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A binary ionic liquid system composed of *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide and lithium bis(trifluoromethanesulfonyl)imide: A new promising electrolyte for lithium batteries

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ABSTRACT

Room temperature ionic liquids are nowadays the most appealing research target in the field of liquid electrolytes for lithium batteries, due to their high thermal stability, ionic conductivity and wide electrochemical windows. The cation structure of such solvents strictly influences their physical and chemical properties, in particular the viscosity and conductivity.

In this paper we report on the preparation and characterization of a complete series of solutions between lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and the promising *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide ($PY_{1,2O1}$) ionic liquid. A wide molality range has been explored in order to identify the optimal compositions in terms of conductivity and electrochemical stability. Our thermal results show that the solutions are amorphous independently on the LiTFSI content. Up to salt concentration of 0.4 mol kg^{-1} the solutions have a very low viscosity ($\eta \sim 36$ cP), a high ionic conductivity, even at temperatures below 0 °C, and a good electrochemical stability. Cations transport numbers ranging between 0.05 and 0.39 have been determined as a function of LiTFSI content. The combination of these properties makes the $PY_{1,2O1}$-based solutions potentially attractive liquid electrolytes for lithium batteries.

1. Introduction

In the last years, ionic liquids (ILs) have been widely investigated for their potential applications in numerous fields such as separation processes, catalysis, material science and electrochemistry. Their intrinsic properties, like negligible volatility even at elevated temperature, nonflammability, high chemical and thermal stability, combined to high ionic conductivity and electrochemical stability, make them very attractive candidates as electrolytes in rechargeable lithium batteries [1,2].

ILs are usually quaternary ammonium salts where the cation is mostly derived from a cyclic amine (pyridine, imidazole, piperidine, and pyrrolidine), and either an inorganic or an organic anion. A great variety of side chains can be connected to central N$^+$, thus obtaining a number of cation structural modifications. By combining a wide spectrum of available cations and anions, ionic liquids with very different physicochemical properties can be obtained.

Among the possible anions, $[CF_3(SO_2)_2N]^-$ forms ionic liquids with low viscosity and melting point [3,4]. In particular, many studies on the pyrrolidinium-imide salts have shown high conductivity values, exceeding 1 mS cm^{-1} at room temperature, and wide electrochemical windows [5,6]. Furthermore, several reports point out the influence of the alkyl-chain length on ILs properties [7,8]. For instance, the viscosity of the ionic liquid increases with the carbon atom number of the alkyl group with a consequent drop in conductivity [9].

However, scarce information is available on ether-functionalized ILs as potential solvents for liquid or polymer electrolytes in lithium batteries [10]. Alkylether functionalized imidazolinium and pyrrolidinium salts with trifluoborate and/or hexafluorophosphate anions have been reported. In both cases, it has been shown that the presence of extra-complexing units may improve the viscosity and ionic conductivity of the system, making them particularly appealing for electrochemical applications [11–13]. To date, pyrrolidinium imide salts with alkylether chains have been only marginally described in

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the literature [14], and no detailed data have been given on their solutions with LiTFSI.

In this work we report on the synthesis and characterization of *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide, and on the preparation and characterization of solutions with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). A wide range of solutions with molality ranging between 0 and 5.5 mol kg^{-1} has been explored. Each solution has been carefully characterized as far as concerns density, viscosity, ionic transport. The electrochemical measurements have been performed on selected compositions.

2. Experimental

2.1. Synthesis of *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($PY_{1,2O1}$)

The ionic liquid $PY_{1,2O1}$ (see Scheme 1) was synthesized by using a modification of the procedure introduced by Passerini et al. [15] for the synthesis of analogous derivatives. *N*-Methylpyrrolidine (60 g, 0.7 mol) and 1-iodo-2-methoxyethane 115 g (0.62 mol) in ethyl acetate (215 mL) were stirred overnight under a nitrogen flux. The solvent and excess pyrrolidine were then removed in vacuo to afford *N*-methoxyethyl-*N*-methylpyrrolidinium iodide (98 g, 58% yield) as a pale yellow solid. The iodide was suspended in ethyl acetate (20 mL) in a flask covered with an aluminum foil under nitrogen flux, and a deaerated (by nitrogen bubbling) water solution (100 mL) of lithium bis(trifluoromethanesulfonyl)imide (103.5 g, 0.36 mol) was then added.

The resulting suspension was vigorously stirred overnight. The organic phase was separated while the aqueous phase was extracted three times (20 mL each) with ethyl acetate. The resulting organic phases were collected and evaporated in vacuo. Crude $PY_{1,2O1}$ was purified three times over an active coal (Darco® G-60, 100 mesh powder) column (ethyl acetate as the eluant), then dried by stirring in vacuo at 80 °C for 24 h, to afford 106 g of the title compound ($PY_{1,2O1}$, colorless, 69% yield). *N*-Methylpyrrolidine, lithium bis(trifluorometanesulfonyl)imide, and ethyl acetate (purum for analysis) were commercially available. 1-Iodo-2-methoxyethane was synthesized from 1-methoxy-2-tosylethane [16] by reaction with sodium iodide as previously reported [17].

