Electrochemical and In Situ Raman Spectroscopic Doping Level Determination of Poly(3-methylthiophene) and Polythiophene in Nonaqueous Solution

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비수용액에서의 폴리 3-메칠사이오펜과 폴리 사이오펜의 전기화학적 인시투 라만 분광학적 도우핑 준위의 결정

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Abstract

A Nernstian thin-layer cell model or a Nernstian adsorption model was employed in order to derive the equations to find electrochemical parameters, which are useful for judging performance of conducting polymer films, poly(3-methylthiophene) (P-3-MTh) and polythiophene (PTh) thin films, in acetonitrile solution cotaining tetrabutylammonium tetrafluoroborate. From the potential difference between the peak and the half-peak on the cyclic voltammetric wave for the first oxidation reaction of the P-3-MTh, doping level per monomer unit (DLMU) was found to be ranged from 0.25 to 0.65. The DLMU of PTh was also ranged from 0.25 to 0.60. In order to compare the electrochemical data with in situ Raman data, the in situ Raman spectroscopic study of the P-3-MTh doped with trifluoromethanesulfonate ($TFMS^-$), as well as tetrafluoroborate (BF_4^-), has been also performed in both acetonitrile and propylenecarbonate solutions with tetrabutylammonium trifluoromethanesulfonate. The DLMU was found to be ranged from 0.36 to 0.62. These in situ Raman

results are thought to be very reliable, and consistent with electrochemical data. Therefore, the thin-layer cell model or the adsorption model can be applied as a convenient fast tool to determine the DLMU.

1. Introduction

Poly(3-methylthiophene) (P-3-MTh) and polythiophene (PTh) organic conducting polymers have been shown to be good candidates for potential applications in the field of rechargeable batteries, conductors, electrochromic devices, solar energy conversion, chemical sensors, semiconducting devices, information storage, and catalysis[1-2]. They exhibit high chemical and electrochemical stability in air and in moisture in both doped and undoped states, high reversible doping level per monomer unit (DLMU), and a highly regular polymeric backbone obtained by varying (a) the nature of the dopant and (b) the structure of the monomer[1, 3]. 3-Methylthiohene forms the polymer electrochemically by the coupling of monomeric units in 2, 5-positions[1-2]. Tourillon et al.[1, 3] reported a partial crystallinity in the P-3-MTh doped with trifluoromethanesulfonate ($CF_3SO_3^-$).

Among the parameters which control the physicochemical and electrical properties of organic conducting polymers, the doping level (DLMU) is critical, because it determines the performance in the devices, such as a rechargeable battery. Tourillon, et al.[1, 3] reported that, by elemental microanalysis, the maximum DLMU of P-3-MTh with $CF_3SO_3^-$ anion was found to be 0.50. For polythiophene system, the maximum DLMU of 0.60 was reported by Afanas'ev, et al.[4].

No theoretical method to determine the doping level of conducting polymer using an electrochemical technique has not been well defined. In order to treat this problem, the equations were derived applying a thin-layer cell model. With these the doping levels (DLMU) of the conducting polymer thin films were determined and compared in the organic electrolyte solutions.

2. Experimental

All chemicals were commercially available and purchased. Poly(3-methylthiophene) (P-3-MTh) or polythiophene (PTh) was grafted on the gold substrate by electrochemical oxidation at the constant potential from the electrolyte solutions containing 0.01～0.5 M 3-methylthiophene or thiophene. Supporting electrolyte was 0.1 M $TBABF_4$ or 0.1 M TBATFMS in acetonitrile (AN) or propylenecarbonate (PC). For electrolyte solutions to perform electrochemical studies, the same solutions, except that no 3-methylthiophene or thiophene was included, were used.

Electrochemical measurements were made using an EG & G PARC Model 173 potentiostat with an PARC Model 179 digital coulometer, a PARC Model 175 signal generator, and a Houston Instrument Model x-y recorder. All potentials were referenced to an Ag/0.1 M $AgNO_3$ (acetonitrile) reference electrode or an Ag wire (Ag/Ag^+) reference electrode. All experiments were performed at room temperature, under atmospheric pressure.

Raman measurements, as described in reference [5], were made using a system consisting of a homemade sample stand with optics, a Spex Model 1877 triplemate polychromator, an EG & G PARC Model 1420 ISPD (intensified photoarray diode) detecter with an EG & G PARC Model 1218 controller, an OMA2 console system, and Tektronix Model 4662 interactive digital plotter. As an excitation source, a Spectra Physics Model Ar^+ laser was used. Wavelength of 514.5 nm was employed.

