Electrochemistry Communications 43 (2014) 5–8

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

An advanced ionic liquid-lithium salt electrolyte mixture based on the bis(fluoromethanesulfonyl)imide anion

Y. Deguchi [a,b], J. Serra Moreno [c], S. Panero [c], B. Scrosati [d], H. Ohno [a,b], G.B. Appetecchi [c,e,*]

[a] Department of Biotechnology, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan
[b] Functional Ionic liquid Laboratories, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei, Tokyo 184-8588, Japan
[c] Department of Chemistry, University of Rome La Sapienza, P.le Aldo Moro 5, 00185 Rome, Italy
[d] Elettrochimica ed Energia, Italy
[e] ENEA, Agency for New Technologies, Energy and Sustainable Economic Development, UTRINN-IFC, via Anguillarese 301, Rome 00123, Italy

ARTICLE INFO

Article history:
Received 23 December 2013
Received in revised form 25 February 2014
Accepted 26 February 2014
Available online 6 March 2014

Keywords:
N-butyl-*N*-ethylpyrrolidinium
Bis(trifluoromethanesulfonyl)imide
Bis(fluorosulfonyl)imide
Ionic liquid electrolytes

ABSTRACT

An innovative electrolyte mixture, based on the novel *N*-butyl-*N*-ethylpyrrolidinium bis(fluoromethanesulfonyl) imide ($PYR_{24}FSI$) ionic liquid and the LiFSI lithium salt, was prepared and its thermal and ion-transport properties were investigated. The FSI-based mixture showed fast crystallization kinetics with melting point around −40 °C. A conductivity close to 4×10^{-3} S cm^{-1} was reached at room temperature. This PYR_{24}FSI-LiFSI mixture family has been found to be an appealing electrolyte for high safety and performance lithium battery systems.

1. Introduction

There is a strong request to improve the safety of lithium battery systems, and researches towards novel generation solvents have been aimed. Among these, ionic liquids (ILs) occupy a front row position due to their unique properties such as non-flammability, negligible vapor pressure, wide chemical/electrochemical/thermal stability, high ionic conductivity, and in some cases, hydrophobicity [1]. Particularly, ILs are excellent candidates as electrolytes and/or electrolyte components in the place of volatile and hazardous alkyl carbonates [2]. For these, numerous IL-lithium salt mixtures have been extensively investigated [3–18].

ILs based on *N*-alkyl-*N*-ethylpyrrolidinium cations $(PYR_{2A})^+$ (the subscripts indicate the number of carbon atoms in the alkyl side chains) have been favorably used as electrolyte components for lithium batteries because of their sub-ambient melting point, high room temperature conductivity, and wide electrochemical stability [1,2,19]. With respect to ILs based on unsaturated cyclic and non-cyclic quaternary ammonium cations, PYR-based ILs show much lower cathodic decomposition potential [15]. For example, ethylmethylimidazolium (EMI)-based IL electrolytes, i.e., generally displaying fast ion transport properties, exhibit poor cycling efficiency in graphite electrode [20] due to reduction of the EMI cation at low potential [3,6,15,20]. Also, EMI-based ILs have an unfavorable compatibility with lithium metal anode due to the presence of acidic protons and double bounds in the cation [21].

The feasibility to reversibly cycling lithium into graphite anodes using ILs, based on the bis(fluorosulfonyl)imide (FSI) anion, was previously reported in various papers [13,16,22,23], thus demonstrating the capability of FSI to form stable passive layer which prevents reduction of unstable EMI cations [13]. In particular, the FSI anion was found to be attractive especially if coupled with PYR cations. For instance, PYR_{1A}FSI-LiFSI electrolyte mixtures showed outstanding performance in contact with both graphite [16] and $LiCoO_2$ [24] electrodes in combination with an excellent lithium stripping/plating cycling behavior [17,25]. In addition, it is well known that FSI-based ILs display fast transport properties (due to their lower viscosity) [13,24,26] and low melting point.

Therefore, we combined the PYR_{24} cation with the FSI anion to synthesize a novel IL (PYR_{24}FSI), which was used for preparing PYR_{24}FSI-LiFSI innovative electrolyte. Thermal and transport properties of this mixture were investigated.

