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Electrochemical Synthesis of Polythiophene in an Ionic Liquid

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Abstract: Polythiophene (PTh) was prepared by the direct electrochemical synthesis in an ionic liquid ([BMIM]PF_6) containing 0.1 mol/L thiophene by cyclic voltammetry, constant potential and constant current techniques. It is found that smooth and blue–green PTh films can be obtained at a potential of *ca*. +1.75 V (*vs*. Ag/AgCl) or a current of *ca*. 1.5 mA cm^{-2} in the ionic liquid.

Keywords: Polythiophene, electrochemical synthesis, ionic liquid.

Polythiophene (PTh) has drawn much attention in recent years because of its attractive applications such as conductors, electrode materials, and organic semiconductors[1]. Electrochemical polymerization is a convenient way to prepare PTh, polypyrrole (PPy) and polyaniline (PAn)[1]. However, in contrast to PPy and PAn which can be obtained in aqueous medium, PTh is generally synthesized by electrochemical oxidation of the monomer in an organic medium. Ionic liquids are a class of novel environmentally benign “green solvents” that have remarkable properties and promising applications in many fields[2]. The air- and moisture-stable ionic liquid, 1-butyl-3-methylimidazolium hexafluoro-phosphate ([BMIM]PF_6), is an excellent solvent for many organic compounds and an electrolyte having wide electrochemical window (*ca*. 4.5 V). In this work, we report for the first time on the direct electropolymerization of thiophene in the [1]ionic liquid–[BMIM]PF_6 used as solvent and electrolyte.

Thiophene(Alfa Aesor) was purified by distillation, 1-methylimidazole was from ACROS, [BMIM]PF_6 was prepared as previously described[3]. The electrochemical synthesis and electrochemical examination were performed in a one-compartment cell with the use of an EG & G PARC model 283 potentionstat/galvanostat under computer control. The working and counter electrodes were a Pt disk (0.07 cm^2) and a Pt coil. The anodic potentials were measured *versus* an Ag/AgCl electrode. The working electrodes were carefully polished on polishing cloth with alumina water mixture before each synthesis.

Cyclic voltammograms (CVs) of thiophene in [BMIM]PF_6 are shown in **Figure 1 A**. By scanning the potential between –0.4 V and +1.8 V *vs.* Ag/AgCl, the CVs corresponding to the growth of a conducting polymer were observed and blue-green

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homogeneous films were formed. As seen from this figure, the strong oxidation of thiophene starts at *ca*. +1.6 V, a couple of redox waves appeared at *ca*. +0.4 V and +1.1 V could be ascribed to the doping and dedoping of PTh, respectively, and their current strengths increased with potential scan continued because of the increase in the thickness of the PTh film on the electrode. On the other hand, the CV of the pure [BMIM]PF_6 showed no current waves in the same potential scale (**Figure 1 B**). This behavior conformed that the CV waves in **Figure 1 A** could be assigned to the oxidation polymerization of thiophene and the redox reaction of polythiophene.

Likewise, PTh films were also prepared using constant potential and constant current techniques. It was found that smooth and blue–green films were obtained when the potential for the electropolymerization was controlled between +1.7 V and +1.9 V. At potentials more than +2.0 V, the films appeared to be destroyed due to overoxidation of the polymer. When the current density was between 1.5 mA • cm^{-2} and 3.0 mA • cm^{-2}, the potential measured during constant current electrolysis experiments was +1.7V to +1.9 V, and smooth and blue-green films could be prepared. The electroactivity of the PTh films obtained at constant current density (j=1.5 mA • cm^{-2}, t=600s) was tested in pure [BMIM]PF_6 (**Figure 2**). It can be seen that the dedoping (reduction at *ca.* +0.4 V) and re-doping (re-oxidation at *ca.* +1.1 V) of the PTh film are reversible in the ionic liquid.

Further work on the synthesis and characterization of conducting polymer in ionic liquids is under way in our laboratory.

Figure 1 Cyclic voltammograms of 0.1 mol/L thiophene in [BMIM]PF_6(**A**) and that of pure [BMIM]PF_6(**B**) on Pt disk electrode at a potential scan rate of 50 mV • s^{-1}

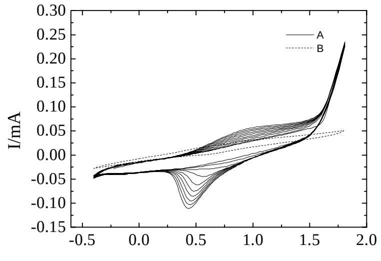
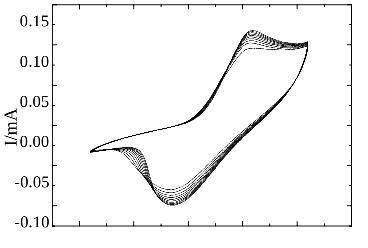


Figure 2 Cyclic voltammograms of PTh film at Pt disk electrode in pure [BMIM]PF_6 at a potential scan rate of 50 mV • s^{-1}



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