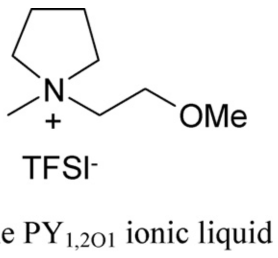
^{1}H NMR (see Ref. [14]) ($CDCl_3$): 2.20–2.30 (br s, 4H), 3.10–3.20 (br s, 3H), 3.30–3.40 (br s, 3H), 3.50–3.60 (m, 6H), and 3.75–3.85 (br s, 2H). ^{13}CNMR (δ, $CDCl_3$): 21.0 (CH_2), 48.6 (CH_3), 58.6 (CH_3), 63.2 (CH_2), 65.4 (CH_2), 66.0 (CH_2), and 115.0 (q, CF_3, $J = 307$ Hz). Anal. Calcd. for $C_{10}H_{18}F_6N_2O_5S_2$: C 28.30, H 4.28. Found: C 28.2, H 4.3.

2.2. Preparation of $(1-\chi)$ $PY_{1,2O1}$–χ LiTFSI solutions

The lithium salt-ionic liquid solutions were prepared in a dry-box (MBRAUN $O_2 < 1$ ppm, $H_2O < 1$ ppm), under argon atmosphere, by adding to $PY_{1,2O1}$ proper amounts of LiTFSI previously dissolved in acetone. The solutions were dried at 70 °C in order to completely remove the solvent. The chosen salt concentrations, in terms of both molality and lithium molar fraction, are reported in Table 1.

Table 1
Salt molar fraction, χ, and molality, m, of the $PY_{1,2O1}$–LiTFSI solutions.

$(1-\chi)$ $PY_{1,2O1}$	χ LiTFSI	m_{LiTFSI} (mol kg^{-1})
1	0.00	0.00
0.95	0.05	0.12
0.90	0.10	0.26
0.85	0.15	0.41
0.75	0.25	0.78
0.60	0.40	1.57
0.50	0.50	2.36
0.375	0.625	3.93
0.30	0.70	5.50



Scheme 1. The $PY_{1,2O1}$ ionic liquid.

2.3. Characterization

NMR spectra of $PY_{1,2O1}$ were recorded on a 300 MHz spectrometer (Bruker). The attributions of the signals of the ^{1}H and ^{13}C NMR spectra were supported by DEPT-135 experiments; chemical shifts are reported in ppm downfield from tetramethylsilane (TMS).

The DSC measurements were performed with a 2910 MDSC (TA Instruments) by using aluminium pans, at a rate of 5 °C min^{-1} under nitrogen purge. TGA scans were recorded at 10 °C min^{-1} under nitrogen flow with a 2950 TGA (TA Instruments).

The viscosity was measured at 20 ± 1 °C by means of a rotational viscosimeter (Rheotec, mod. RC20) with a cone-plate configuration, in control shear rate mode. The density was determined at 20 °C by a helium pycnometer (Micromeritics).

The ionic conductivity was measured by means of the impedance spectroscopy technique, using a frequency response analyser (FRA Solartron 1255), connected to an electrochemical interface (Solartron 1287), over the frequency range 1 Hz/1 MHz, by applying a voltage of 100 mV. The impedance scans were carried out in the temperature range between −28 and 70 °C, by using a two-probes liquid cell with silver electrodes and cell constant of 0.5 cm^{-1}. The stability of the pure IL and the solutions against lithium was investigated by monitoring the time evolution of the impedance response of a symmetric Li|electrolyte|Li cell.

Both linear and cyclic voltammetry were performed by means of an Electrochemical Interface Solartron 1287 with a three electrodes cell, using lithium as both the counter and the reference electrodes, and nickel as the working one. A Whatman glass microfiber filter was used as the separator.

The lithium transference number, $T_{\text{Li}}{}^+$, was determined by a dc polarization combined with impedance spectroscopy, as proposed by Bruce et al. and Evans et al. [18,19]. The method consists in applying a small dc pulse to a symmetrical Li|electrolyte|Li cell and measuring the initial, I_0, and the steady-state, I_{ss}, current which flow through the cell. The same cell was also monitored by impedance spectroscopy to detect the initial, R_0, and the final, R_{ss}, resistance of the two Li interfaces, this to account for the resistance of passivation layers and the eventual increase of this value upon the duration of the dc pulse. Under these circumstances, the lithium transference number, $T_{\text{Li}}{}^+$, is given by:

$$T_{\text{Li}}^{+} = \frac{I_{\text{ss}}}{I_0}\,\frac{\Delta V - I_0 R_0}{\Delta V - I_{\text{ss}} R_{\text{ss}}}$$

The limitations of this method when applied to ionic liquids will be addressed in Section 3.