

Ionic liquid mixtures with tunable physicochemical properties



J. Serra Moreno^a, S. Jeremias^b, A. Moretti^{b,c,d}, S. Panero^a, S. Passerini^{c,d}, B. Scrosati^e, G.B. Appetecchi^{a,f,*}

^a University of Rome "La Sapienza", Department of Chemistry, Piazzale Aldo Moro 5, 00185 Rome, Italy

^b University of Muenster, Institute of Physical Chemistry, Corrensstrasse 28, 48149 Muenster, Germany

^c Helmholtz Institute Ulm (HIU), Electrochemistry I, Helmholtz Strasse 1, 89081 Ulm, Germany

^d Karlsruhe Institute of Technology, P.O. Box 3640, 76021 Karlsruhe, Germany

^e Italian Institute of Technology, Rome, Italy

^f ENEA, Agency for New Technologies, Energy and Sustainable Economic Development, UTRINN-IFC, via Anguillarese 301, Rome 00123, Italy

ARTICLE INFO

Article history:

Received 7 November 2014

Accepted 10 November 2014

Available online 13 November 2014

Keywords:

N,N-dimethylpyrrolidinium
N-butyl-*N*-methylpyrrolidinium
N-methyl-*N*-octylpyrrolidinium
bis(trifluoromethanesulfonyl)imide
ionic liquid mixtures

ABSTRACT

Innovative ionic liquids (ILs) can be prepared by properly combining pure ILs, thus obtaining materials with improved characteristics. For instance, three different mixture families, namely $\text{PYR}_{11}\text{TFSI-PYR}_{14}\text{TFSI}$, $\text{PYR}_{11}\text{TFSI-PYR}_{18}\text{TFSI}$ and $\text{PYR}_{14}\text{TFSI-PYR}_{18}\text{TFSI}$, were prepared and investigated in terms of thermal behavior, ionic conductivity and ion self-diffusion coefficient as a function of the mole composition. The physicochemical properties, including mechanical consistency, of these mixed ionic liquids were found to be enhanced and/or finely tuned by properly varying the aliphatic chain length and/or the mole ratio of the pyrrolidinium cations. This issue might be profitably exploited to match the electrolyte requirements of electrochemical devices operating under particular or hard conditions, not always achievable by single materials.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

There is growing up interest in replacing the volatile and hazardous organic solvents, currently used in electrochemical devices such as lithium batteries [1], electrochemical capacitors [2], electrochemical actuators [3], light-emitting electrochemical cells [4], with ionic liquids (ILs) because of their negligible flammability and vapor pressure in conjunction with wide chemical, electrochemical and thermal stability, high ionic conductivity and heat capacity, good solvent capability, possibility of modulating hydrophobicity/hydrophilicity by suitable choice of cation-anion pairs. These requirements, pushing ILs far beyond the initially envisaged role of green solvents [5–9], are basic for the realization of high safety energy storage devices without depleting their energy and power density. Ionic liquid electrolytes were found to show good compatibility and high performance with a large variety of anodes (including lithium metal, graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$) [1] and cathodes (LiCO_2 , LiMn_2O_4 , LiFePO_4) [1]. Recently, it was demonstrated that IL incorporation such as *N*-alkyl-*N*-methyl pyrrolidinium bis(trifluoromethanesulfonyl)imide in PEO-based polymer electrolytes increases the room temperature ionic

conductivity by two orders of magnitude [10], thus allowing a significant extension of the operative temperature range of lithium metal polymer batteries.

