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Electrochemical polymerization of aniline in a protic ionic liquid with high proton activity

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ABSTRACT

Electrochemical polymerization of aniline in conventional protic ionic liquids (PILs) usually requires an exogenous proton source or the aniline monomer pre-protonation to obtain high quality polyaniline (PANI). In the present work, a proton functionalized ionic liquid pyrrolidinium hydrogenosulfate ([Pyrr][HSO_4]), which has high proton activity, has been tried for the first time as an electrolyte for the aniline electropolymerization. It is shown that in this medium the electropolymerization of aniline is facile and the resulting PANI has porous structure and high electrode specific capacitance. The electropolymerization in pyrrolidinium nitrate ([Pyrr][NO_3]) as control experiment demonstrates that the high efficiency of the electropolymerization in [Pyrr][HSO_4] is due to the high proton activity of HSO_4^-. The present work is of significance for simplifying pre-existing ionic liquid media for aniline electropolymerization and further improving the electrochemical performance of PANI obtained in ionic liquid media.

1. Introduction

Room temperature ionic liquids (RTILs) are liquid salts composed of organic cations and organic or inorganic anions at room temperature. They have unique properties such as high conductivity, good stability, wide electrochemical window, low volatility, strong ability to dissolve substances, *etc.* Therefore, they are suitable media for electrochemical synthesis. For a specific task, a suitable functionalized ionic liquid can be designed by selective combination of anions and cations or modification of different alkyl chain lengths for specific anions and/or cations [1–3]. In recent years, the use of RTILs to replace the conventional molecular solvent for the electrochemical synthesis of conducting polymers has attracted extensive attention of researchers [4–12].

Fuchigami et al. studied the electrochemical polymerization of pyrrole, thiophene and aniline in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIm][CF_3SO_3]) aprotic ionic liquids (AIL). It is found that for pyrrole and thiophene the AIL is superior to the conventional aqueous solution system [13]; for aniline, however, the AIL is a poor medium for the electropolymerization as compared with the aqueous solution system. In order to make an efficient electropolymerization of aniline, the concentration of the aniline monomer must be high enough (*ca.* 1.0 M) and an exogenous proton source (1.0 M CF_3SO_3H) is also required [13]. In other neat AILs such as 1-butyl-3-methylimidazolium tetrafluorobrate ([BMIm][BF_4]) and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ([BMMIm][NTf_2], the continuous growth of the polymer is found to be poor [14–16]. Proton-deficiency may be responsible for the result. For this reason, some protic liquids are tried as media for the electrochemical polymerization [17,18]. In ethylammonium nitrate (EAN) (a PIL with proton on the cation), Snook et al. have found that the rate of the electropolymerization of aniline is also slow. They argue that the main reason for the slowness is its low proton activity (the equivalent pH is *ca.* 5). In order to enhance the proton activity of EAN, anilinium nitrate is synthesized through the pre-protonation of aniline to satisfy the acidity requirement [11]. The electropolymerizations of aniline in *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([C_4MPyr][NTf_2]), EAN and neutral aqueous solution demonstrate that only EAN results in a PANI film with high electrochemical performance [11]. These studies indicate that the electropolymerization of aniline in ionic liquids requires sufficient proton activity to obtain high quality PANI film with high specific capacitance.

In the past, the proton deficiency in the electropolymerization of aniline in PIL or AIL is circumvented by adding an exogenous proton source or pre-protonating aniline monomers. These strategies are effective for the electropolymerization but the systems are relatively not simple enough. Since ionic liquids are designable, it should be possible theoretically to design a functionalized ionic liquid with high proton activity such that the basic conditions for the electropolymerization of

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aniline could be satisfied. Pyrrolidinium hydrogenosulfate ([Pyrr][HSO_4]), a RTIL reported by Anouti et al. [19], seems to be good condidate for the electropolymerization of aniline. In this work, [Pyrr][HSO_4] is tried as a medium for the first time for the electropolymerization of aniline. A nanoporous PANI film with good capacitance performance is obtained facilely due to the high proton activity of [Pyrr][HSO_4]. The present work is helpful for improving the performance of PANI-based electrochemical devices [20–22].

2. Experimental section

2.1. Materials

Pyrrolidine (Pyrr, 98%) was purchased from TCI (Shanghai) Chemical Industry Development Co., Ltd. Ferrocene was purchased from Sigma-Aldrich (now Merck). *N*-butyl-*N*-methypyrrolidinium bis (trifluoromethanesulfonyl)imide ([C_4MPyr][NTf_2]) was purchased from Shanghai Chengjie Chemical Co. Ltd. Sulfuric acid (H_2SO_4, 98%). Nitric acid (HNO_3, 68%), hydrochloric acid (HCl, 36%), and aniline (99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All reagents used were of analytical grade. Triply distilled water was used throughout the experiments.

2.2. Preparation and characterization of functionalized ionic liquids

[Pyrr][HSO_4] and [Pyrr][NO_3] ionic liquids were prepared by acid-base neutralization (Scheme 1). The brief steps are as follows: Pyrrolidine (21.77 g; 0.3 mol) was first introduced in a round-bottom flask and the flask was then immerged in an ice bath. After that, an equivalent moles of sulfuric acid or nitric acid were added dropwise to the flask. After the complete addition, the mixture was kept for stirring at ambient temperature for 4 h. The resulting solution was subsequently subjected to rotary evaporation under reduced pressure to remove water, and then placed in a vacuum drying oven for 24 h.

