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ORIGINAL PAPER

Electropolymerization of benzotriazole in room temperature ionic liquid [bmim]PF_6

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Abstract The electropolymerization of benzotriazole on an Au electrode was investigated via cyclic voltammetry and chronoamperometry in a room temperature ionic liquid medium, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) containing glacial acetic acid. The chronoamperometric investigation revealed that the instantaneous nucleation predominated the potentiostatic electropolymerization of benzotriazole at the oxidation peak potential. Scanning electron microscopy indicated that the polymer film was compact and relatively smooth and infrared spectroscopy suggested the polymer chains were formed mainly via coupling of the unsaturated nitrogen atoms. The polymer was found to be highly electroactive, showing a quasi-reversible and stable pair of redox peaks centering at 0.9 V versus Ag/AgCl in 0.1 mol L^{-1} H_2SO_4.

Keywords Poly(benzotriazole) · Room temperature ionic liquid [bmim]PF_6 · Electropolymerization · Chronoamperometry

1 Introduction

Room temperature ionic liquids (RTILs) are ionic melts with a melting point below 100 °C [1]. RTILs exhibit many excellent physical and chemical properties, e.g. high electrical conductivity, low volatility, excellent thermal and electrochemical stability, excellent solubility properties and they are widely applied in analytical chemistry, electrochemistry, organic synthesis and other fields [2–6]. Air and water stable RTILs such as 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) have attracted much attention in recent years [7, 8].

Some RTILs have been shown to be excellent media for the syntheses of some conducting polymers. Polypyrrole has been successfully synthesized in RTIL medium [9]. Polyaniline prepared in RTIL exhibited excellent electrochemical stability [10]. It has been proven that the RTILs own wide electrochemical windows and unique solvent capability, in which the growth of some conducting polymers that cannot be electrosynthesized in aqueous solution because of oxygen evolution may become successful. Thus thiophene and benzene have also been polymerized in RTILs [11–13].

Benzotriazole as a heteropolycyclic compound has been widely used to inhibit metal corrosion [14–16] and it is also used as an important additive for metal plating [17]. So far, studies on benzotriazole have mainly focused on the adsorption behavior and bonding structure with the substrate metal [18]. In this work we aim at the polymerization of benzotriazole without metallic ions. Benzotriazole is oxidized in [bmim]PF_6 containing glacial acetic acid to form a polymer film on an Au electrode by chronoamperometry. Glacial acetic acid is chosen here to control the medium acidity for its high purity and low viscosity. The Au electrode as working electrode can avoid the formation of a metallic ion-benzotriazole surface complex through the metal oxide. The initial stage of electropolymerization process is investigated by chronoamperometry. The morphology and structure of the polymer film are analyzed and the electrochemical characteristics of the polymer are tested by cyclic voltammetry.

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2 Experimental

[bmim]PF_6 was prepared according to the reported procedure [8], the final product of which was dried under vacuum for 48 h to control the water content below 3 ppm, as determined by Karl-Fischer titration. The result of NMR of [bmim]PF_6 was the same as that reported [19] and no multi-resonance peaks of impurities were observed.

The electrochemical tests were carried out in a one-compartment cell with use of a CHI 660B electrochemical workstation (CH Instrument, Inc.). The working electrode was an Au electrode (3.14 mm^2). A Pt coil was used as counter electrode. The reference electrode was a prototype Ag/AgCl electrode. Before the electrochemical measurements the surface of the Au electrode was polished with 0.5 μm alumina powder, then washed with redistilled water, ethanol and acetone. The cell was cleaned in a mixture of 50/50 vol% concentrated H_2SO_4 and aqueous hydrogen peroxide (30%). [bmim]PF_6 was used as the medium for the electropolymerization of benzotriazole and glacial acetic acid was added to obtain acidic conditions. The electropolymerization experiments were performed under a nitrogen atmosphere.

