



Short communication

Novel functionalized ionic liquid with a sulfur atom in the aliphatic side chain of the pyrrolidinium cation

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ABSTRACT

A novel ionic liquid, never reported in literature until now, was properly designed, synthesized and preliminary investigated. This material was prepared combining the *N*-methylpyrrolidinium cation (PYR_{1(2S1)})⁺, exhibiting a sulfur atom in the alkyl side chain, with the bis(trifluoromethanesulfonyl)imide anion, (TFSI)⁻, to be addressed as safer electrolyte component for sulfur-based battery systems. The presence of sulfur within the cation side chain was found to prevent the crystallization of the ionic liquid even in the presence of lithium salt. Cyclic voltammeteries have clearly indicated that Li⁺ cation exhibits good mobility and is reversibly plated/stripped in PYR_{1(2S1)}TFSI–LiTFSI electrolytes with high efficiency.

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1. Introduction

Ionic liquids (ILs), constituted by organic cations and inorganic/organic anions, represent a very interesting new class of room temperature fluids [1,2]. One of the main peculiarities of ILs is the possibility of finely tuning their physicochemical properties by properly designing the ionic liquid architecture, e.g., varying the cation/anion side chain length [3,4] and/or introducing suitable functional groups and/or foreign atoms in the cation/anion structure [5]. This unique characteristic allows synthesizing suitable ILs able to satisfy very different requirements and/or operative conditions. Therefore, ILs were proposed for a very wide variety of applications, in particular as "green and safer" solvents for chemical reactions, bi-phasic catalysis, chemical synthesis, separation/extraction processes, advanced high-temperature lubricants, transfer fluids in solar thermal energy systems and electrochemical devices including lithium batteries.

Li/S devices are among the most promising advanced lithium battery systems because of their large theoretical energy density, e.g., 5 times higher with respect to commercial Li-ion battery. In addition, sulfur is cheap, non-toxic and largely available. However, Li–S batteries suffer of severe drawbacks, both at the cathode (sulfur lost as polysulfide dissolution) and the anode (poor safety in standard electrolytes) sides [6,7]. ILs based on *N*-alkyl-*N*-methylpyrrolidinium cations, (PYR_{1A})⁺, and the bis(trifluoromethanesulfonyl)imide, (TFSI)⁻, anion have been favorably proposed for lithium batteries [8], including Li/S systems. Recently, many works [9–13] have demonstrated beneficial effects of

IL-based electrolytes in mitigating/minimizing the unwelcome behaviors (including self-discharge) occurring in lithium–sulfur devices.

With the aim of facing such issues, a novel ionic liquid material, PYR_{1(2S1)}TFSI (namely *N*-methyl-*N*-methylthioethylpyrrolidinium bis(trifluoromethanesulfonyl)imide, containing a sulfur atom in the alkyl side chain of the cation and never reported in literature, was originally designed (Fig. 1) and synthesized through a properly developed procedure route. Regarding Li/S systems, the sulfur functionalizing the pyrrolidinium cation is expected to reduce the polysulfide diffusion and precipitation onto the lithium anode, limiting also the self-discharge effect. In addition, looking to a larger variety of potential applications, an enhanced selectivity towards sulfur compounds is expected, allowing possible exploitation to PYR_{1(2S1)}TFSI for efficient purification of hydrocarbons and gases [14,15].

The novel S-based RTIL was preliminary investigated in terms of thermal and electrochemical properties. The addition of the LiTFSI salt was also considered.

2. Material and methods

The PYR_{1(2S1)}TFSI ionic liquid was synthesized through a three step procedure route. A particular care was devoted in order to avoid oxidation of the sulfur atom in the cation alkyl side chain. Therefore, all synthesis stages were carried out at room temperature (or below) in inert (nitrogen or argon) atmosphere and minimizing exposure to the sunlight.