3. Results and Discussion

3.1 Doping level per monomer unit (DLMU) determination using a thin-layer cell model

Figure 1 shows typical cyclic voltammograms vs. scan rates of potential for (a) P-3-MTh doped with BF_4^- (thickness of 1400 Å), and (b) PTh doped with BF_4^- (thickness of 1200 Å), in the AN solution containing 0.1 M $TBABF_4$.

A single-electrode thin-layer cell model can be applied to P-3-MTh and PTh polymer film electrode systems, as is the solution case applied in the reference

[6], because the electroactive species are confined to a thin layer of a thin thickness of ℓ (for example, less than $2\mu m$), and a volume of V at the electrode surface under the conditions consisting of bulk electrolysis, a large area/volume ratio, and no convective mass transfer. If one consider the reaction $R \rightleftarrows O + ne$, and the conditions where the concentrations of R and O can be considered uniform [$C_R(x, t) = C_R(t)$ and $C_O(x, t) = C_O(t)$ for $0 \leq x \leq \ell$], the anodic current is given by

$$i_a=-nFV[dC_R(t)/dt] \qquad (1)$$

For a Nernstian reaction,

$$E=E^{o'}+(RT/nF)\ln[(C_o(t)/C_R(t)] \qquad (2)$$

$$C_R^*=C_R(t)+C_O(t) \qquad (3)$$

Combination of the equation (2) and the equation (3) yields:

$$C_R(t)=C_R^*\exp[-(nF/RT)(E-E^{o'})]/[1+\exp\{-(nF/RT)(E-E^{o'})\}] \qquad (4)$$

Differentiation of equation (4) and the scan rate, $\nu=(dE/dt)$, yields:

$$dC_R(t)/dt=(-nF\nu C_R^*/RT)\exp\{-(nF/RT)(E-E^{o'})\}/[1+\exp\{-(nF/RT) \\ x(E-E^{o'})\}]^2 \qquad (5)$$

The substitution of equation (5) into equation (1) yields the expression for the current:

$$i_a=(n^2F^2\nu VC_R^*/RT)\exp\{-(nF/RT)(E-E^{o'})\}/[1+\exp\{-(nF/RT) \\ x(E-E^{o'})\}]^2 \qquad (6)$$

The peak current occurs at $E=E^{o'}$ and is given by

$$i_{pa}=n^2F^2\nu VC_R^*/4RT \qquad (7)$$

For an ideal Nernstian reaction, the potential difference between the peak and the half-height of the anodic wave is given by

$$1/8=\exp\{-(nF/RT)(E_{1/2p}-E_p)\}/[1+\exp\{-(nF/RT) \\ x(E_{1/2p}-E_p)\}]^2 \qquad (8)$$

If one solves the equation (8) and assuming 25°C, it is simplified as follows:

$$\triangle E_{p,1/2p}=45.3 \text{ mV/n (at 25°C)}, \qquad (9)$$

where $\triangle E_{p,1/2p}=E_{pa}-E_{1/2p}$. If one calculate the number of electrons involved in the overall reaction, using the equation (9), since $\triangle E_{p,1/2p}$ value of 70 mV is obtained from the fresh first potential cycle, the DLMU is found to be 0.65 (0.33 for the tenth cycle). The DLMU data were summarized with the different techniques in Table 1. With increased scan rates, the DLMU values were also decreased, showing that it was ranged from 0.25 for 500 mV to 0.31 for 5 mV.

Generally, the low DLMU values were obtained from the different scan rate experiments, compared to the multiple scan experiments. It was found that the polymer film had aging effects because the different scan rate experiment was performed after the multiple scan experiments. The DLMU value was decreased with repeated scans (see Table 1).

The single-electrode thin-layer cell model can also be applied to the PTh polymer electrode system of a film thickness of ℓ, as in the P-3-MTh case. If one should try to calculate the DLMU, using the equation (9), since $\triangle E_{p,1/2p}$ value is found to be 75 mV from the fresh first cycle, it is found to be 0.60. As the scan was repeated, the $\triangle E_{pa,1/2p}$ was increased. Thus, the DLMU value was decreased, and it was 0.33 for the tenth cycle. With increased scan rates, the DLMU value was also decreased, showing that it was ranged from 0.25 for 500 mV to 0.31 for 5 mV. Therefore, the maximum DLMU of 0.60 is obtained, and it is interestingly well consistent with the value reported by Afanas'ev, et al.[4].

