

18-Crown-6를 포함하는 KPF_6 Acetonitrile 용액에서 전도성
Poly(3-methylthiophene) 막전극의 특이한 전기화학적 성질

李仁鍾
한림대학교 화학과
(1998. 4. 15 접수)

An Unusual Electrochemical Response of Conducting
Poly(3-methylthiophene) Film Electrodes in KPF_6 Acetonitrile
Solution Containing 18-Crown-6

Ihn Chong Lee
Department of Chemistry, Hallym University, Chunchon 200-702, Korea
(Received April 15, 1998)

Conducting polymers, such as poly(pyrrole), poly(thiophene), poly(aniline), etc., have received considerable attention because of their wide range of applications in many areas.¹ So there are several papers dealing with the electrochemical properties of the conducting polymer in various electrolyte solutions,² and the charge transport mechanisms through the polymer.³ However, few papers on the chemical natures of ions in the polymer films have been published.^{4,5} Recently an ionic behavior of electrolytes in the conducting polymer film electrodes has been investigated by radioelectrochemical method.⁶ But the studies on ionic behavior of electrolyte in the presence of ligand for the electrolyte cation are rare.⁷

In this study, using a KPF_6 electrolyte solution containing radioactive $^{42}K^+$ and 18-crown-6, a pronounced complexing reagent for K^+ , we have determined mass changes of the electrolyte cations in conducting polymer film during electrochemical operations. Also, a directional property of current fluctuations in current-time transient curves, and decay and regeneration of CVs on the basis of mass changes of the K^+ incorporated in the polymer film have been discussed.

EXPERIMENTAL

Poly (3-methylthiophene) was electrochemically synthesized on a glassy carbon working electrode at a constant potential of +1.7 V vs. Ag/AgCl reference electrode in acetonitrile with concentration of both monomer, 3-methylthiophene, and supporting electrolyte, lithium tetrafluoroborate, of 0.05 M. Total charge for the polymerization was 250 $mC\ cm^{-2}$. The electrochemical analysis for the polymer film electrode was performed in one compartment cell containing 0.02 M KPF_6 acetonitrile in the presence and absence of 18-crown-6. The concentration of 18-crown-6 was adjusted to 0.02 M. The potential for current-time transient curves and potential range for cyclic voltammograms were +0.9 V and -0.2 to +1.2 V vs. Ag/AgCl, respectively. The electrochemical synthesis of the polymer films and their electrochemical analysis were performed with a potentiostat (BAS CV-27) equipped with an X-Y recorder (Uchida Model: YR-41T) and a flatbed recorder (Cole-Parmer Instrument Company Model: 8373-10).

Preparation of $^{42}KClO_4$ electrolyte solution was following; A small amount of KOH was irradiated

in rotary specimen racks of Triga Mark III Reactor for 9 hours. The sample was dissolved in distilled water and neutralized by an equivalent amount of concentrated HClO_4 , and the solution was used for the tracer works. The measurements of radioactivity of the $^{42}\text{K}^+$ incorporated in the polymer film electrode after each electrochemical operation - that is, polarizing the electrode at +0.9 V vs. Ag/AgCl for 10 min in combination of a consecutive potential scanning between -0.2 V to +1.2 V vs. Ag/AgCl - were performed with a scintillation counter (Canberra, Tennelec TC 952) connected to an NaI detector (Canberra, Model 727).