The reagent 2-bromoethylmethylthioether, Br–CH₂CH₂–S–CH₃, was prepared starting from 2-(methylthio) ethanol, HO–CH₂CH₂–S–CH₃ (Aldrich, 98 wt.%), which was reacted with PBr₃

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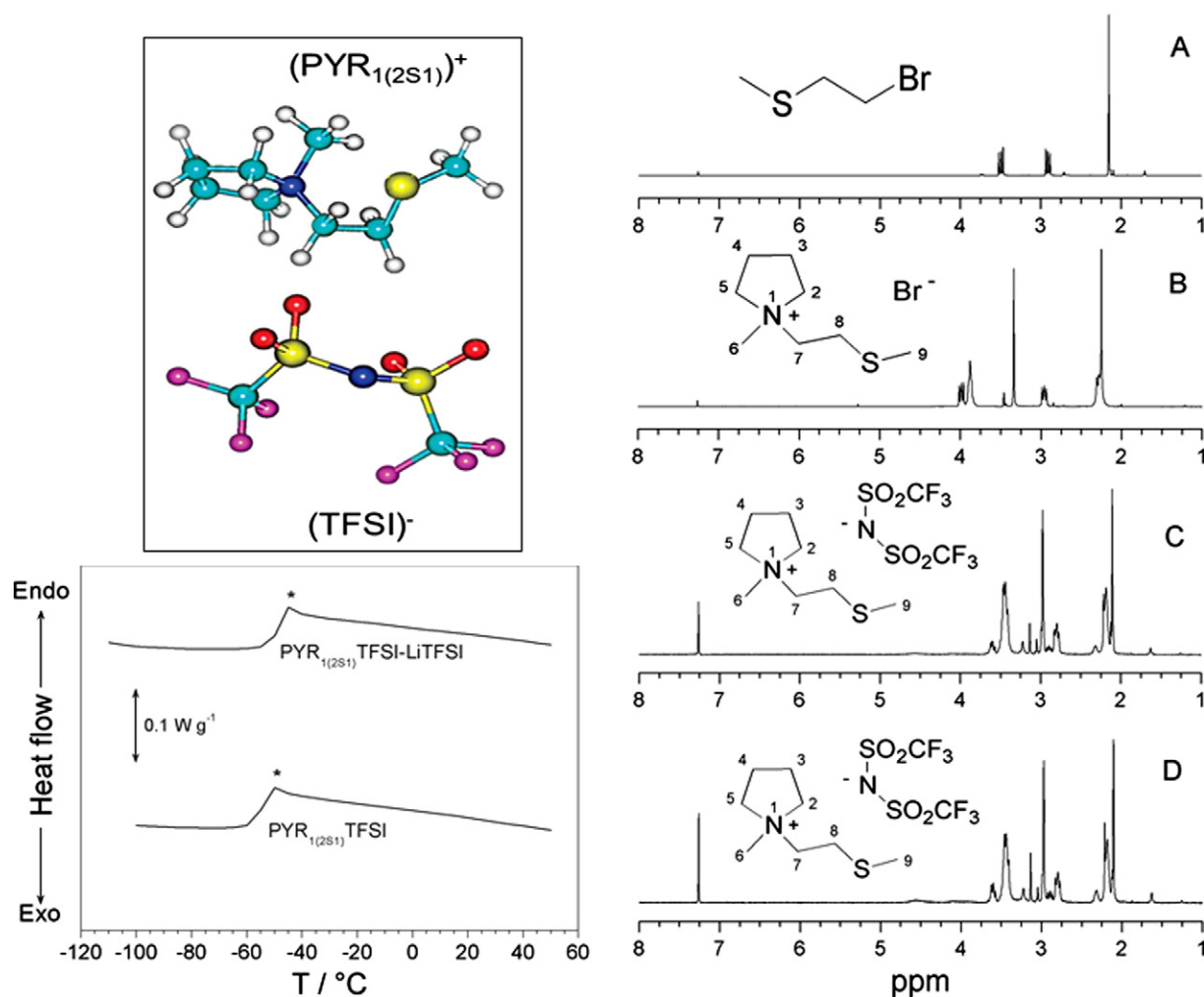


Fig. 1. Upper left panel: chemical structure of the $\text{PYR}_{1(2S1)}\text{TFSI}$ ionic liquid. Magenta: carbon; blue: nitrogen; red: oxygen; yellow: sulfur; purple. Right panel: $^1\text{H-NMR}$ spectra of $\text{Br-CH}_2\text{CH}_2\text{-S-CH}_3$ (A), $\text{PYR}_{1(2S1)}\text{Br}$ (B) and $\text{PYR}_{1(2S1)}\text{TFSI}$ upon vacuum drying at 20°C (C) and 110°C (D). Lower left panel: DSC trace of $\text{PYR}_{1(2S1)}\text{TFSI}$ and $\text{PYR}_{1(2S1)}\text{TFSI-LiTFSI}$ mixture. Scan rate: $10^\circ\text{C min}^{-1}$.

