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Electropolymerization in a novel proton functionalized room temperature ionic liquid anilinium acetate

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ABSTRACT

A novel proton functionalized room temperature ionic liquid–anilinium acetate ([HANI]Ac) with high ionic conductivity and low viscosity has been synthesized and used for the first time for aniline electropolymerization without any additives. The electropolymerization process reveals that the onset potential for anilinium oxidation (E_{onset}) in neat [HANI]Ac is +0.45 V *vs.* SCE, which is lower than those in aqueous and nonaqueous (ionic liquid as solvent/electrolyte) solutions. The control experiments and theoretical calculations indicate that the low E_{onset} in neat [HANI]Ac should be attributed to charge balancing counter-ion Ac^-. Compared with [HANI]Ac/[BMIM]PF_6 binary system, the mass transfer resistance of anilinium in neat [HANI]Ac is small, therefore the electropolymerization can be kept on at a high rate in a period. The cyclic voltammograms and Fourier transform infrared spectra demonstrate that the obtained PANI is highly conductive. The PANI has moderate solubility in [HANI]Ac and its adherence to the electrode is poor. During the electropolymerization, the accumulated PANI diffuses from the electrode/solution interface to the bulk phase which leads to different current signals of PANI under different conditions. Stirring slightly increases the oxidation current signal of anilinium but greatly reduces the redox current signal of PANI. Under quiescent conditions, lowering the upper switching potential reduces the redox current signal of PANI. The potential scan rate has great effect not only on the current signal of PANI but also on the redox peak shape. The electropolymerization process of [HANI]Ac in the presence of triethylamine further demonstrates that proton deficiency can result in a significant reduction of the rate of aniline polymerization.

1. Introduction

Conducting polymers are very useful for the development of electronic devices due to its unique physical and chemical properties [1–3]. Common conducting polymers are polyacetylene, polyaniline, polythiophene, polypyrrole, *etc.* [4–8]. Among them, polyaniline (PANI) is one of the most promising conducting polymers [9–14]. The synthesis of PANI and its electrochemical characterization are well documented. Compared with the chemical synthesis, the process of the electrochemical synthesis of PANI is easy to control and the PANI with different electrochemical properties could be obtained by changing the conditions for the electropolymerization.

As far as the electrochemical synthesis of PANI is concerned, an electrolyte is a very important factor that affects not only the process of the polymerization (*e.g.*, the onset potential for aniline oxidation (E_{onset}), the polymerization rate), but also the physical and chemical properties of the resulting PANI. Because of the unique properties of room temperature ionic liquids (ILs), such as good conductivity, low volatility, *etc.* [15–17], ILs have been tried as an electrolyte for the electrochemical synthesis of conducting polymers [18–24]. The IL electrolytes tried in aniline electropolymerization can be roughly divided into two categories: one is aprotic ILs, and the other is proton functionalized ILs. In aprotic ILs, exogenous protons are needed for the aniline polymerization. Sekiguchi et al. [25] have studied the electropolymerization of aniline in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM]CF_3SO_3) with CF_3SO_3H as proton source, and found that the polymerization rate is controlled by the diffusion of aniline from the bulk phase to the surface of an electrode. Because the viscosity of [EMIM]CF_3SO_3 is larger than that of water, the aniline polymerization rate in this IL is much lower than that in aqueous solutions. Wei et al. [26,27] have obtained conducting PANI nanotubes in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6) with CF_3CO_2H as proton source. In proton functionalized ILs, no exogenous protons are needed for the anilinepolymerization. Li et al. [28] have synthesized

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a novel 1-ethylimidazolium trifluoroacetate ([HEIM]Tfa) and used this proton functionalized IL as reaction medium for the electropolymerization of aniline without adding exogenous protons. Interestingly, the E_{onset} in [HEIM]Tfa is significantly lower than that in aqueous H_2SO_4 solution. Unfortunately, the authors have not mentioned how the protons on 1-ethylimidazolium cation get involved in the polymerization. It follows that protons are indispensable to the electropolymerization of aniline though the debate on the protons involved PANI growth mechanism is still in progress.

In order to realize the electropolymerization of aniline in aprotic ILs without adding exogenous protons, Snook et al. [29] have first synthesized a proton functionalized anilinium salt–anilinium nitrate to ensure that every aniline molecule has one available proton for the involvement in the polymerization. The success of this novel attempt means that it is quite probable to electropolymerize aniline without any additives. As anilinium nitrate is solid at room temperature, it cannot be used for aniline electropolymerization directly. In the present study, we have synthesized a novel proton functionalized anilinium salt, *i.e.*, anilinium acetate ([HANI]Ac), which is liquid at room temperature. The electropolymerization process of neat [HANI]Ac without any additives is first reported.