RESULTS AND DISCUSSION

Fig. 1 is a typical CV of poly(3-methylthiophene) film electrode in 0.02 M KPF_6 electrolyte acetonitrile solution, in which the severe current fluctuations are observed. Also the CVs obtained in the electrolyte solution containing 0.02 M of 18-crown-6 show the current fluctuation, but the frequency of the fluctuation in the 18-crown-6 system reduced so much that sometimes we rarely found the fluctuations. It has been reported that repetitive potential scans of polymer film electrode in the aqueous⁸ and acetonitrile^{6,9} electrolyte solution result in the concentration increase of the elec-

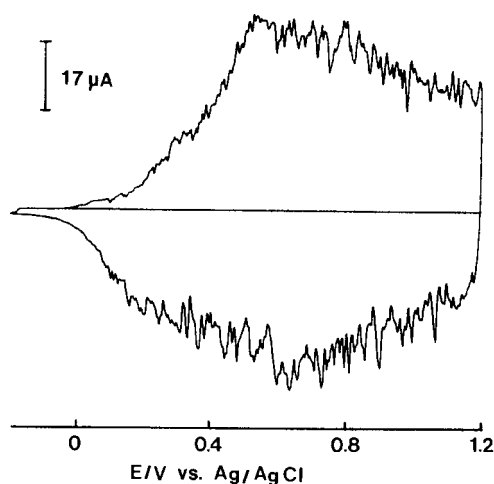


Fig. 1. A typical cyclic voltammogram of poly(3-methylthiophene) film electrode in 0.02 M KPF_6 acetonitrile. Scan rate: 0.05 V s^{-1} .

trolyte in the conducting polymer film electrode. Also, in this study, the concentration increase of electrolyte in the polymer film electrode during potential scans was observed; The concentration of K^+ in the electrode after the successive eight potential scans reached about 5 M (the surface area of the electrode was $7.1 \times 10^{-2} \text{ cm}^2$, the thickness of the polymer film was 500 nm, calculated from the charge consumed for electropolymerization according to the previously established relationship between charge and thickness,¹⁰ and the amount of K^+ incorporated in the polymer film was $3.1 \times 10^{-6} \text{ g}$), which far exceeds its solubility, 0.39 M, at 20°C in acetonitrile. This suggests that the current fluctuations are attributed to movement of the charged crystalline aggregates (nonstoichiometric sizeable particles) formed by concentration increase of the electrolyte during potential scans.

Fig. 2 is a typical pattern of current - time transient curves, obtained by polarizing the polymer film electrode at +0.9 V vs. Ag/AgCl in the 0.02 M KPF_6 acetonitrile solution, as a function of the potential scan numbers of the electrode. When a fresh polymer film electrode was subject to polarizing after a couple of potential scans, the severe current fluctuations were observed as shown in Fig. 2-1. In this case, it should be noted that, although the down fluctuations are slightly pronounced with time, the fluctuations are almost evenly divided to upward and downward. However, increase of the number of potential scans prior to the polarization caused the down fluctuations - that is, undopings of charged particles - to dominate over the up fluctuations - that is, dopings of charged particles - and further increase of the potential scans resulted in the complete down fluctuations as shown in Fig. 2-2, and finally the current - time curve without fluctuations was obtained as shown in Fig. 2-3.

Fig. 3 is a typical pattern of current - time transient curves, obtained by polarizing the polymer film electrode at +0.9 V vs. Ag/AgCl in the 0.02 M KPF_6 acetonitrile solution containing 18-crown-6 of 0.02 M, as a function of the potential scan numbers of the electrode. The 18-crown-6 had