The morphology of the polymer film was examined by a JSM-6700F scanning electron microscope (SEM). Infrared (IR) measurements were carried out on a Perkin Elmer Spectrum One spectrophotometer. For this purpose the polymer film was removed from the electrode surface and embedded in a KBr tablet. The electrochemical characteristics of the polymer film were investigated in 0.1 mol L^{-1} H_2SO_4.

Benzotriazole and other chemicals were of analytical grade (Sinopharm Chemical Reagent Co., Ltd.). All aqueous solutions were prepared with double-distilled water. All experiments were performed at ambient room temperature.

3 Results and discussion

3.1 Cyclic voltammograms of benzotriazole

Cyclic voltammograms of the Au electrode in [bmim]PF_6 containing 0 or 0.5 mol L^{-1} glacial acetic acid medium were measured to examine the effect of the acid on the electrochemical characteristics of [bmim]PF_6. As shown in Fig. 1, the electrochemical window of [bmim]PF_6 was as wide as 4.2 V (from −2.2 to 2.0 V) in pure [bmim]PF_6, though being limited by the decomposition of PF_6^- and the reduction of $[bmim]^+$. With glacial acetic acid the anodic limiting potential was the same, but the cathodic limiting potential was positively shifted to ca. −0.70 V, because of hydrogen evolution at more negative potentials. Therefore, the medium of [bmim]PF_6 containing 0.5 mol L^{-1} glacial acetic acid ([bmim]PF_6-HAc) showed a stable potential range from −0.70 to 2.0 V.

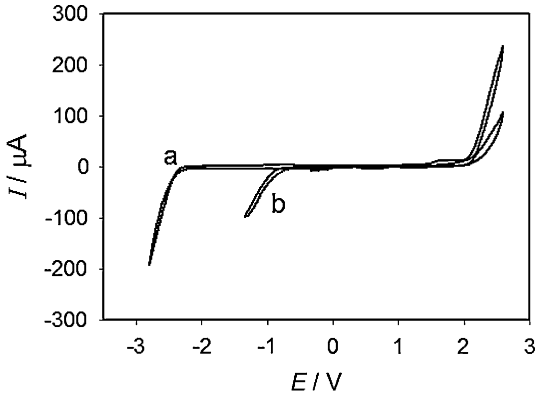

Fig. 1 Cyclic voltammograms in [bmim]PF_6 containing 0 (a) or 0.5 (b) mol L^{-1} glacial acetic acid. Scan rate: 0.005 V s^{-1}

A cyclic voltammogram of benzotriazole in the [bmim]PF_6-HAc medium is shown in Fig. 2. An obvious anodic peak was observed at 1.67 V, which may indicate the oxidation of benzotriazole monomer to form a polymer. In the reverse scan a small reduction peak was also observed. A trace-crossing was observed at potentials near the positive limit of the medium (1.85–2.0 V), at which the oxidation of benzotriazole is expected to be gradually weakened but the oxidation of the [bmim]PF_6 medium was gradually enhanced. It is difficult to explain the nature of the trace-crossing with the nucleation-and-growth mechanism [20, 21] of conducting polymers only, which may also be related with the new monomer and the new medium. The nature of the trace crossover is a matter requiring further investigation.

3.2 Poly(benzotriazole) prepared by chronoamperometry

Chronoamperometry is an important diagnostic technique for the initial stage of electrocrystallization [22–24]. Figure 3 shows a current transient (CTT) recorded during the

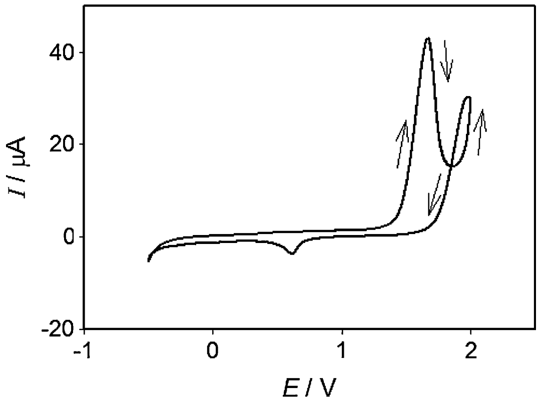

Fig. 2 Cyclic voltammogram in [bmim]PF_6 containing 0.5 mol L^{-1} benzotriazole and 0.5 mol L^{-1} glacial acetic acid. Scan rate: 0.1 V s^{-1}

