



Comparative electrochemical performance of electrodeposited polypyrrole in protic and aprotic ionic liquids



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ABSTRACT

Polypyrrole (Ppy) thin films were obtained by pyrrole (py) electropolymerization in ionic liquid (IL) media. The charge compensation dynamics as well as the electrochromic behavior of the obtained films were studied in two ILs with similar structures, being one containing $-\text{CH}_3$ (aprotic IL) and the other containing $-\text{H}$ (protic IL) attached to the ethylimidazolium cation. The results obtained with quartz crystal microbalance with dissipation combined with cyclic voltammetry have shown that in spite of the presence of protons in the PIL, which could favor both electropolymerization and electrochemistry of Ppy in this media, these processes are more effective in the aprotic IL, leading us to conclude that other factors must be taken into account when choosing the most appropriated IL as electrolyte. Also, electrochemical reactions in both ILs were successfully associated to the transformation of chromogenic species by evaluating the electrochromic activity of the polymeric films.

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1. Introduction

Protic ionic liquids (PILs) are ionic liquids (ILs) which are formed through proton transfer from a Brønsted acid to a Brønsted base, resulting in materials bearing protons attached to their cations. They have some characteristic properties of the aprotic ionic liquids (AILs), i.e. high ionic conductivity and low vapor pressure, depending on the extent of proton transfer, but can be easier obtained when compared to the aprotic analogues [1].

Another particular interest in this subclass of IL is related to the ability to conduct protons under anhydrous conditions [2], and it has been growing interest to understand the relationship between its ionicity and several physicochemical properties [3,4]. Recent contributions have shown that the PILs are promising electrolytes for improving electrochemical performance of modified electrodes in applications such as electrolytes for safer lithium-ion batteries [5] solar cells [6] and non-humidified fuel cells [7].

Another interesting application could be as electrolytes for electropolymerization of conducting polymers. Previous contributions have shown successful electropolymerization of conducting polymers in AIL: in Ref. [8], pyrrole (py) was electropolymerized in an AIL containing the anion hexafluorophosphate, showing good polymerization rates and electrochemical response toward ascorbic acid and dopamine; in Ref. [9], it was possible to obtain

electropolymerized thin films of polyaniline in AIL based electrolyte and the addition of an acid to the electrolytic media promoted the conversion from the base (non-conducting) to the salt (conducting) form. Once PILs already possess protons available in their cations, they are interesting electrolytes for the obtention of thin films of conducting polymers [10]. In fact, anilinium nitrate salt was dissolved in a PIL and in an AIL, and electropolymerization has shown superior performance when the PIL was employed [11]. Concerning polypyrrole (Ppy), in general, electropolymerization can undergo at any pH, being favorable in acid conditions although very low pH values can result in films with low conductivity [12].

As far as we are concerned, electropolymerization and electrochemistry of Ppy were only conducted in AIL [13–18]; so that, in the present work, the factors affecting the electropolymerization of py to produce the conducting polymer Ppy, as well as the role of the species participating in the charge balancing process of the obtained Ppy films in both AIL and PIL were studied. For that, two structurally similar ILs, differing only by the presence of $-\text{CH}_3$ (AIL) or $-\text{H}$ (PIL) attached to the cation ethylimidazolium were employed. Additionally, the electrochromic behavior of these systems was evaluated and discussed.

2. Experimental

The PIL, ethyl-imidazolium bis(trifluoromethylsulfonyl)imide (HEITf₂N) was obtained by acid-base reaction. Equimolar amounts

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of the acid, trifluoromethanesulfonimide (HTf₂N – Fluka), dissolved in dichloromethane were added slowly (at a speed of 1 mL min⁻¹) to previously distilled 1-ethyl-imidazole (Aldrich) under stirring in a round bottom flask placed into ice bath. The temperature during the reaction was maintained below 40 °C. The AIL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITf₂N) was obtained by mixing aqueous solutions of 1-ethyl-3-methylimidazolium bromide (Aldrich) and lithium bis(trifluoromethanesulfonyl)imide (LiTf₂N – Aldrich), followed by purification processes [19]. The water content, determined by Karl-Fischer titration using a Karl-Fischer Coulometer (Metrohm) was 2000 ppm for the PIL and the water content of the AIL was adjusted to the same value for comparison purposes. Remaining water becomes strongly coupled to PILs by hydrogen bond and is more difficult to be removed when compared to AILs [20]. The viscosities of both ILs were measured with an Anton Paar viscosimeter model SVM 3000, being the values obtained at 25 °C 45.3 mPa s for the AIL and 21.3 mPa s for the PIL. The chemical structures of the two ILs are disclosed in Fig. 1.

All electrochemical measurements were performed with an AUTOLAB PGSTAT 30 potentiostat, using Pt mesh and Ag wire as counter and reference electrodes respectively and voltammetric studies of ILs containing Ferrocene/Ferrocenium (Fc/Fc⁺) as an internal reference were previously performed in order to define the potential windows.

