



Towards improvement of the electrochemical properties of ionic liquid-containing polyethylene oxide-based electrolytes



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ABSTRACT

We report an investigation on quaternary, polyethylene oxide (PEO)-based electrolytes as separators for lithium polymer batteries. The target is the development of Li⁺ conducting membranes, containing large fraction of the *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)imide ionic liquid, able to combine fast ion transport properties with improved electrochemical stability. The PEO electrolytes, prepared through a fully-dry solvent-free procedure, exhibited good aging resistance and conductivity values equal to 3.46×10^{-4} and $2.43 \times 10^{-3} \text{ S cm}^{-1}$ at -20 and 20°C , respectively, combined with an anodic stability up to 4.5 V (vs. Li⁰/Li⁺). These results represent the best performance, in terms of ion transport properties and electrochemical stability, reported till now for PEO electrolytes.

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1. Introduction

The development of solvent-free polymer electrolytes (SPEs) is undoubtedly appealing from the safety and engineering point of view and opens new perspectives to applications in electrochemical devices [1–5]. SPEs, minimizing dendritic growth onto the lithium anode and avoiding liquid leakage, are much safer than the liquid ones because of the absence of volatile, flammable, and reactive organic solvents. Also, they can be easily and cheaply manufactured into low thicknesses ($<100 \mu\text{m}$) and shapes not allowed for supported liquid electrolytes, offering a new concept of solvent-free, all-solid-state, thin-layer, flexible (both mechanically and in design), robust, lithium polymer batteries (LPBs). However, the room temperature performance of LPBs is still limited by the low ionic conductivity of solvent-free polymer electrolytes. Conduction values suitable for practical applications are approached only at temperatures higher than 70°C .

The addition of ionic liquids (ILs), e.g., molten salts at room temperature or below, as co-salts was found as one of the most successful approaches for overcoming the conductivity limitation

of SPEs [6,7] and, therefore, for relevantly improving the lithium battery performance at ambient temperature [6]. In particular, ILs formed by *N*-alkyl-*N*-methylpyrrolidinium, (PYR_{1A})⁺, cation and perfluorosulfonylimide, (PFSI)[−], anions were seen to enhance the room temperature ion conduction of polyethylene oxide (PEO) electrolytes above $10^{-4} \text{ S cm}^{-1}$ and improve the compatibility with respect to the lithium metal anode [7].

However, fast transport properties in combination with compatibility towards high voltage cathodes are required for realizing high energy density devices operating at high powers. In previous work [8] we have properly designed and developed quaternary SPEs based on PEO as the host and incorporating large fraction of *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)imide, PYR₁₃FSL. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and ethylene carbonate (EC) were chosen as the lithium salt and additive, respectively. The purpose of incorporating high IL amounts was to promote creation of 3-D conductive networks, due to ionic liquid phase separation phenomena evidenced by thermal and impedance investigation [8], with the aim to enhance the ion transport properties. For instance, conductivity values equal to 1.5×10^{-4} and $1.6 \times 10^{-3} \text{ S cm}^{-1}$ were exhibited at -20°C and 20°C , respectively, i.e., not commonly reported for ionic liquid-based PEO electrolytes, and no degradation of the mechanical and transport properties was observed even upon prolonged storage time periods. EC was incorporated as additive for promoting, in combination with the

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FSI anion, the formation of a stable, protective SEI onto anodes [9,10]. The presence of this flammable solvent in a rather small amount is not detrimental for the safety of the battery system because it is mostly consumed during the first half-cycle [11].

Nevertheless, PEO electrolytes are known to be electrochemically unstable with high voltage cathodes [7], being subjected to oxidation processes already at 3.7–3.8 V [12]. The quaternary PEO-LiTFSI-PYR₁₃FSI-EC electrolytes were developed with the purpose to promote liquid leakage (due to the high IL excess); the ionic liquid film released by the electrolyte membrane is expected protecting the polymer host from high voltage cathode material, this extending the operative voltage of SPE and improving the interfacial compatibility with electrodes.

In the present work we have extended the investigation on the thermal and ion transport properties of the PEO-LiTFSI-PYR₁₃FSI-EC electrolyte system as function of the lithium salt concentration and we have studied the electrochemical stability as well as the compatibility with cathodes operating above 4 V.

2. Experimental

2.1. Materials

A synthesis route reported elsewhere [13], which uses water as the only processing solvent, was followed for preparing the PYR₁₃FSI ionic liquid with high purity level (Li⁺, Br⁻ and H₂O content below 2 ppm).

The PEO-LiTFSI-PYR₁₃FSI-EC electrolytes were prepared through a solvent-free hot-pressing process described elsewhere [7,8] and carried out in a controlled environment dry room (moisture content <20 ppm at 20 °C). LiTFSI (3 M, battery grade, >99.9%), PYR₁₃FSI, PEO (Dow Chemicals, WSR 301, M_w = 4,000,000) were vacuum dried at 120 °C (24 hours), 70 °C (2 days) and 50 °C (2 days), respectively. EC (Merck, battery grade, >99.9%, moisture content <20 ppm) was used as received. Electrolytic tapes from 50 to 100 μm thick were obtained. On the basis of the results previously reported [8], the (PYR₁₃)⁺:Li⁺ mole ratio was kept equal to 2.2:1 whereas the Li:EO mole ratio was ranged from 0.05:1 (EO:Li = 20:1) to 0.1:1 (EO:Li = 10). The EC content was kept equal to 7.4 wt.% (8% with respect to the PEO-LiTFSI-PYR₁₃FSI overall mass), corresponding to a volume fraction around 8.9%. The formulation (in terms of mole ratios and weight contents) of the PEO-LiTFSI-PYR₁₃FSI-EC quaternary polymer electrolyte samples is reported in Table 1.