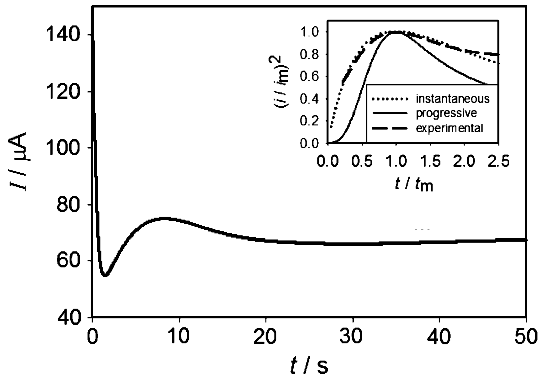

Fig. 3 Current transient for benzotriazole electropolymerization at 1.67 V in [bmim]PF_6 containing 0.5 mol L^{-1} benzotriazole and 0.5 mol L^{-1} glacial acetic acid. Inset: comparison of the experiment curve with theoretical curves from the Scharifker–Hills model

oxidation of benzotriazole monomer in [bmim]PF_6-HAc medium at 1.67 V, which corresponds to the potential of the anodic oxidation peak in Fig. 2. The electropolymerization process should be hardly affected by other reactions. The CTT can be divided into three regions. In the first region ($t < 1.5$ s), the decrease in oxidation current is related to charging of the double layer due to the specific adsorption of benzotriazole on the Au electrode. The second region corresponds to the increase in the oxidation current up to a maximum, which is typical of nucleation and growth processes. The third region corresponds to the decrease in the oxidation current, which is typical of a diffusion controlled process. An analysis of the CTT was performed by fitting the experimental data to a dimensionless theoretical curve for crystal nucleation and diffusion controlled growth in three dimensions (3D), as proposed by Scharifker and Hills [25]. The instantaneous and progressive theoretical transients are given by Eqs. 1 and 2, respectively,

$$\frac{i^2}{i_m^2} = \frac{1.9542}{t/t_m}\{1 - \exp[-1.2564(t/t_m)]\}^2 \qquad (1)$$

$$\frac{i^2}{i_m^2} = \frac{1.2254}{t/t_m}\{1 - \exp[-2.3367(t/t_m)^2]\}^2 \qquad (2)$$

where t and i are the time and current density with their maxima of t_m and i_m, respectively.

The experiment data are fitted as shown in the inset of Fig. 3. The experimental curve conforms to the theoretical curve of the instantaneous nucleation model. Therefore, it can be concluded that instantaneous nucleation predominated at the oxidant peak potential for the electropolymerization of benzotriazole.

3.3 Morphology and structure of poly(benzotriazole)

Chronoamperometry was used for the polymerization of benzotriazole to avoid the uncertain effect of the trace crossover observed in the cyclic voltammogram. A dark red polymer film prepared by chronoamperometry was observed by the naked eye. The film color did not change after washing with acetone and double-distilled water several times, demonstrating that the film was not simply an adsorbed layer of benzotriazole. The SEM picture of the electrosynthesized polymer film on the Au electrode is shown in Fig. 4. The polymer film was prepared by chronoamperometry at 1.67 V for 1,000 s. The film is highly compact, almost grain-free, and relatively smooth, though several flaws can also be observed. This morphology is similar to that of poly(bithiophene), a smooth and dense polymer film obtained using RTILs as the electrolyte [26].

