



Mixed organic compound-ionic liquid electrolytes for lithium battery electrolyte systems



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H I G H L I G H T S

- Electrolytes based on proper combination of ionic liquid with organic solvents.
- Enhanced safety in conjunction with fast ion transport properties.
- Conductivity approaching 10^{-3} S cm⁻¹ at -20 °C.
- No flammability up to an organic compound mole fraction equal to 0.3.

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The thermal, transport, rheological and flammability properties of electrolyte mixtures, proposed for safer lithium-ion battery systems, were investigated as a function of the mole composition. The blends were composed of a lithium salt (LiTFSI), organic solvents (namely EC, DEC) and an ionic liquid (PYR₁₃TFSI). The main goal is to combine the fast ion transport properties of the organic compounds with the safe issues of the non-flammable and non-volatile ionic liquids. Preliminary tests in batteries have evidenced cycling performance approaching that observed in commercial organic electrolytes.

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1. Introduction

The low safety is one of the main drawbacks of commercially available lithium-ion batteries because of the presence of flammable and volatile organic solvents in the electrolyte, e.g., namely ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC) [1], resulting in possible fire and/or explosion of the electrochemical device. In addition, the safety issue dramatically decreases with increasing the battery size, this preventing commercialization for stationary (smart grid, renewable power source) and automotive (electric/hybrid vehicles) uses [2].

A promising approach for solving this problem is partial or total replacement of organic solvents (in the electrolytes) with a new class of fluid materials, acting as poorly flammable and/or flame retardant components, called ionic liquids (ILs). The latter are molten salts at room temperature or below, composed by organic cations combined with inorganic/organic anions [3,4]. The main advantages of ILs toward organic solvents are: low flammability, negligible vapor pressure, high chemical, electrochemical and thermal stability and, in some cases, hydrophobicity [3,4]. Despite these undoubtedly favorable characteristics, the ion conductivity of IL-based electrolytes is, however, still lower than that of organic solutions, with negative effect on the high rate performance of electrochemical devices. In this scenario, mixtures of ILs in combination with organic compounds have been proposed as electrolyte components for lithium batteries. Such an approach may represent a good compromise among fast ion transport properties (low viscosity) and improved safety (low flammability) of the resulting electrolyte [1,5–7]. Also, the incorporation of proper

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organic compounds (such as vinyl carbonate), even in moderate amount (5–15 wt.%), into ionic liquid electrolytes was found to enhance the cycling battery performance [5–11].

In the last fifteen years, various ILs, in combination with organic solvents, have been proposed and tested as components for lithium battery electrolytes. Particularly, ionic liquids based on the bis(trifluoromethanesulfonyl)imide (TFSI) anion and the *N*-alkyl-*N*-methyl pyrrolidinium (PYR_{1A}) cation (the subscripts indicate the number of carbon atoms in the alkyl side chains) have been extensively studied because of their wide thermal and electrochemical stability and good ion conduction [12–14]. Furthermore, pyrrolidinium cations show some advantages if compared with the non-cyclic and unsaturated cyclic quaternary ammonium ones such as higher stability on reduction and better compatibility at the interface with electrodes because of the absence of acidic protons and double bonds [15,16].

This manuscript reports a physicochemical study on electrolyte mixtures composed by a lithium salt (LiTFSI), two of the most common organic solvents employed in lithium-ion battery systems (namely EC and DEC) and a pyrrolidinium TFSI ionic liquid (namely PYR₁₃TFSI). These quaternary mixed electrolytes were investigated in terms of thermal, transport, rheological and flammability properties by modulating the mole ratio of the different components. Also, the performance of the mixed electrolytes were tested in Li/LiFePO₄ and Li/Li₄Ti₅O₁₂ half-cells and compared with that of commercial organic solutions.

2. Experimental

2.1. Preparation of the electrolyte mixtures

The PYR₁₃TFSI ionic liquid was synthesized in our laboratory following a procedure route developed at ENEA and described in details elsewhere [17]. The lithium salt, LiTFSI (3 M, battery grade), was dried under high vacuum ($>10^{-6}$ mbar) at 120 °C for 24 h. The organic solvents, EC and DEC (Merck, battery grade), were mixed in mole ratio equal to 1:1. Then, the EC/DEC blend was stirred with zeolites to reduce the initial water content (50 ppm) below 20 ppm and stored in presence of zeolites.