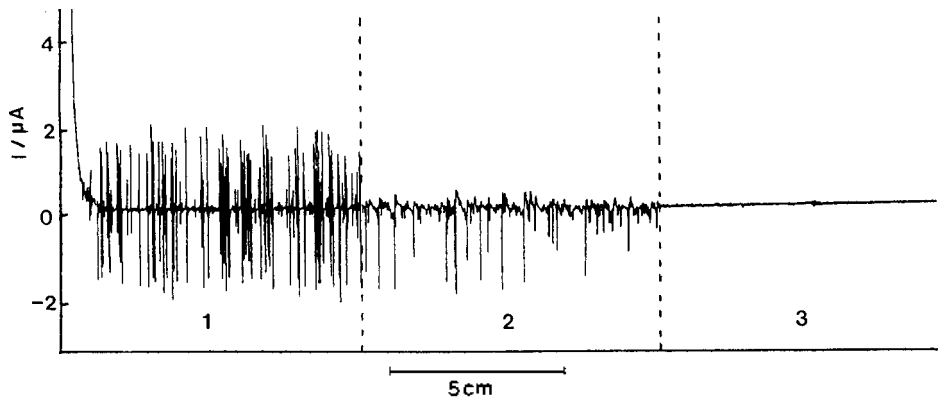


Fig. 2. A typical fluctuation pattern of current-time transient curves of poly(3-methylthiophene) electrode as a function of the potential scan numbers in 0.02 M KPF₆ acetonitrile. Applied potential: +0.9 V vs. Ag/AgCl. Chart speed: 5 cm/min. Current-time transient curves obtained after cycle no. 6, 45, and 120 are shown.

been chosen as a representative compound for the crown ether analogues because the stability constant,¹¹ $10^{5.72}$, of K (18-crown-6)⁺ complex is larger than that of any other K (crown ether)⁺ complexes in acetonitrile solution. The characteristics of the crown ether system are the reduced frequency of the fluctuation and the reversed directional property - that is, the complete up fluctuations, dopings of negatively charged particles - as shown in Fig. 3-2, which is corresponding to Fig. 2-2. Another interesting observation in the current-time transient curves is that residual currents in 18-crown-6 system are much larger than that in 18-crown-6 free system. It means that dopings in

the 18-crown-6 system are easier than that in the 18-crown-6 free system. If this is the case, the concentrations of not only PF₆⁻ but also K⁺, which are accompanied by the doping anion as co-ion, will increase. In order to confirm that, determinations of the incorporated K⁺ in the polymer film electrode were carried out as a function of the number of electrochemical operations and the results are plotted in Fig. 4 (KClO₄, less than 5% in weight of total electrolyte concentration, containing ⁴²K was added to KPF₆ acetonitrile solution to perform the tracer works). It should be noted from Fig. 4 that the amounts of the incorporated K⁺ in the polymer film electrode in the

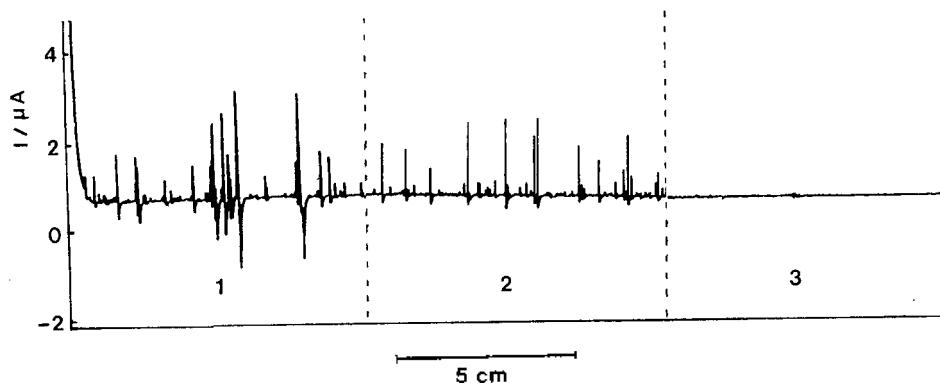


Fig. 3. A typical fluctuation pattern of current-time transient curves of poly(3-methylthiophene) film electrode under the same experimental conditions of Fig. 1 except addition of 18-crown-6 to be 0.02 M. Current-time transient curves obtained after cycle no. 4, 14, and 60 are shown.