It is accepted that the substitution pattern in the polymer can be analyzed by IR spectrophotometry [27, 28]. In order to gain further insight into the structure of the poly(benzotriazole) film, the IR spectrum of the polymer powder was collected, as shown in Fig. 5. The main peak at 1,483 cm^{-1} corresponds to the C–C vibrations in the aromatic ring [29]. The bands at 1,263, 991, and 790 cm^{-1} can be assigned to

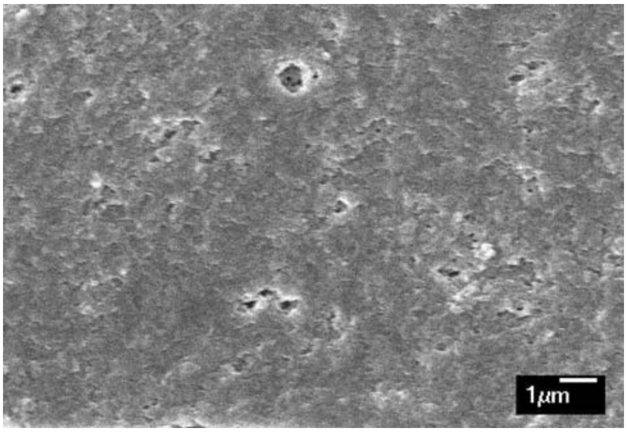

Fig. 4 SEM micrograph of poly(benzotriazole)

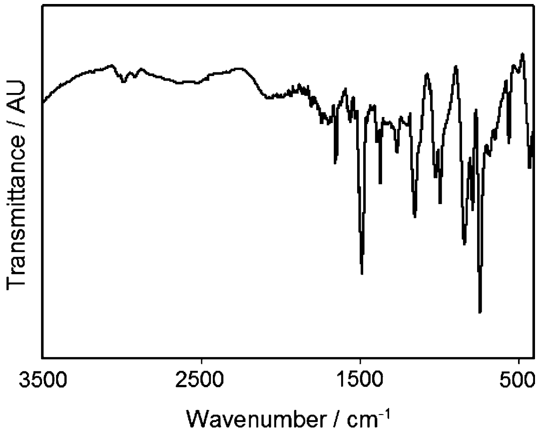

Fig. 5 IR spectrum of the prepared polymer film

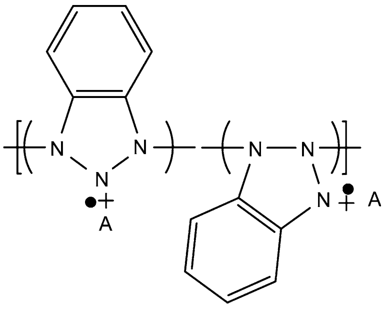

Fig. 6 The potential structure of poly(benzotriazole)

the C–N vibration [30], in plane C–H vibration at the benzene ring, and out of plane C–H vibration at the benzene ring [31], respectively. However, the characteristic band of the N–H vibration over 3,100 cm^{-1} is not clearly observed. It was also found that the N–H vibration of benzotriazole disappeared in the investigation of the structure of the films on copper surfaces in the presence of benzotriazole by Poling [32], and the study indicated that the copper was bonding with the amino N of the benzotriazole molecule, and the film was composed of a copper ion-benzotriazole complex. However, the metallic ion is absent in the present reaction. So it is possible that the poly(benzotriazole) is connected by unsaturated N atoms, and the potential structure of the polymer is represented in Fig. 6.

3.4 Electrochemical characteristics of poly(benzotriazole)

Cyclic voltammograms of the poly(benzotriazole) film in 0.1 mol L^{-1} H_2SO_4 aqueous solution are shown in Fig. 7. The film was prepared by chronoamperometry at 1.67 V for 1,000 s. The film was thoroughly washed several times with acetone and double-distilled water, and cyclic voltammograms of the film were then acquired at potential scan rates from 0.005 to 0.1 V s^{-1}. The reduction (de-doping) and re-oxidation (re-doping) of the polymer film exhibited a nice quasi-reversible electrochemical behavior, indicating that the polymer is highly electroactive here. The anodic and cathodic peak currents ($I_{p.a}$ and $I_{p.c}$) rose linearly with square root of potential scan rate (correlation coefficient $r_{p.a} = 0.9970$, and $r_{p.c} = 0.9972$), indicating mainly diffusion control, e.g. cation and/or anion diffusion in the polymer film during oxidation and reduction.