The carbon working electrodes and the composite cathodes were prepared (in the dry room) through a solvent-free procedure analogous to that followed for the polymer electrolytes. The PEO (vacuum dried at 60 °C for 48 hours) polymer was milled in a mortar with KJB carbon (Akzo Nobel, previously vacuum dried at 150 °C for 24 hours). For the cathode preparation, the KJB carbon was previously (intimately) blended with the LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂, NMC (LinYi-Gelon) active material (previously vacuum dried at 150 °C for 24 hours) in a ball-miller and, then, PEO was added (and milled) to the NMC-KJB blend. Successively, LiTFSI

(vacuum dried at 120 °C for 24 hours), PYR₁₃FSI (70 °C for 48 hours) and EC (used as received) were added in the proper proportions. Upon further mixing, the electrode blend paste was housed in vacuum-sealed pouch envelope and annealed at 70 °C overnight in order to homogenize the components. A plastic-like bulk paste, having a thickness from 4 to 5 mm, was obtained, which was then hot-pressed at 80 °C for 2 minutes to form about 300 μm thick preliminary film. Successively, the film was consecutively cold-calendered to remove all porosity and reduce the thickness down to 50–60 μm. Finally, 12 mm diameter discs (active area equal to 1.13 cm²) were punched from the electrode tape for the electrochemical tests. The weight composition of the working electrodes and composite cathodes was KJB:electrolyte = 50:50 and NMC:KJB:electrolyte = 40:7:53, respectively. The active material mass loading for the composite cathode ranged from 4 to 5 mg cm⁻², corresponding (accounting for a theoretical capacity of NMC equal to 160 mA h g⁻¹) to a capacity from 0.6 to 0.8 mA h cm⁻². The polymer electrolyte (acting as the binder and ionic conductor), contained both in the working electrodes and in the composite cathodes, has identical weight composition to that of cell (electrolyte) separator.

2.2. Methods

Images (50x) were taken on the cross-section of quaternary polymer electrolyte membranes (properly cut by sharp knife) by a LEICA MeF3 optical microscope.

Differential scanning calorimetry (DSC) measurements were run by a thermal analyzer system DSC TA Instruments. The polymer electrolyte samples (about 5 mg), housed in sealed aluminum pan (inside the dry room), were initially cooled at 10 °C min⁻¹ from room temperature down to -140 °C and, then, heated at 10 °C min⁻¹ up to 150 °C with 50 mL min⁻¹ helium flow rate.

Impedance spectroscopy was used to determinate the ionic conductivity of the PEO-LiTFSI-PYR₁₃FSI-EC electrolytes. The AC measurements, taken on two-blocking electrode (symmetrical) cells kept in open circuit voltage (OCV) condition, were conducted in the -40/80 °C temperature range by a F.R.A. Schlumberger Solartron 1260. Sinusoidal amplitude equal to 10 mV was applied to the cells (thermally controlled by climatic chamber Binder GmbH MK53) in the 65,000 – 1 Hz frequency range. Prior the measurements, the cells were held at -40 °C for at least 24 hours and, then, subjected to a heating scan (up to 80 °C) at 10 °C day⁻¹ (scan) rate.

Thermogravimetric analysis (TGA) was carried out by SDT 2960 equipment. The temperature and mass were calibrated using the nickel Curie point as the reference and ceramic standards provided with the instrument, respectively. The samples (10–12 mg), handled and weighed in the dry room, were housed in high purity aluminum oxide crucibles (cross sectional area of 0.24 cm²). The TGA measurements were carried out in synthetic air atmosphere, which was flown over the samples at 100 ml min⁻¹ rate. The thermal stability was investigated by running a heating

Table 1
Weight composition and ionic conductivity values (referred to the equilibrium state) of the PEO quaternary electrolyte samples. The lithium salt:EO monomer and ionic liquid:lithium salt mole ratios are also reported.

Sample	Li:EO mole ratio	PYR ₁₃ :Li mole ratio	PEO/wt.%	LiTFSI/wt.%	PYR ₁₃ FSI/wt.%	EC/wt.%	Conductivity/S cm ⁻¹	
							-20 °C	20 °C
PEO-A	0.050	2.2	44.2	14.4	34.0	7.4	1.36 × 10 ⁻⁴	1.18 × 10 ⁻³
PEO-B	0.057	2.2	41.1	15.3	36.2	7.4	1.49 × 10 ⁻⁴	1.20 × 10 ⁻³
PEO-C	0.067	2.2	37.6	16.4	38.6	7.4	1.53 × 10 ⁻⁴	1.24 × 10 ⁻³
PEO-D	0.080	2.2	33.6	17.5	41.5	7.4	1.75 × 10 ⁻⁴	1.33 × 10 ⁻³
PEO-E	0.100	2.2	29.0	18.9	44.7	7.4	3.46 × 10 ⁻⁴	2.43 × 10 ⁻³

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