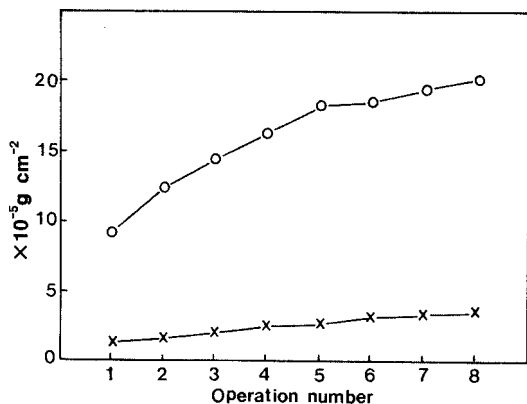


Fig. 4. Variations of incorporated K cation contents in poly(3-methylthiophene) film electrode as a function of the number of electrochemical operations. O: in 0.02 M KPF_6 acetonitrile in the presence of 18-crown-6 (0.02 M), X: in 0.02 M KPF_6 acetonitrile in the absence of 18-crown-6. Scan rate: 0.05 V s^{-1} .

18-crown-6 system steadily increase with the electrochemical operation number, and are about 5.3–6.4 times larger than that of the 18-crown-6 free system throughout the electrochemical operations. It seems that this phenomenon is attributed to complexation of cations of the electrolyte with 18-crown-6 molecules in the crown ether system. The complexation makes increase of the cation size by wrapping around the cation, resulting in decreasing the tendency of ion-pairing and aggregate formation of the electrolyte in the solution. Under the such condition, dopings of single anions as well as negatively charged small particles would be easier than the crown ether free system, showing the larger residual currents and the upward fluctuations as shown in Fig. 3-2.

A unique property of conducting polymer film electrode is the equality in magnitude of doping and undoping charges in electrolyte solution of the low polar organic solvent, acetonitrile.¹² But, in this study, the doping charges in the 18-crown-6 system were always larger than the undoping one in each potential cycle of the electrochemical operations, finally showing a complete decay of the CV as shown in Fig. 5 (8th CV). This phenomenon is obviously opposite to the generally recognized behavior of conducting polymer, that is, the conductivity

of conducting polymer increases with the dopant concentration.¹³ At this stage, even if we do not understand the unusual behavior exactly, it is supposed to be that the complexed cations and anions, penetrating deeply into the polymer film during potential scanning and polarizing of the electrode, stuff almost all of the porous holes of the polymer film. In that case, mobility of the inside ions will be greatly limited in such a way that the undopings could be partially achieved, resulting in decrease of magnitudes of faradaic currents at about +0.89 V with the electrochemical operations as shown in Fig. 5.

When the polymer film electrodes, showing the completely decayed CV as shown in Fig. 5 (8th CV), were immersed in the radioactivity-free 0.02 M KPF_6 or $(\text{Bu})_4\text{NPF}_6$ acetonitrile solution more than 10 min and were subject to the potential scans in the same solution, they show gradual regeneration of the CVs as shown in Fig. 6. After the successive seventeen potential scans, a determination of the incorporated K^+ content in the polymer film electrode was performed, and its value was $1.1 \times 10^{-4} \text{ g cm}^{-2}$, showing decrease from $2.0 \times 10^{-4} \text{ g cm}^{-2}$, corresponding to that of the final electrochemical operation in Fig. 4. This indicates that the regeneration is attributed to displacement of the complexed K^+ by bare cations or

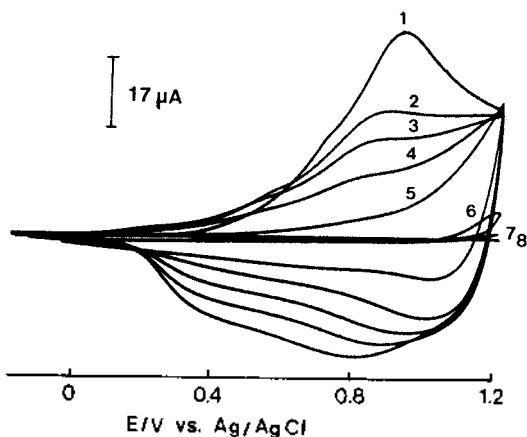


Fig. 5. Decay of cyclic voltammogram of poly(3-methylthiophene) film electrode as a function of the number of electrochemical operations in 0.02 M KPF_6 acetonitrile in the presence of 18-crown-6 (0.02 M). Scan rate: 0.05 V s^{-1} .