2. Material and methods

The PYR_{24}FSI was synthesized according to a procedure route reported in details elsewhere [17,18,25]. *N*-butylpyrrolidine (Sigma-Aldrich, 98%) and bromoethane (Fluka, ≥98.0%) were previously purified through an activated carbon (Aldrich)–acidic alumina (Aldrich) blend. LiFSI (Solvionic) and ethyl acetate (Sigma-Aldrich, ≥99.5%)

---

[*] Corresponding author at: Department of Chemistry, University of Rome La Sapienza, P.le Aldo Moro 5, 00185 Rome, Italy.
E-mail address: gianni.appetecchi@enea.it (G.B. Appetecchi).

http://dx.doi.org/10.1016/j.elecom.2014.02.017
1388-2481/

were used as received. Deionized ultrapure water (Milli-Q, Millipore) was used as co-solvent.

The IL/lithium salt (mole ratio equal to 9:1) mixture was prepared by dissolving (at 50 °C) LiFSI (previously vacuum dried overnight at 120 °C) in $PYR_{24}FSI$ [17,18,25]. The water content was measured by an automatic Karl Fischer titrator (Metrohm) in a glove box (MBraun, <1 ppm O_2, <1 ppm H_2O) at room temperature.

Differential scanning calorimetry (DSC) measurements were carried out using a DSC 821 (Mettler-Toledo). The IL samples (housed in Al pans, which were sealed in the glove box) were cooled down to −140 °C with cooling rate of 2 °C min^{-1} and, then, fully crystallized by thermal cycling [27] from −140 °C to the cold crystallization feature temperature (cooling rate: 2 °C min^{-1}, heating rate: 10 °C min^{-1}). Finally, a heating scan (10 °C min^{-1}) was run from −140 °C to 100 °C.

Ionic conductivity was determined by impedance spectroscopy measurements, using a potentiostat/galvanostat (Biologic instrument), carried out from room temperature to 90 °C at 10 °C day^{-1} step. A 5 mV amplitude signal was applied to two blocking platinum electrode cells (loaded with the IL samples) with the frequency range from 100 kHz to 10 Hz.

3. Results and discussion

The procedure route, followed in the previous work, allowed synthesizing transparent, colorless and odorless IL with moisture content below 2 ppm. NMR measurements (Fig. 1), performed to verify the synthesis of the IL, indicated that the $PYR_{24}FSI$ ionic liquid was correctly obtained. Elemental analysis, performed on the IL material, has revealed a lithium (Li^+) and bromide (Br^-) content below 2 ppm. The IL-lithium salt mixtures exhibited a homogeneous appearance with no evidence of solid precipitate even after prolonged storage.

Fig. 2 depicts the thermal heating trace of pure $PYR_{24}FSI$ (panel A) and the $PYR_{24}FSI$-LiFSI mixture (panel B). DSC measurements were run both after quenching (not crystallized materials) and slow cooling/annealing (fully crystallized materials) from room temperature (see Material and methods). The appearance of an exothermal feature (marked with an asterisk), e.g., ascribable to cold crystallization, in the thermal curve of the not-crystallized materials (dotted traces) was taken as a test of the uncompleted crystallization (i.e., uncompleted disappearance of amorphous and/or metastable phases) of the samples before the DSC measurements [27]. The glass transition temperature (T_g) was detected around 174 K (−99 °C) only in the DSC trace of the amorphous samples. The $PYR_{24}FSI$ material exhibited an endothermic melting peak due to the fusion of the IL around −30 °C (onset value, Table 1), representing the lowest melting temperature recorded until now in FSI-based IL materials [17,18]. Addition of LiFSI led to increase the T_g value (Table 1) from −99 °C (174 K) to −88 °C (185 K), and more importantly, it was seen to hinder the crystallization process of the mixture. This is highlighted by a shift of the melting feature, which exhibits a broader shape, from −30 °C to −38 °C, as a result of unfavorable ion packing ascribable to the different size of Li^+ and $(PYR_{24})^+$ cations [17,18]. The latter issue is able to counterbalance the stronger $Li^+\cdots FSI^-$ interactions (most likely due to lithium cations and anion oxygen atoms) with respect to the $PYR_{24}^+\cdots FSI^-$ ones (due to higher charge surface density of smaller lithium cation) which, conversely, lead to increase the melting temperature. It is worthy to note here that the crystallized $PYR_{24}FSI$ and $PYR_{24}FSI$-LiFSI mixtures (solid traces) do not show any shift of the endothermic melting peak with respect to not-crystallized corresponding samples. This behavior, previously observed in other PYR FSI materials [17,18], clearly indicated that crystallization took place very quickly on cooling. Conversely, bis(trifluoromethanesulfonyl)imide (TFSI)-based ILs, supercooled and/or relatively quickly cold-crystallized during the heating scan, exhibited a shift of the melting feature down to lower temperature side [27] with respect to the fully crystallized samples. This indicates that, with rapid crystallization, a meta-stable crystalline phase may form, addressed to kinetically favored *cis* conformer of the TFSI anion [27]. The latter displays a lower fusion temperature with respect to the thermodynamically favored *trans* TFSI conformer, which is promoted by repeatedly cycling (cooling and heating) the IL sample at sub-melting temperatures (e.g., IL material crystallizes in a single phase).

