/cm^2) in a 1 M CsCl solution containing 0.1 M pyrrole, in a 1 M CsCl solution. The full line (–) and the dashed line (···) indicate the amperometric response and the gravimetric response, respectively.

that solvent or neutral salt insert into film during first oxidation. This feature is not observed on second scan, where the mass decreased and then increased during the second cathodic sweep. These gravimetric responses illustrate that a PPy/PSS film is not Na$^+$ permselective and that ClO_4^- takes part in anion transport.

Complex plane plots of capacitance and electrogravimetric transmittance at 0.1 V, -0.1 V, and -0.3 V are shown in Fig. 5. Table 1 summarizes the results fitted by considering $Z_m(c)$, $Z_m(a)$, and R_{sm} in the equivalent circuit of Fig. 2c. The fitted curves on the basis of the equivalent circuit are also depicted in electrogravimetric plots. The charge capacitances ($C(a)+C(c)$ in Table 1) summed each ionic capacitance have small difference with the capacitances (C_D in Table 1) obtained from capacitance plot. This result illustrates that the mass change at electrogravimetric impedance study is caused largely by charge-compensating anion or cation transport, if considering experimental error and fitting error. The diffusion coefficients of cation are in the range of 10^{-7} - 10^{-8} cm^2/s. These values are over 1 order of magnitude larger than those (10^{-3} - 10^{-9} cm^2/s) of anion. It has been presented that cation-dominated transport of a PP/PSS film at low potential (E < -0.2 V) is altered to anion-dominated one at the high potential (E > 0.0 V)[12]. In this result, though anion contribution to ion transport ($C(a)/(C(c)+C(a))$ in Table 1.) decreases as potential is lowered, the anion transport occurs over a wide potential range.

The amperometric and gravimetric responses of a PPy/Cl film during the first two times of CV sweep in a 1 M CsCl solution are shown in Fig. 6. The first amperometric and gravimetric responses are similar to the second ones. As reduction proceeds, the mass decreases and then increases. No obvious break-in phenomenon appears on the contrary to the PPy/PSS case, because film swelling doesn't occur during ion expulsion.



(a)

(b)

Figure 7. Complex plane plots of capacitance and electrogravimetric transmittance at two dc potentials (a, 0.2 V; b, -0.4 V) for a PPy/Cl film in 1 M CsCl solution. These data were obtained after two times of CV sweep (Figure 6). Experimental plots (∘) and plots (•) expected for the permselective situations ((a) Cl$^-$ ion transport; (b) Cs$^+$ ion transport) are presented together for electrogravimetric plot.

Table 1. Parameter fitted. by using the equivalent circuit of Fig. 2c.

E	$R_n(c)C_m(c)$	$C_m(c)$	$D(c)$	$R_m(a)C_m(a)$	$C_m(a)$	$D(a)$	$C(a)+C(c)^a$	$C_D{}^b$	$C(a)/(C(a)+C(c))$	R_{sm}
V	s	μg/V	cm^2/s	s	μg/V	cm^2/s	mF	mF		Vs/μg
0.1	0.27	-1.1	$6.6*10^{-8}$	4.3	2.6	$2.3*10^{-9}$	7.1	7.7	0.35	$-4.0*10^{-2}$
-0.1	0.28	-1.4	$6.4*10^{-8}$	6.1	1.8	$1.0*10^{-8}$	8.0	8.5	0.23	$-1.0*10^{-1}$
-0.3	0.57	-2.7	$3.2*10^{-8}$	5.7	2.0	$3.2*10^{-9}$	13	10	0.15	$-7.1*10^{-2}$

[a] $C(a)=FC_m(a)/M(ClO_4^-)$, $C(c)=-FC_m(c)/M(Na^+)$, [b] obtained from electrochemical impedance.

Complex plane plots of capacitance and electrogravimetric transmittance at 0.2 V and -0.4 V are shown in Fig. 7. The solid lines for electrogravimetric transmittance are not the plots fitted with the model circuit, but the plots expected for the permselective situations (Cl^- transport in 0.2 V and Cs^+ transport in -0.4 V). It has been known that a PPy/Cl film is not permselective over a wide range of potential, and many evidences of cation transport in low potential have been presented[3, 13]. The experimental data and the calculated data of electrogravimetric plot at 0.2 V have small difference, but the calculated data at -0.4 V draws larger semicircle than the experimental data. It shows that the charge compensation is carried out largely by Cl^- at 0.2 V and by Cs^+ as well as Cl^- at -0.4 V.

Acknowledgement

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