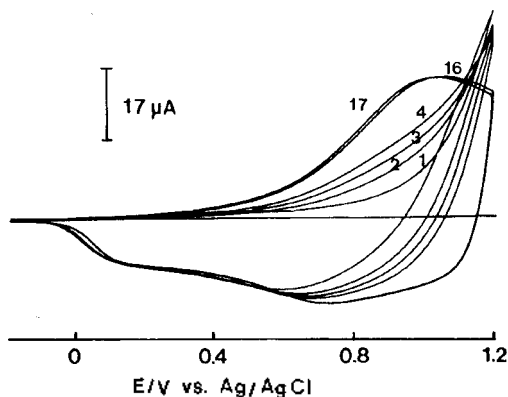


Fig. 6. Regeneration of cyclic voltammogram of poly(3-methylthiophene) film electrode in 0.02 M KPF₆ acetonitrile (the electrode was immersed in 0.02 M KPF₆ acetonitrile for 20 min and subsequently subject to potential scans in the same solution). Scan rate: 0.05 V s⁻¹.

release of the cations from the polymer film electrode in KPF₆ or (Bu)₄NPF₆ electrolyte solution, suggesting that, in either case, the cations play an important role in doping and undoping. In addition, the steady increase of the capacitive currents with potential scan numbers, as shown in the first CVs of Fig. 6, indicates that the displacement or release occur at the polymer film electrode/electrolyte solution interface at first. The regeneration of CV-doping and undoping charges to its virginal magnitudes is almost impossible, probably, due to the porous structure of the polymer film as well as the partial film degradation by oxidation.¹⁴ Also other crown ether-KPF₆ systems were studied, but the decays of the polymer film electrode in those systems were less pronounced than the 18-crown-6 system.

Acknowledgment. The author would like to thank Dr. K. B. Park and H. S. Bang, working for Korea Atomic Energy Research Institute, for making his laboratory available for this work.

REFERENCES

1. Waltman, R. J.; Bargon, J. *Can. J. Chem.* **1986**, *64*, 76.
2. (a) Stilwell, D. E.; Park, S.-M. *J. Electrochem. Soc.* **1989**, *136*, 427. (b) Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W.-Y. *J. Electroanal. Chem.* **1981**, *129*, 115.
3. Saveant, J. M. *J. Electroanal. Chem.* **1986**, *201*, 211.
4. Daum, P.; Lenhard, J.; Rolison, D.; Murry, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 4649.
5. Kaufmann, J. H.; Kanazawa, K. K.; Street, G. B. *Phys. Rev. Lett.* **1984**, *53*, 2461.
6. Lee, I. C. *J. Electroanal. Chem.* **1992**, *340*, 333.
7. Lee, I. C.; Zimmer, H.; Mark, H. B. Jr. *J. Chem. Soc., Chem. Commun.* **1989**, 497.
8. (a) Sunde, S.; Hagen, G.; Odegard, R. *J. Electroanal. Chem.* **1993**, *345*, 59. (b) Sunde, S.; Hagen, G.; Odegard, R. *J. Electrochem. Soc.* **1992**, *138*, 2561.
9. Servagent, S.; Vieil, E. *J. Electroanal. Chem.* **1990**, *280*, 227.
10. Roncali, J.; Yassar, A.; Garnier, F. *J. Chem. Soc. Chem. Commun.* **1988**, p. 581.
11. Takeda, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 866.
12. Marque, P.; Roncali, J.; Garnier, F. *J. Electroanal. Chem.* **1987**, *218*, 107.
13. Roth, S.; Bleier, H.; Pukacki, W. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 223.
14. Deng, Z.; Smyrl, W. H.; White, H. S. *J. Electrochem. Soc.* **1989**, *136*, 2152.