The electrolytic mixtures were prepared by mixing (in the proper mole fractions) LiTFSI, PYR₁₃TFSI and EC/DEC, which were successively stirred at 40–50 °C until to obtain homogeneous samples (e.g., full dissolution of LiTFSI in ionic liquid and organic solvents). Two different sample sets (Table 1) were prepared:

set A: binary mixtures $(x)\text{LiTFSI}-(1-x)\text{PYR}_{13}\text{TFSI}$ where x and $(1-x)$ represent the mole fraction of the two components;

set B: quaternary mixtures $(0.1)\text{LiTFSI}-(0.9-x)\text{PYR}_{13}\text{TFSI}-(x)\text{EC/DEC}$ where x is the overall mole fraction of EC/DEC (the EC:DEC mole ratio was fixed equal to 1:1).

The mixtures were prepared and characterized in a controlled environment dry room (humidity content below 10 ppm at 20 °C).

2.2. Water content

The water content was measured using the standard Karl Fisher method. The titrations were performed by an automatic Karl Fisher coulometer titrator (Mettler Toledo DL32) located inside the dry room. The Karl Fisher titrant was a one-component reagent (Hydranal 34836 Coulomat AG) provided from Aldrich.

2.3. Thermal analysis

The thermal measurements were performed using a TA Instruments (Model Q100) differential scanning calorimeter (DSC).

Table 1

Mole composition of the investigated electrolyte mixtures. The mole concentration values, with the respect to the Li⁺, (PYR₁₃)⁺, (TFSI)⁻ ion species, are reported.

	Mole fraction			Molarity/mole dm ⁻³		
	LiTFSI	PYR ₁₃ TFSI	EC/DEC	Li ⁺	(PYR ₁₃) ⁺	(TFSI) ⁻
Set A						
A1	0.1	0.9	–	0.37	3.32	3.69
A2	0.2	0.8	–	0.78	3.11	3.89
A3	0.3	0.7	–	1.23	2.88	3.11
Set B						
B1	0.1	0.8	0.1	0.40	3.17	3.57
B2	0.1	0.7	0.2	0.42	2.97	3.39
B3	0.1	0.6	0.3	0.46	2.78	3.24
B4	0.1	0.6	0.4	n.a.	n.a.	n.a.
B5	0.1	0.4	0.5	0.57	2.29	2.86
B6	0.1	0.3	0.6	n.a.	n.a.	n.a.
B7	0.1	0.2	0.7	0.73	1.46	2.19
B8	0.1	–	0.9	1.02	–	1.02

Hermetically sealed, aluminum pans were prepared in the dry room. In order to allow a complete crystallization [18], the materials were thermally annealed in the DSC instrument by repeatedly cycling and/or holding the samples at sub-ambient temperatures for varying time periods. Successively, the samples were cooled (10 °C min⁻¹) down to –140 °C and, then, heated (10 °C min⁻¹) up to 100 °C. The appearance of a cold recrystallization peak during the heating scan was taken as test of uncompleted crystallization of the sample.

2.4. Ionic conductivity

The ionic conductivity was determined by a conductivity meter AMEL 160 in the temperature range from –40 °C to 100 °C (60 °C for the set B samples) using a climatic test chamber (Binder GmbH MK53). The entire setup was controlled by a software developed at ENEA. The mixtures were housed (in the dry room) in sealed, glass conductivity cells (AMEL 192/K1) equipped with two porous platinum electrodes (cell constant equal to 1.0 ± 0.1 cm⁻¹). In order to fully crystallize the materials [18], the cells were immersed in liquid nitrogen for a few seconds and, then, transferred in the climatic chamber at –40 °C. After few minutes of storage at this temperature, the solid samples turned again liquid. This route was generally repeated until the samples remained solid at –40 °C. After a storage period at –40 °C for at least 18 h the conductivity of the materials was measured by running a heating scan at 1 °C h⁻¹.

2.5. Viscosity measurements

The viscosity measurements were carried out using a rheometer (HAAKE RheoStress 600) located in the dry room. The tests were performed from 20 °C to 80 °C (1 °C min⁻¹ heating rate) in the 100 s⁻¹ to 2000 s⁻¹ rotation speed range. Measurements were taken after 10 °C steps.

2.6. Density measurements

The density measurements were performed from 90 °C to 20 °C at 10 °C step using a density meter (Mettler Toledo DE40) located in the dry room. The samples were previously degassed under vacuum at 50 °C overnight to avoid bubble formation during the cooling scan tests.

2.7. Flammability tests

The flammability tests were carried out on the electrolyte mixtures of set B (e.g., differing in the organic solvent content). The

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