

Effect of polar solvent acetonitrile on the electrochemical behavior of polyaniline in ionic liquid electrolytes

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Abstract

Polyaniline film was electropolymerized in organic acidic media (CF_3COOH) and then investigated by cyclic voltammetry, AC impedance, and galvanostatic charging and discharging tests in ionic liquid—1-methyl-3-butylimidazolium hexafluorophosphate (BMIPF_6) and the mixture electrolytes of BMIPF_6 and acetonitrile (ACN) with different ratios. The results showed that the polymer in mixture of BMIPF_6 and ACN have lower solution resistance, higher cycle life, and higher electrochemical capacitance. The relationship of the peak current to the scan rates provides some insight into the nature of the polyaniline film switching reaction in different electrolytes.

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1. Introduction

Air-stable 1,3-dialkylimidazolium-based room-temperature molten salts have been extensively utilized for a variety of electrolytes in batteries and capacitors [1–4]. These ionic liquids possess several properties, which make them attractive alternatives to traditional nonaqueous electrolytes. Chief among these were nonvolatility, nonflammability, and high thermal and electrochemical stability [5–7]. They were also recyclable and more environmentally benign than most conventional organic solvents. The films prepared in conventional solvents but cycled in an ionic liquid showed the improved electrochemical performance and significantly increased lifetimes, to up to a million cycles [8].

From the above points of view, ionic liquids were expected to be peculiar media for electroorganic syntheses and electropolymerization. The alkyylimidazolium-based ionic liquids have been investigated as possible electrolytes for electrochemical synthesis and electropolymerization [9–14]. Ionic liquid could also be used for electrolytes in electro-

chemical apparatus. Because the nature of the alkyylimidazolium-based ionic liquids is greatly affected by the anion component, not all imidazolium-based ionic liquids are suitable for the electropolymerization and electrochemical apparatus [8]. It has been proved that the imidazolium ionic liquid having CF_3COO^- is a much superior electrolyte for polymerization as compared to those having either the tetrafluoroborate (BF_4^-) or hexafluorophosphate (PF_6^-) anions, because the greater diffusion of cations than of anions was a useful factor improving the cation-exchange behavior of the polymer [14–16].

In this work, electropolymerized polyaniline film grown from organic media was investigated in BMIPF_6 and BMIPF_6 containing ACN. Mixtures of IL and ACN have the lower viscosity and higher conductivity, which result in the improved lifetimes and electrochemical capacitance of the polyaniline film.

2. Experimental

2.1. Chemicals

Acetonitrile was dried with P_2O_5 and distilled before use. BMIPF_6 from ACROS ORGANICS was dried at 70 °C for 12 h under vacuum before use.

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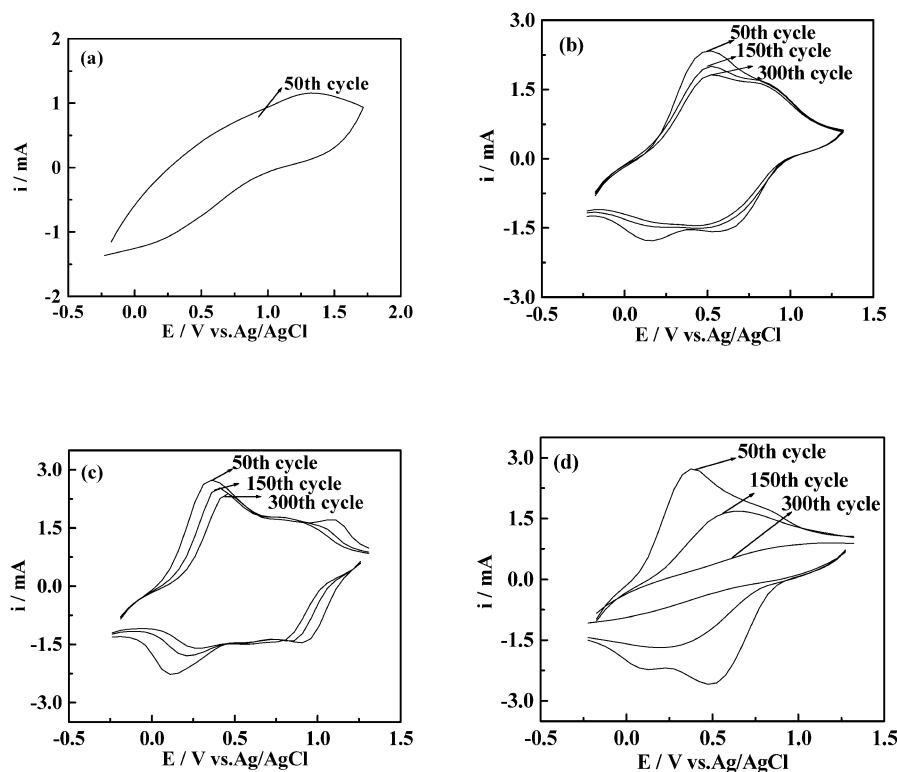