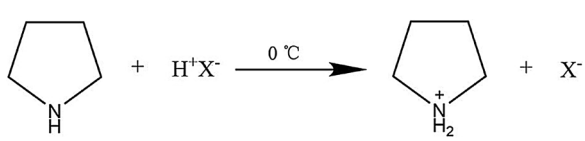
The functionalized ionic liquids were characterized by ^{1}H NMR. The spectra were shown in Fig. S1. The chemical shifts (ppm) corresponding to the characteristic peaks are listed in Table 1.

The ^{1}H NMR spectrum confirms that one proton from sulfuric acid/nitric acid has been transferred to the nitrogen atom in pyrrolidinium, *i.e.* the resulting RTILs are [Pyrr][HSO_4] and [Pyrr][NO_3], respectively.

2.3. Electrochemical polymerization of aniline in functionalized ionic liquid

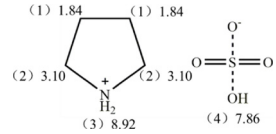
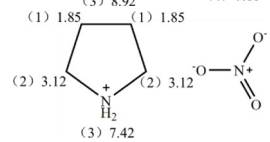
The functionalized ionic liquid [Pyrr][HSO_4] (2.0 mL) was used as a medium for the electropolymerization of aniline (0.3 M). The electropolymerization was carried out at ambient temperature (~ 25 °C). Prior to the electropolymerization, the solution was purged with high purity nitrogen for 20 min. During the electropolymerization the nitrogen atmosphere was maintained.

The electropolymerization of aniline was performed on a CHI660E electrochemical workstation. The three-electrode system was composed of a working electrode (Pt disk electrode, 25 μm in diameter), a Pt wire counter electrode, and a Ag|Ag^+ (~10 mM $AgNO_3$ dissolved in [C_4MPyr][NTf_2]) electrode as a reference. Prior to use, the working electrode was polished to a mirrorlike surface in the following steps: Firstly, polished with 0.5 μm and 0.05 μm Al_2O_3, respectively, then washed with ultrapure water and ethanol, and finally sonicated in ultrapure water for 5 min. The electropolymerization of aniline in an



Scheme 1. Preparation of functionalized ionic liquids. X^- denotes HSO_4^- or NO_3^-.

Table 1
^{1}H NMR spectrum characteristics of PILs.

PILs, δ / ppm	Characteristics
	(1)quartet, 4H (2)triplet, 4H (3)broad signal, 2H (4)broad signal, 1H
	(1)quartet, 4H (2)triplet, 4H (3)broad signal, 2H

ionic liquid medium was carried out using cyclic voltammetry. The setting of the parameters for the electropolymerization was described in figure captions. After the electropolymerization, the obtained PANI/Pt electrode was rinsed with ultrapure water and dried for later use.

The calibration of the electrode potential of the reference electrode (Ag|Ag^+ electrode) was carried out by cyclic voltammetry in [C_4MPyr][NTf_2] containing ~10 mM ferrocene (Fc) (Fig. S2). The cyclic voltammogram in Fig. S2 shows a pair of reversible redox peaks of ferrocene. The cathodic peak potential (E_{pc}) was −258 mV *vs.* Ag|Ag^+ and the anodic peak potential (E_{pa}) was −335 mV *vs.* Ag|Ag^+. The peak separation potential (ΔE_p) and the formal potential ($E^{o\prime}$) was 77 mV and −297 mV *vs.* Ag|Ag^+, respectively. Because the potential of the Fc^+/Fc pair is 0.40 V *vs.* NHE, the electrode potential of the present Ag|Ag^+ reference electrode is calculated to be 0.70 V *vs.* NHE.

2.4. Electrochemical characterization of PANI/Pt electrode

The PANI deposited on Pt electrode was characterized by cyclic voltammetry in neat [Pyrr][HSO_4]. The PANI/Pt was used as a working electrode, a Pt wire as a counter electrode, and a Ag|Ag^+ electrode as a reference electrode. The setting of experimental parameters was shown in the figure captions.

2.5. FTIR and SEM characterization of PANI

The PANI for the characterization was prepared according to the procedures descried in section 2.3. After the electropolymerization, the potential was set at 0.1 V (*vs.* Ag|Ag^+) for 10 s. The detachable GC electrode (3 mm diameter) with PANI was rinsed with ultrapure water, and then dried for later characterization. The SEM of PANI was recorded on the field emission scanning electron microscope (JEOL JSM-6700F, Japan) under high vacuum conditions. Imaging was conducted using secondary electron signals. Beam energy used was 3.0 kV. The FTIR spectrum of the PANI was recorded on an FTIR spectrometer (Thermo scientific Nexus 670, America) in an ATR mode.

2.6. Characterization of proton activity of PILs

The measurement of the proton activity of a PIL and its equivalent pH was performed on a CHI660E electrochemical workstation at ~ 25 °C using the corresponding PIL as supporting electrolyte. The three-electrode working system was composed of a Pt disk electrode (25 μm in diameter), a Pt wire counter electrode, a Ag|Ag^+ electrode as reference. Cyclic voltammetry was adopted to determine the hydrogen evolution potential of the ionic liquid. The Nernst equation was used to calculate the proton activity and the equivalent pH of the PIL.