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## CATION-SIEVING AND ANION-SIEVING OF ELECTROSYNTHESIZED POLYTHIOPHENE FILM

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### ABSTRACT

A polythiophene film which was electrosynthesized in  $\text{BF}_3$ -dithier ether solution of thiophene under optimized conditions possesses such a compact structure instead of its fibrous structure obtained in other systems that the large ions can be prevented from incorporating into the polymer. Not only anion-sieving but also cation-sieving effect was observed.

### INTRODUCTION

A conducting polymer, such as polypyrrole, is electrochemically oxidized to be doped with anions and is neutralized to dedope these anions<sup>[1,2]</sup>. This charging and discharging processes involve simultaneous transport of charges and ions in the polymer matrix. The transport of anions is affected by their sizes. The larger anions may be prevented from doping the polymer film owing to their sizes. This was called as “ion-sieving” effect. The anion-sieving effects are found for

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polypyrrole<sup>[3,4]</sup> and poly(3-methylthiophene)<sup>[5]</sup>. No anion-sieving effect on polythiophene has been mentioned due to its fibrous structure, which is less compact than polypyrrole and poly(3-methylthiophene). Furthermore, no cation-sieving effect has been reported for any conductive polymer.

Recently, we developed a technique to electropolymerize thiophene in freshly distilled BF<sub>3</sub>-diethyl ether(BFEE). Under optimized conditions, a conductive polythiophene film with very compact structure has been obtained<sup>[6]</sup>. This makes it possible that selective permeability for ions diffusing into this polymer. In this communication, we report that the electrosynthesized polythiophene in BFEE is the first example of conducting polymers which shows both cation- and anion-sieving effects.

### EXPERIMENTAL

All electropolymerization and electrochemical measurements were performed in a one-compartment cell using an EG & G potentiostat/galvanostat model 273 under computer control. Thiophene was distilled under argon atmosphere. Freshly distilled BFEE was used as solvent. Each solution was deoxygenated by bubbling argon before the experiment and maintained a slight argon overpressure during the experiment. A platinum disc (0.2 mm<sup>2</sup>) was utilized as working electrode, which was polished with diamond paste(1.5μm) and cleaned in an ultrasonic acetone bath before use. A platinum plate and Ag/AgCl electrode were employed as the counter electrode and the reference electrode, respectively. A thin polythiophene film was synthesized on working electrode by galvanostatic polymerization at 1mA/cm<sup>2</sup> and the deposition charge was controlled as 150 mC/cm<sup>2</sup>. The polythiophene coated electrode had been kept at 0 V for at least 20 min to remove the doped anions, then the film was well washed with distilled water and acetonitrile before electrochemical measurements for anion-doping or cation-doping. Aqueous solutions containing 0.2M NaBF<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, and CH<sub>3</sub>COONa were used for anion-doping, and acetonitrile solutions containing 0.2 M LiClO<sub>4</sub>,

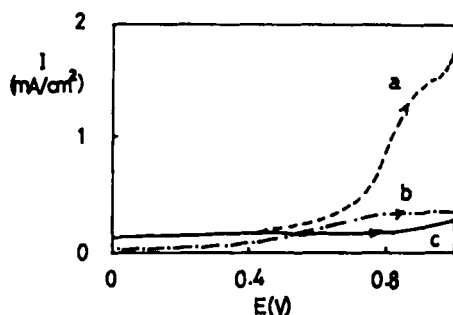


Figure 1. The differential pulse voltammograms of polythiophene film in aqueous solutions containing (a)  $\text{NaBF}_4$ , (b)  $\text{Na}_2\text{SO}_4$  and (c)  $\text{CH}_3\text{COONa}$

$\text{N}(\text{Et})_4\text{ClO}_4$  and  $\text{N}(\text{Bu})_4\text{ClO}_4$  were used for cation-doping experiments, respectively.

## RESULTS AND DISCUSSION

Different pulse voltammetries were used to evaluate the rate of electrochemical doping. Figure 1 shows the differential pulse voltammograms of a polythiophene film in three aqueous solutions.

The film used in Figure 1 was first set a potential of 0 V and then scanned from 0 to 1 V at a scan rate of 5 mV/S in various solutions. The anodic current is attributed to the oxidation of polythiophene, which is accompanied by anion-incorporation into the polymer matrix. The sequence of the diameter of these hydrated ions in aqueous solution is



it is noted that the anodic current decreased dramatically with an increase in anion size. The cut-off radius of ion which can pass through the film is about 0.40 nm. Clearly, the polythiophene film synthesized in BFEE solution has an anion-sieving effect.

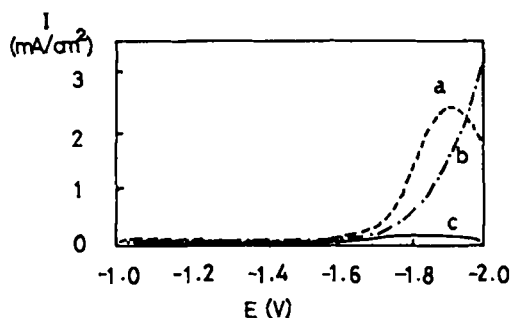


Figure 2. The differential pulse voltammograms of polythiophene film in acetonitrile solutions containing (a)  $\text{N}(\text{Bu})_4\text{ClO}_4$ , (b)  $\text{N}(\text{Et})_4\text{ClO}_4$ , (c)  $\text{LiClO}_4$

Figure 2 illustrates the differential pulse voltammograms of polythiophene film in acetonitrile solutions containing 0.2M  $\text{LiClO}_4$ ,  $\text{N}(\text{Et})_4\text{ClO}_4$  and  $\text{N}(\text{Bu})_4\text{ClO}_4$ , respectively.

The potential in Figure 2 was first at -1 V and then scanned to -2 V at a rate of 5 mV/S in various electrolyte solutions. The polythiophene film was electrochemically reduced to give cathodic current, which was followed by cation-incorporation into the film. The cation-doping current of  $\text{N}(\text{Et})_4^+$  and  $\text{N}(\text{Bu})_4^+$  are comparable. In sharp contrast, the suddenly decreased current of cation-doping for  $\text{Li}^+$  was observed. It is well known that the size of non-solvated  $\text{Li}^+$  is small. However, the radius of the solvated  $\text{Li}^+$  in acetonitrile is much larger than  $\text{N}(\text{Bu})_4^+$  and  $\text{N}(\text{Et})_4^+$  due to its strong solvability. Obviously, the polythiophene film shows a notable cation-sieving effect.

From the above experimental results, we concluded that polythiophene film electrosynthesized in thiophene/BFEE solution under optimized conditions exhibits both anion-sieving and cation-sieving effects.

## REFERENCES

1. K.K.Kanazawa, A.F.Diaz, W.D.Gill, P.M.Grant, G.B.Street, G.P.Gardini and J.F.Kwak, *Synth.Met.*, 1,329(1979/80).

2. B.Rasch, W.Vielstich, *J.Electroanal.Chem.*,**370**,109(1994).
3. P.Burgmayer, R.W.Murray, *J.Am.Chem.Soc.*,**104**,6139(1982).
4. H.Shinohara, M. Aizawa and H. Shirakawa,  
*J.Chem.Soc.,Chem.Comm.*,**87**(1986).
5. W.Zhang, S.Dong, *J.Electroanal. Chem.*, **284**, 517(1990).
6. G. Shi, S. Jin, G. Xue and C. Li, *Science*, **267**,994(1995).