Ppy films were electropolymerized at constant current in 0.1 mol L⁻¹ of distilled py (Aldrich) mixed with both ILs. The films were deposited over glass substrates covered with indium tin oxide (ITO) (Delta Technologies) or AT-cut 5 MHz piezoelectric quartz crystals (14 mm diameter) coated with platinum (Qsense).

For the spectro-electrochemical studies, transmittance-potential profiles were obtained simultaneously with cyclic voltammetry. As light source an incident light (electromagnetic radiation) spot at a specified wavelength generated by a solid-state light source (World Precision Instruments) was used. Optical fibers were used to transport the light that passes through the sample from the electrochemical cell to a photodiode amplifier PDA1 (World Precision Instruments), linked to an ADC port in the potentiostat.

For the electrogravimetric studies, the cyclic voltammetry data was simultaneously recorded with frequency and dissipation changes using a Quartz Crystal Microbalance with Dissipation (QCM-D) from Q-Sense (model E4). An electric field applied to

the quartz crystal causes it to oscillate at a specific frequency and when the oscillation frequency change is only related with mass change on the quartz surface (i.e. no viscoelastic changes), they are related through the Sauerbrey equation: $\Delta f = -\Delta m/CA$ [21], where Δf is the measured shift in frequency in Hz, Δm is the mass change, A is the active area of the quartz crystal and C is the theoretical mass sensitivity. C was calculated by relating the charge and mass change during electrodeposition of cooper and using the quartz crystal parameters the value obtained was 17.7 ng cm⁻² Hz⁻¹ [22]. Cooper was chose because its reduction potential is higher enough to disregard the water reduction, so the charge can be directly related with the deposited mass. Nevertheless, when the frequency change is also associated with viscoelastic changes in the film, the Sauerbrey equation can no longer be applied and an appropriated viscoelastic model must be used [23].

Atomic force microscopy (AFM) images were taken with a Pico SPM-LE molecular imaging system with cantilevers operating in the intermittent contact mode (AAC mode), slightly below their resonance frequency of approximately 305 kHz in the air. Topographic images refer to scan areas of 25 μm × 25 μm and 2 μm × 2 μm. Image processing and root mean square roughness parameter (Rq) were performed with Pico Scan Software. Rq is the statistical function that represents the standard deviation of the distribution of surface heights [24]. Each film obtained at different current densities was analyzed at four different topographic positions on the surface.

3. Results and discussion

3.1. Electropolymerization of py in ILs

The frequency and dissipation changes at different overtones were monitored by QCM-D during the electropolymerization of py at constant current of 190 μA cm⁻² in both PIL and AIL. The frequency variation during the process is the same independently on the overtone and the obtained data for the 3rd one is presented in Fig. 2a and b as an example. In addition, there is no dissipation change during the measuring, which means that the obtained films are thin enough to be considered as rigid ones and Sauerbrey equation can be employed for obtention of mass of the polymer [18]. The mass variation as a function of time during the electrodeposition in both AIL and PIL are presented in Fig. 2c.

In spite of similar polymerization rate for both ILs, it was not possible to obtain Ppy films with good reproducibility in the protic one. When the monomer is added to the PIL, the mixture acquires a dark yellow coloration after few minutes being brown after one day possibly due chemical polymerization of py in the PIL as it has been previously observed in strong acid solutions such as calix-6-arenehexasulfonic acid [25] and hydrochloric acid [26].

On the other hand, thin and uniform Ppy films were obtained with good reproducibility in the AIL. The electropolymerization of py was run galvanostatically at different current densities ranging from 65 μA cm⁻² to 190 μA cm⁻² and it was monitored by QCM-D measurements. In Fig. 3a the mass variations at the different current densities during deposition in the EMITf₂N are shown. During the electrochemical synthesis, the anions Tf₂N⁻ are incorporated (p-doping) into the polymer structure to balance the positive charges present along the polymer backbone as previously observed for a similar AIL containing the same cation and the CF₃SO₃⁻ anion [27]. During the polymer synthesis a constant potential value of ca. 0.80 V (vs. Fc/Fc⁺) is reached for all employed current densities and the mass increases linearly with time until the current supply is stopped. These results indicate that, in the range of current densities employed, higher applied currents produce

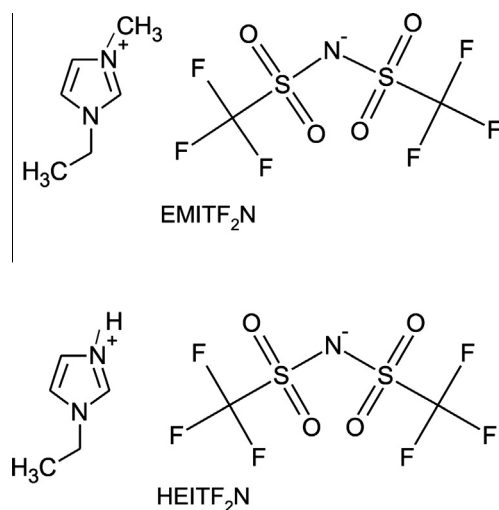


Fig. 1. Chemical structure of ILs: 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide (EMITf₂N) and 1-ethyl-imidazolium bis(trifluoromethylsulfonyl)imide (HMITf₂N).

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