Fig. 1. Cyclic voltammograms for polyaniline films at 100 mV/s. The volume ratios of ACN/IL: (a) neat ionic liquid, (b) 1:3, (c) 1:1, and (d) 3:1. Polymer films were grown under the following conditions: electropolymerized galvanostatically at a current density of 0.1 mA/cm² for a deposited charge of 0.18 C/cm², A = 1 cm² from 0.5 M aniline/2 M CF₃COOH/0.1 M Bu₄NBF₄/acetonitrile solution.

2.2. Electropolymerization of polyaniline

The polymer film was grown from a solution containing aniline 0.5 and 0.1 M tetrabutylammonium tetrafluoroborate (Bu₄NBF₄). Trifluoroacetic acid (2 M) was also added to this solution. The electropolymerization was performed galvanostatically on an EG&G Potentiostat/Galvanostat 273A model at 0.1 mA/cm². The film were then washed in ACN in order to remove soluble species from the film and cycled in a series of monomer-free electrolytes.

2.3. Electrochemical measurements

All the measurements were performed in a closed one-compartment three-electrode cell and N₂ was saturated before test. Cyclic voltammetry, AC impedance, and galvanostatic charging and discharging tests were performed on an AUTOLAB PGSTAT30. A platinum wire was used as the counterelectrode and the reference electrode was Ag/AgCl/0.3 MKCl electrode. A platinum plate (1 × 1 cm²) was used as the working electrode to deposit the polymer and also as the working electrode to investigate the electrochemical behavior of the polymer. Prior to any measurements, the working electrode was polished by alumina slurry and then washed in acetone in an ultrasonic bath for 1–2 min and dried at 50 °C. Conductivities of electrolytes were measured by a DDSJ-308 conductivity detector.

3. Results and discussion

3.1. Cyclic voltammetry

The cyclic response of polyaniline films containing CF₃COOH was dependent on the electrolytes used during tests. Polyaniline films were tested in five different kinds of electrolytes: neat BMIPF₆, IL:ACN = 3:1, 1:1, 1:3, respectively (IL was BMIPF₆, ratio was volume ratio) (shown in Fig. 1). The polyaniline (CF₃COOH) film showed strong electroactivity during the first 50 cycles in the neat BMIPF₆ at 10 mV/s between 1.7 and –0.4 V. Nevertheless, the observed rapid decreases in electroactivity during the first 150 cycles indicated the difficulty of insertion of anion PF₆[–] into the polymer matrix from ionic liquid BMIPF₆. This also suggests that the composition of ionic liquids plays an important role in determining the electroactivity and performance of conjugated polymers. The gradual loss of redox activity in the BMIPF₆ could be due to loss of melt from the film (deswelling) producing a more compact polymer with restricted ion mobility. Fig. 1a is the CV plot of polymer in pure ionic liquid at 100 mV/s. From the shape of Fig. 1a, we could see that it has a weak oxidation peak and no reduction peak, which also means difficulty of anion exchange. For ionic liquids containing small anions (BF₄[–], PF₆[–]), the insertion/deinsertion of the anions into/out of the polymer was the dominant effect in the processes of oxidation/reduction.

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