One could apply an adsorption model for the P-3-MTh and the PTh systems, and the same results as those obtained with the thin-layer cell model would be obtained for a Nernstian reaction.

3.2 Chronocoulometric data

Charge vs. repeated scan data of the P-3MTh film electrode (thickness of 670 Å, area of 0.055 cm^2) were obtained from the chronocoulometric experiments. If one neglects a contribution of capacitive charge to the total charge and assumes the n value of 2.25 for polymerization of 3-methylthiophene monomer, the DLMU in the oxidation reaction can be calculated from the total charge from the forward scan. The highest DLMU value was found to be 0.52 for the initial scan, and the lowest, 0.16. However, it seems hard to get a right net charge originated from Faradaic reaction with this technique due to capacitive contribution. It will be shown below that the oxidized P-3-MTh film contains high capacitance at the positive potentials.

Figure 2 shows plots of charge, Q_F, vs. forward step potential (E_j - E_i) of 5000 Å film of P-3-MTh. From the slope of the plot, the double layer capacitance, C_{dl}, can be obtained, and from the intercept on the charge axis, the Faradaic component of the adsorbed species of the total charge can be obtained

[7]. The potential was varied from E_i = -0.4 V, or 0.7 V to E_j in 0.05 V step with the PARC Model 173, and Q_F was determined from charge vs. time curve with the PARC Model 179 digital coulometer. The C_{dl} determined from the slope of the curve representing the negative potential region before the anodic peak was 2.5 $mFcm^{-2}$ (see curve 2(1)). The C_{dl} determined from the slope of curve 2(2), representing the positive potential region after the anodic peak, was 14.8 $mFcm^{-2}$. The C_{dl} values from the two segments of the potentials are different, suggesting different C_{dl} values for different oxidation states of the conducting polymer. The intermediate potential region over 100 mV from low slope to high slope shows a rapid change in the slope, representing a fast oxidation reaction. Thus, the capacitance cotribution is expected to be high in the positive potential region of cyclic voltammogram, compared to the negative potential region. A sudden change of sign of current occurs due to a high capacitance, when the potential is switched from the positive scan direction to negative scan direction at the positive switching potential (see Figure 1). The capacitance of oxidized P-3-MTh also shows a higher value than the reduced P-3-MTh due to the charged species. The capacitance is proportional to the amount of charged species in the film.

3.3 Doping level determination using in situ Raman data

In situ Raman spectra of P-3-MTh film electrode in the acetonitrile solution containing 0.1 M $TBABF_4$ were obtained in a two-compartment cell, using a wavelength of 514.5 nm of Ar^+ laser as an excitation source and OMA2 system in the potential range from -0.6 V vs. Ag/Ag^+ to +1.1 V vs. Ag/Ag^+. The intensity of resonant 1452 cm^{-1} band (symmetric ring stretching) was clearly changed with potential change. The band was strongest at -0.6 V vs. Ag/Ag^+, and according to degree of oxidation of the film with positive potentials, the intensity became decreased, and finally became negligible at +1.1 V vs. Ag/Ag^+. When the potential was switched back to more negative potentials from +1.1 V vs. Ag/Ag^+, the intensity was increased, and finally gained with almost the same value as the original reduced form at -0.6 V vs. Ag/Ag^+. The 1452 cm^{-1} band was very strong and sensitive to the potential change. The intensity of symmetric ring stretching band changes proportionately to the degree of potential change of the polymer film. Upon oxidation of the P-3-MTh polymer film, 495 nm

UV-visible absorption band also decreased in intensity. These indicate a decrease in the number of π electrons upon electrochemical oxidation without development of extra signal.

Tourillon, et al.[1, 3], as discussed in the introduction section, reported the highest DLMU (0.50) of P-3-MTh was found with the dopant, $TFMS^-$. In situ Raman experiments were carried out for both BF_4^- and $TFMS^-$ anions to compare the results (see Table 1).

Figure 3 shows log[x/(a-x)] vs. applied potential, where x is Raman intensity at a certain potential and a is the Raman intensity of fully reduced form of the film at -0.6V vs. Ag/Ag^+. In situ Raman intensity (at 1452 cm^{-1} band) was measured after waiting 30 seconds to reach a steady state. The potential was set manually using PAR. The intensity was corrected with respect to the background.