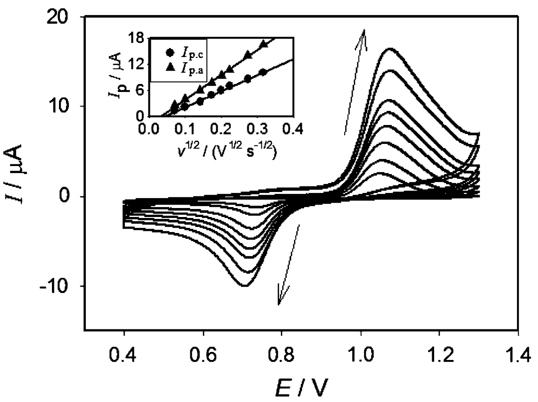

Fig. 7 Cyclic voltammograms of a poly(benzotriazole) film in 0.1 mol L^{-1} H_2SO_4 at various potential scan rates. Scan rates: 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.075, and 0.1 V s^{-1} from inner to outer. Inset: the absolute values of the anodic and cathodic peak currents versus the square root of scan rate

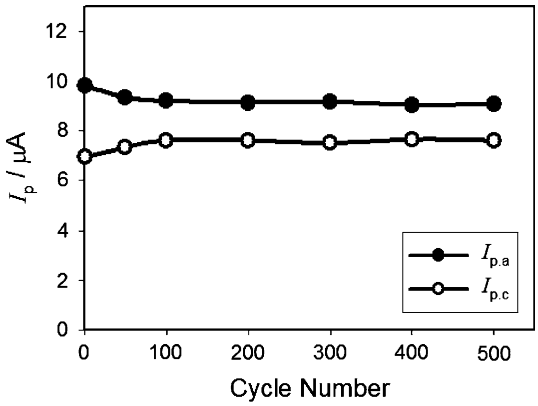

Fig. 8 Relationship between the peak currents ($I_{p.a}$ and $I_{p.c}$) of the polymer film and the cycle number. Scan rate: 0.05 V s^{-1}

In practical application, the long-term cycling stability of electrochemical activity is very important. Therefore, the long-term cycling stability of poly(benzotriazole) was evaluated by cyclic voltammetry in 0.1 mol L^{-1} H_2SO_4 aqueous solution and the results are shown in Fig. 8. In the initial 100 cycles, the oxidation peak current of the polymer ($I_{p.a}$) decreased gradually but the reduction peak current ($I_{p.c}$) increased gradually with increase in cycle number, resulting from the change of the surface structure of the polymer film. After the 100th cycle, the values of $I_{p.a}$ and $I_{p.c}$ remained almost unchanged. The $I_{p.a}$ and $I_{p.c}$ at the 500th cycle were 9.058 and 7.588 µA, which are 98.93 and 99.89% of those at the 100th cycle, respectively. The excellent long-term cycling stability of the polymer suggests that poly(benzotriazole) should be a good electrode material.

4 Conclusions

Poly(benzotriazole) was prepared by chronoamperometry in [bmim]PF_6 containing glacial acetic acid. The polymer exhibited excellent electrochemical activity and stability in 0.1 mol L^{-1} aqueous H_2SO_4. The monomer and solvent employed in this work are believed to be highly environmentally friendly, and the suggested method for electropolymerization of benzotriazole in RTILs, which are water stable and excellent in extraction performance, may offer a potential solution for treatment of the vast amount of benzotriazole in industrial waste water. Also, the electrosynthesized poly(benzotriazole) as a new conducting polymer material is expected to have broad application prospects, including its potential photoelectric application.

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