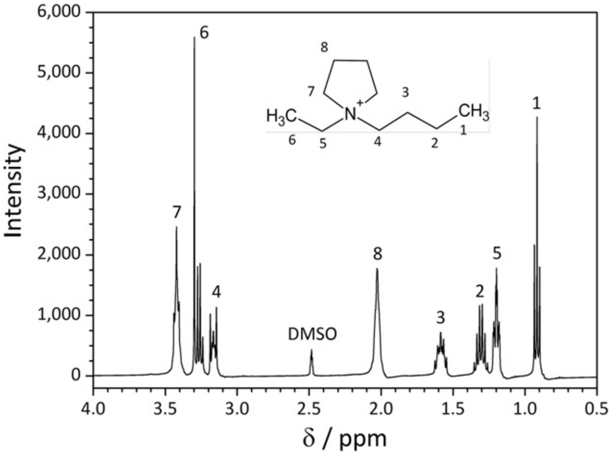

Fig. 1. ^1H-NMR spectrum of the $PYR_{24}FSI$ ionic liquid.

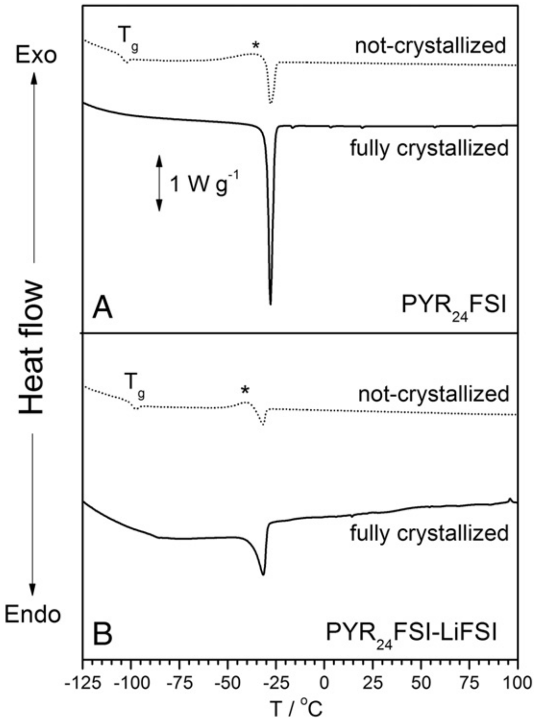

Fig. 2. DSC traces, obtained after quenching (dotted traces) and slow cooling/annealing (solid traces) from room temperature, of the $PYR_{24}FSI$ ionic liquid (panel A) and the $PYR_{24}FSI$-LiFSI mixture (panel B).

The ionic conductivity vs. temperature dependence of neat $PYR_{24}FSI$ and the $PYR_{24}FSI$-LiFSI mixture is plotted in Fig. 3A. Conductivity above 5×10^{-3} S cm^{-1} (Table 1) was reached at 23 °C for the pure IL, which achieved 1×10^{-2} S cm^{-1} at 50 °C. These fast ion transport properties

Table 1
Melting point (m. p.), conductivity (σ), glass transition temperature (T_g) and T_0 parameter of the pure IL and $PYR_{24}FSI$-LiFSI mixture.

IL sample	m. p./K	σ (23.5 °C)/S cm^{-1}	T_g/K	T_0/K
$PYR_{24}FSI$	243 ± 1	$(5.3 \pm 0.6) \times 10^{-3}$	174 ± 1	75 ± 1
$PYR_{24}FSI$-LiFSI	235 ± 1	$(3.6 \pm 0.1) \times 10^{-3}$	185 ± 1	116 ± 1