Raman intensity of 1452 cm^{-1} is proportional to the amount of the ring stretching modes in the polymer, and one can treat the Raman intensity data according to the Nernst equation:

$$E=E^o+0.059/n \log(C_o/C_R) \text{ (at 25℃)}, \qquad (10)$$

where E^o is the formal potential, n, the number of electrons involved in the overall redox reaction. C_o and C_R are concentrations of oxidized form and reduced form, respectively. The plot of log[x/(a-x)] vs. applied potential was found to be linear. From the slope (0.059/n), the number of electrons involved in the overall oxidation reaction (n) was calculated to be 0.44 ± 0.08, and from the intercept on the potential axis, the formal potential (E^o) of +0.99 V vs. Ag/Ag^+ was obtained. The E^o was close to the half-wave potential ($E_{1/2}$ of 0.96 V) from the CV. But, for the negative scan it was found to be 0.11 ± 0.01.

In order to compare effects of another kinds of anions on the n values of P-3-MTh, $TFMS^-$ doping was also carried out. The n value (DLMU) for the positive scan was found to be 0.48 ± 0.09 in acetonitrile solution, and it was found to be 0.50 ± 0.12 in propylenecarbonate solution. However, for the negative scan it was 0.45 ± 0.11 in the acetonitrile solution, and 0.37 ± 0.07 in the propylenecarbonate. The DLMU value from the P-3-MTh doped with $TFMS^-$ is higher than that from the P-3-MTh doped with BF_4^- (see Table 1). The P-3-MTh doped with $TFMS^-$ was reported to give a high value of 0.50, which was obtained from an elemental microanalysis, by Tourillon, et al.[1, 3]. It is interesting to know that our results are consistent with their results.

The DLMU value is found to be ranged from 0.36 to 0.62 from in situ Raman data. The in situ Raman data are thought to be very reliable, because the in situ Raman is a direct measurement of change in the amount of symmetric ring stretching modes upon redox reaction. Since, when the P-3-MTh system is assumed to be Nernstian, reasonable DLMU values are obtained, the oxidation reaction of the P-3-MTh system can be considered to be reversible.

4. Conclusions

A Nernstian thin-layer cell model or a Nernstian adsorption model can be applied to determine the doping level per monomer unit (DLMU) of conducting polymers. It was ranged from 0.25 to 0.65 for P-3-MTh based upon the CV data. For PTh it was ranged from 0.25 to 0.60 by the same technique. According to chronocoulometric results, as comparison experiments, the DLMU values of P-3-MTh from 0.16 to 0.52 was obtained, decreasing with repeated scans, and from the PTh film, a typical value of 0.32 was obtained. However, these values, based upon the total charge, may include errors due to high double layer capacitance of oxidized form. In the case of the P-3-MTh, the capacitance of oxidized form was 14.8 $mFcm^{-2}$, that of the reduced form being 2.5 $mFcm^{-2}$. The DLMU of P-3-MTh by in situ Raman measurements, as comparison experiments, was ranged from 0.36 to 0.62. The thin-layer cell reversible model, in situ Raman results, and chronocoulometric results showed the same range of DLMU values as those reported by Tourillon, et al. Interestingly, PTh showed the same highest DLMU value (0.60) as that reported by Afanas'ev et al.

Acknowledgments

This work was supported in part by the Office of Naval Research (Grant N00014-89-J-1339) and the National Institutes of Health (Grant S06G08047).

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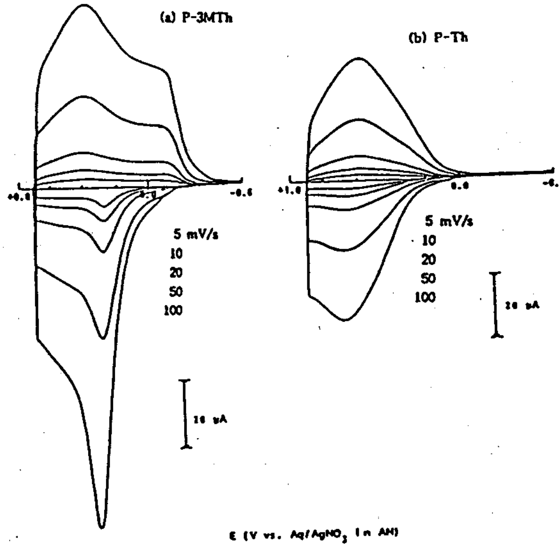

Fig. 1. (a) Cyclic voltammetric curves for poly(3-methylthiophene) in the acetonitrile solution of 0.1 M TBABF$_4$ at different scan rates of potential (5 mV/s to 100 mV/s); (b) cyclic voltammetric curves for polythiophene (1200 Å) with the same conditions as poly(3-methylthiophene). The reference electrode was Ag/0.1 M AgNO$_4$, acetonitrile.