2. Experimental

2.1. Materials

Aniline, glacial acetic acid (≥99.5%), triethylamine and acetanilide were purchased from Sinopharm Chemical Reagent Co., Ltd., China. 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6, 99%), 1-butyl-3-methylimidazolium nitrate ([BMIM]NO_3, 99%), 1-butyl-3-methylimidazolium acetate ([BMIM]Ac, 99%) were purchased from Shanghai Chengjie Chemical Co., Ltd., China. All other reagents were of analytical grade. Triply distilled water was used throughout the experiments.

2.2. Preparation and characterization of [HANI]Ac

The liquid state [HANI]Ac was obtained just by mixing and stirring 1.86 g (0.02 mol) aniline and 1.20 g (0.02 mol) glacial acetic acid at room temperature for 30 min. The conductivity of this proton functionalized IL was measured on a DDS-307 conductometer with a Pt/platinized electrode at 25 °C. The viscosity of [HANI]Ac was measured on a Thermo Scientific MARS III rheometer at 25 °C. The NMR spectra were recorded on a Bruker AV300 spectrometer. The ^1H NMR spectrum of neat [HANI]Ac was recorded using the peak of D_2O (99.9%, sealed in a capillary) as the reference. The ^{13}C NMR spectrum of neat [HANI]Ac was recorded using the peak of $CDCl_3$ (99.8%, sealed in a capillary) as the reference. The ^{13}C NMR of acetanilide was recorded after dissolving acetanilide (solid) in $CDCl_3$ (99.8%).

2.3. Electropolymerization in neat [HANI]Ac and FTIR characterization

The electropolymerization of [HANI]Ac was performed on a CHI660E electrochemical workstation at room temperature. The three-electrode system was composed of a working electrode (GCE, 3 mm in diameter), a Pt wire counter electrode, and a saturated calomel electrode (SCE) sheathed with a glass tube as reference. All the potentials given in this paper were *vs.* SCE. The electropolymerization was carried out in neat [HANI]Ac using cyclic voltammetry. The setting of the parameters for the electropolymerization is detailed in figure captions.

When the electropolymerization was stopped, the glassy carbon electrode was taken out and put on the sample holder of VERTEX-70 spectrophotometer without washing. The FTIR spectra of the resulting PANI were recorded in the total reflection testing mode.

2.4. Electropolymerization of aniline in 0.50 M H_2SO_4

A 27 μL aliquot of aniline was dissolved in 3 mL H_2SO_4 (0.50 M), forming 0.10 M aniline in H_2SO_4. Cyclic voltammetry was performed in this system as in neat [HANI]Ac. The potential window was 0∼1.0 V and the scan rate was 50 mV s^{-1}.

2.5. Electropolymerization of [HANI]Ac in [BMIM]Ac, [BMIM]NO_3 and [BMIM]PF_6

Three aliquots of [HANI]Ac (0.062 g) were added to 4.0 mL [BMIM]Ac, [BMIM]NO_3 and [BMIM]PF_6, respectively (the final concentration of [HANI]Ac was 0.10 M), and the electropolymerization was carried out in these homogeneous mixtures using linear sweep voltammetry under quiescent condition. The potential window was −0.5∼0.8 V and the scan rate was 50 mV s^{-1}.

2.6. Effect of the protons available to aniline for electropolymerization

Triethylamine (0.81 g, *ca.* 1.12 mL) was added to [HANI]Ac (3.06 g), forming a homogenous [HANI]Ac/triethylamine ($n_{[HANI]Ac}$: $n_{triethylamine}$ = 5:2) liquid mixture. Glacial acetic acid (1.12 mL) was added to [HANI]Ac (3.06 g), forming a homogenous [HANI]Ac/glacial acetic acid liquid mixture. These mixtures were separately used as electrolytes for electropolymerization (saturated calomel electrode was sheathed in a tube containing the corresponding solution).

2.7. Density functional theory calculations

In the present work, all of the density functional theory (DFT) calculations were implemented by the Gaussian 09 [30] using the B3LYP [31] functional with a 6-31 G (d, p) basis set [32]. Frequency calculations were performed to verify that all the optimized geometries correspond to a local minimum that has no imaginary frequency.

3. Results and discussion

3.1. Synthesis and characterization of [HANI]Ac

When aniline was mixed with equivalent glacial acetic acid, yellowish liquid (room temperature) [HANI]Ac was then obtained (Fig. 1). Conductivity test shows that yellowish liquid is of ions with a conductivity of 0.18 S m^{-1}, which is close to the conductivity

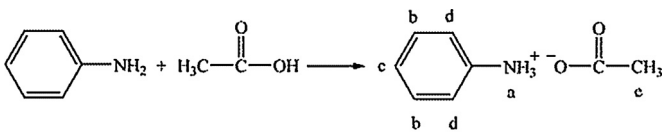

Fig. 1. Formation of proton functionalized room temperature ionic liquid [HANI]Ac and the photo of the product.