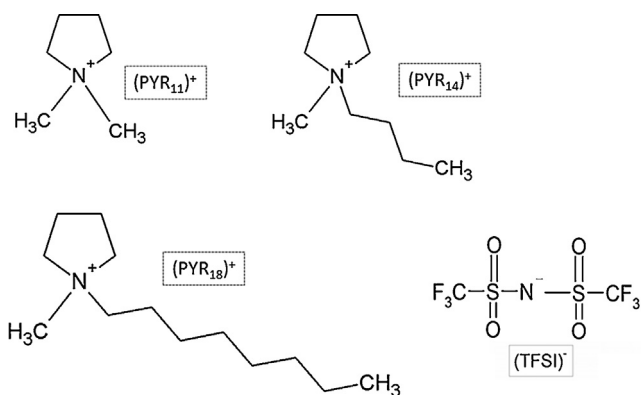
The rational design of novel systems based on ILs requires a deep understanding of the intermolecular interactions and ion transport properties occurring in the ionic liquid bulk. ILs are highly structured fluids with short-range aggregation moieties, correlated to the alkyl side chain length bounded to the nitrogen group of the cation [11,12]. The existence of nanoscale organizations, pointed out by several authors based on the combination of computational and experimental approaches [13–20], has implications in chemical processes, selectivity for gas solubility and ion transport.

Electrochemical devices, especially if operating under particular conditions, may require wide variety of electrolyte characteristics, often non-satisfied by single material components. The possibility of enhancing and/or finely tuning the electrochemical properties of ionic liquids by properly combining neat IL materials appears a very appealing issue [1]. However, the association and ordering of the ions in mixture are more complicated than in pure components, thus affecting the short-range aggregation moieties and, consequently, the IL physicochemical properties.

Our basic idea is to properly combine ionic liquids formed by the *N*-alkyl-*N*-methylpyrrolidinium, e.g., $(\text{PYR}_{1A})^+$ (where the subscripts indicate the number of carbon atoms in the alkyl side chains), cation and the bis(trifluoromethanesulfonyl)imide,

* Corresponding author.

E-mail address: gianni.appetecchi@enea.it (G.B. Appetecchi).



Scheme 1. Chemical structure of the cations and anion of the investigated ionic liquid mixtures.

(TFSI)⁻, anion, aiming to obtain materials with improved characteristics. For instance, pyrrolidinium cations were chosen since their properties are influenced by the aliphatic chain length [1,12,19,20]. The synergic combination of such pyrrolidinium TFSI ionic liquids is expected to positively reflect on the performance of these “innovative” materials. For such a reason, mixtures of pyrrolidinium cations, which differed for the main aliphatic side chain (A) ranging from short (methyl) to long (n-butyl and n-octyl), were studied. Also, the comparison of the physicochemical properties of a given ion in two different environments, i.e., pure liquids and their mixtures (formed by two ILs differing only for the length of the cation alkyl side chain), is expected to provide valuable information on the macroscopic and microscopic aspects of the investigated blends.

Three ionic liquid materials, namely PYR₁₁TFSI, PYR₁₄TFSI and PYR₁₈TFSI, were synthesized, allowing preparing three IL binary mixture families: *i*) PYR₁₁TFSI-PYR₁₄TFSI (hereafter named as PYR₁₁-PYR₁₄), *ii*) PYR₁₁TFSI-PYR₁₈TFSI (PYR₁₁-PYR₁₈) and *iii*) PYR₁₄TFSI-PYR₁₈TFSI (PYR₁₄-PYR₁₈). The thermal (DSC) and ion transport (conductivity and self-diffusion coefficient) properties of the so-obtained IL materials were investigated and compared with those of the pure ionic liquids.

Table 1
Mole composition, melting point (m. p.) and ionic conductivity (σ) values of PYR₁₁-PYR₁₄, PYR₁₁-PYR₁₈ and PYR₁₄-PYR₁₈ ionic liquid mixtures. The m. p. values were obtained from DSC (a) and conductivity (b) measurements.