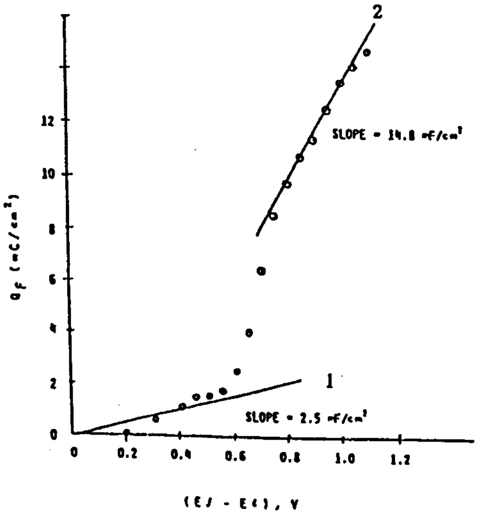

Fig. 2. Charge for forward step (Q_f) vs. step potential (E_j-E_i) of 5000 Å poly(3-methylthiophene) film electrode. The solution was the same as in Fig. 1. The potential was stepped with an increment of 0.05 V from -0.4 V (vs. Ag/0.1 M AgNO$_3$, AN) to more positive potentials.

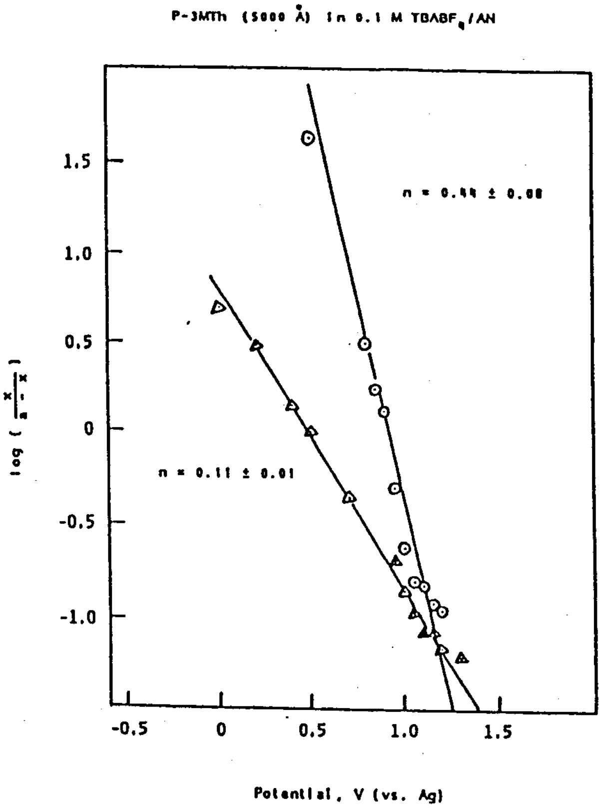

Fig. 3. Log[(x/(a-x)] vs. potential, where x=in situ Raman intensity (at 1452 cm^{-1}), and a=in situ Raman intensity at the initial negative potential (-0.6 V). The potential was versus Ag wire (Ag/Ag^+) electrode, and a two-compartment cell was used.

Table 1. Doping level per monomer unit (DLMU) of P-3-MTh and PTh.

Technique	P-3-MTh DLMU	PTh DLMU
Nernstian thin-layer cell model		
Multiple CV scans	0.65(first) ~	0.60(first) ~
BF_4^-, AN	0.33(tenth)	0.33(tenth)
Different CV scan rate	0.31(5mV/s) ~	0.31(5mV/s) ~
BF_4^-, AN	0.25(500mV)	0.25(500mV/s)
Chronocoulometry		
BF_4^-, AN	0.52(first) ~ 0.16(seventh)	0.32(1)
In situ Raman spectroscopy		
BF_4^-, AN	0.44±0.08(pos.), 0.11±0.01(neg.)	
$TFMS^-$, AN	0.48±0.09(pos.), 0.45±0.11(neg.)	
$TFMS^-$, PC	0.50±0.12 (pos.), 0.37±0.07 (neg.)	
Elemental analysis(2)	0.50	
Afanas'ev(3)		0.60

(1) Only one experiment was performed for comparison; (2) This data was quoted from the reference [1, 3]; (3) This data was quoted from the reference [4].