(Aldrich, 99 wt.%) using anhydrous (through distillation on metallic sodium) ethyl ether as the solvent. The reaction was run for two stirring hours at 0°C and, then, neutralized with aqueous NaHCO_3 . The $\text{Br-CH}_2\text{CH}_2\text{-S-CH}_3$ was rinsed with (anhydrous) ethyl ether, dehumidified through anhydrous Na_2SO_4 and, successively, purified through vacuum distillation. The so-obtained $\text{Br-CH}_2\text{CH}_2\text{-S-CH}_3$ was reacted with a slight excess (1–2 wt.% with respect to the stoichiometric amount) of *N*-methylpyrrolidine (Sigma-Aldrich, 98 wt.%) in ethyl acetate (Sigma-Aldrich, ≥ 99.5 wt.%). Upon overnight stirring, a white solid precipitate of $\text{PYR}_{1(2S1)}\text{Br}$ precursor (insoluble in ethyl acetate) was observed. The latter, previously rinsed with (cold) ethyl acetate, was purified through activated charcoal using dichloromethane, CH_2Cl_2 (Sigma-Aldrich, ≥ 99.5 wt.%), as the solvent (removed by filtration and vacuum distillation, respectively). Successively, the precursor was reacted (overnight) with LiTFSI (Solvionic, > 99.9 wt.%) using CH_2Cl_2 as the medium for obtaining the $\text{PYR}_{1(2S1)}\text{TFSI}$ ionic liquid (miscible with CH_2Cl_2) and LiBr (insoluble) as the side product. The solid phase (LiBr and unreacted LiTFSI are insoluble in CH_2Cl_2) and the solvent were removed by filtration and vacuum distillation, respectively. This procedure was iteratively repeated four times. Finally, the ionic liquid was vacuum dried (120°C overnight) in a dry-room (having moisture content < 10 ppm H_2O).

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ measurements (CDCl_3 as the solvent) were performed by a Bruker AC-300 (300 MHz and 100 MHz, respectively) spectrophotometer on the $\text{Br-CH}_2\text{CH}_2\text{-S-CH}_3$ reagent, on the $\text{PYR}_{1(2S1)}\text{Br}$ precursor and on the $\text{PYR}_{1(2S1)}\text{TFSI}$ ionic liquid to check

the structure of the synthesized materials. The test samples (30 mg each one) were dissolved in 2 ml of CDCl_3 , whose chemical shifts (δ) lie to 7.26 ppm ($^1\text{H-NMR}$) and 77.0 ppm ($^{13}\text{C-NMR}$) in the NMR patterns.

Differential scanning calorimetry (DSC) measurements were carried out using a TA Instruments (Model Q100) calorimeter. The IL samples, housed in aluminum pans (which were sealed in the dry-room), were cooled ($10^\circ\text{C min}^{-1}$) from room temperature down to -120°C and, successively, heated ($10^\circ\text{C min}^{-1}$) up to 100°C .

Ionic conductivity measurements were performed on sealed two blocking stainless steel electrode cells loaded with the ionic liquid sample. The specific ion conduction values were determined by a conductimeter AMEL 160 within the $-40/90^\circ\text{C}$ temperature range at 2°C h^{-1} heating scan. Prior to the conductivity measurements, the cells were dipped in liquid nitrogen for a few seconds and, immediately, stored at -40°C overnight [16].

Cyclic voltammetries (CVs) were run at 5 mV s^{-1} , on lithium metal (counter and reference electrode)/RTIL-based sample/stainless steel (SS, working electrode) sealed coin-cells manufactured in the dry-room. The $\text{PYR}_{1(2S1)}\text{TFSI-LiTFSI}$ electrolyte, trapped in glass fiber separator, was interlayered between the working and the counter electrodes. The CV measurements were performed scanning the cell voltage from the open circuit voltage (OCV) towards more negative (cathodic limit) voltages and, successively, running consecutive cyclic voltammetries between -0.3 and 0.5 V (vs. Li/Li^+). The measurements

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