Mixture sample	Mole fraction			m. p. / °C (a)	m. p. / °C (b)	σ / S cm ⁻¹ (-10 °C)	σ / S cm ⁻¹ (20 °C)
	PYR ₁₁	PYR ₁₄	PYR ₁₈				
<i>Set I</i>							
IA	0	1.00	---	-8.0	-7.6	5.7×10^{-8}	1.8×10^{-3}
IB	0.25	0.75	---	-14.9	-15.4	1.4×10^{-4}	2.2×10^{-3}
IC	0.50	0.50	---	-25.1	n. d.	2.3×10^{-5}	6.0×10^{-5}
ID	0.75	0.25	---	-12.0	n. d.	2.4×10^{-6}	1.8×10^{-6}
IE	1.00	0	---	130.5*	n. d.	9.0×10^{-9}	2.1×10^{-8}
<i>Set II</i>							
II.A	0	---	1.00	-13.6	-12.5	7.4×10^{-5}	5.4×10^{-4}
II.B	0.25	---	0.75	n. d.	-17.6	7.2×10^{-5}	7.4×10^{-4}
II.C	0.50	---	0.50	n. d.	-15.6	2.2×10^{-5}	2.0×10^{-4}
II.D	0.75	---	0.25	n. d.	-15.1	1.7×10^{-5}	1.8×10^{-4}
II.E	1.00	---	0	130.5*	n. d.	9.0×10^{-9}	2.1×10^{-8}
<i>Set III</i>							
III.A	---	0	1.00	-13.6	-12.5	7.4×10^{-5}	5.4×10^{-4}
III.B	---	0.25	0.75	n. d.	n. d.	1.2×10^{-4}	8.9×10^{-4}
III.C	---	0.50	0.50	n. d.	n. d.	1.7×10^{-4}	1.2×10^{-3}
III.D	---	0.75	0.25	n. d.	n. d.	2.5×10^{-4}	1.6×10^{-3}
III.E	---	1.00	0	-8.0	-7.6	5.7×10^{-8}	1.8×10^{-3}

* = from ref. [25].

2. Experimental

2.1. Ionic liquid mixtures

The PYR₁₄TFSI ionic liquids were synthesized through a procedure described in details elsewhere [21]. The chemicals *N*-methylpyrrolidine (97 wt.%), bromomethane (99 wt.%), 1-bromobutane (99 wt.%), 1-chlorooctane (99 wt.%), ethyl acetate (ACS grade, >99.5 wt.%) were purchased by Aldrich and previously purified through activated carbon (Aldrich, Darco-G60) and alumina (acidic, Aldrich Brockmann I). The LiTFSI (99.9 wt.%, battery grade) salt was purchased by Solvionic and used as received. Deionized H₂O was obtained with a Millipore ion-exchange resin deionizer. Scheme 1 depicts the chemical structure of the cations and common anion of the investigated ionic liquid mixtures.

The water content was measured using the standard Karl Fisher method. The titrations were performed by an automatic Karl Fisher coulometer titrator (Metrohm) in a glove-box (H₂O and O₂ content below 1 ppm). The Karl Fisher titrant was a one-component reagent (Hydranal 34836 Coulomat AG) purchased from Aldrich.

The ionic liquid binary mixtures were prepared (within the glove-box) blending the IL materials in the appropriate mole ratio and, then, stirring them at 50 °C for a few minutes. The IL mixtures containing (PYR₁₁)⁺ were stirred at 135 °C, i.e., just above the melting point of this ionic liquid material. Three different IL mixture sets (Table 1) were prepared: (x)PYR₁₁-(1-x)PYR₁₄ (set I); (x)PYR₁₁-(1-x)PYR₁₈ (set II) and; (x)PYR₁₄-(1-x)PYR₁₈ (set III) where (x) and (1-x) represent the mole fraction of the IL components in the binary mixtures.

2.2. Thermal analysis

The thermal measurements were performed using a DSC 821 (Mettler-Toledo) differential scanning calorimeter (DSC). Hermetically sealed, Al pans were prepared in the glove-box. In order to allow complete crystallization [22], the IL materials were thermally annealed in the DSC instrument by repeatedly cycling and/or holding the samples at sub-ambient temperatures for varying periods of time. Successively, the samples were cooled (10 °C min⁻¹) down to -140 °C and, then, heated (10 °C min⁻¹) up to 150 °C. The

Download English Version:

<https://daneshyari.com/en/article/184879>

Download Persian Version:

<https://daneshyari.com/article/184879>

[Daneshyari.com](https://daneshyari.com)