



Pyrrolidinium-based polymeric ionic liquids as mechanically and electrochemically stable polymer electrolytes

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ABSTRACT

A new family of polymeric ionic liquids having pyrrolidinium cation pendant units was synthesized from commercially available poly(diallyldimethylammonium) chloride. A simple anion exchange procedure was applied to the poly(diallyldimethylammonium) chloride using different salts such as LiTFSI, KPF₆, LiBF₄ and NaDBSA. The anion exchange reaction was quantitative as confirmed by NMR, FT-IR and titration experiments. Among these polymers, poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide (TFSI) showed excellent performance as polymer matrix for polymer electrolyte compositions together with pyrrolidinium ionic liquid and lithium salt having a similar TFSI counter-anion. In this sense, free standing mechanically stable transparent polymer films showing an ionic conductivity higher than 10⁻⁴ S cm⁻¹ at room temperature were prepared and characterized. Furthermore, the polymer electrolytes presented a wide electrochemical stability window (7.0 V) which makes them interesting candidates for solid-state lithium batteries.

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1. Introduction

Ionic liquids (ILs) are organic salts with a low melting point (<100 °C) which are widely investigated due to their chemical stability, low flammability, negligible vapor pressure, high ionic conductivity and wide electrochemical window [1,2]. In the last decade, ionic liquids have emerged as one of the most promising candidates as liquid electrolytes in advanced electrochemical devices such as batteries, fuel cells, electrochromic devices and solar cells [3,4]. Among these applications, rechargeable lithium batteries are one of the most popular types of battery for portable electronic devices as cellular phones and laptop computers. Ionic liquids are being proposed as electrolytes in lithium batteries due to their high conductivity and additional advantages in terms of security issues such as its low flammability [5]. However, imidazolium-based ionic liquids, which are mostly investigated in a large range of devices, are not suitable as electrolytes with lithium metal electrode due to the instability of lithium metal in presence of acidic cation protons. Therefore, some authors have recently looked for more stable ionic liquids to overcome that problem and pyrrolidinium-based ionic liquids have recently shown interesting results in terms of electrochemical stability and performance [6–8].

Liquid electrolytes do present some drawbacks difficult to overcome, such as leakage. For that reason, the design of an all-solid-state battery with a solid electrolyte that could present

flexibility, easy handling, safety and performance is needed. Two main strategies have been pursued by the scientific community in an attempt to translate the benefits of ILs to polymer electrolytes for lithium batteries. The first strategy involves designing polymer electrolytes composed of conventional polymer matrices such as poly(ethylene oxide) derivatives and ionic liquids [5,7,9–11]. The second strategy consists of synthesizing new functional polymers by polymerization of ionic liquid monomers and using them as matrices for polymer electrolytes [12–15]. These materials are named polymeric ionic liquids (PILs). Polymeric ionic liquids show the main advantages of tunable solubility, enhanced ionic conductivity and chemical compatibility towards ionic liquid blends. To our knowledge, only polymeric ionic liquids containing imidazolium, tetraalkylammonium or pyridinium cations have been synthesized so far.

In this work, we report the synthesis and characterization of new pyrrolidinium-based polymeric ionic liquids and its application as mechanically and electrochemically stable polymer electrolytes for lithium batteries. The optimization of the thermal and electrochemical properties of transparent and highly conductive polymeric films based on pyrrolidinium polymer, single molecule ionic liquid and lithium salt blends is presented.

2. Experimental

2.1. Materials

N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide, PYR₁₄TFSI (high purity, >99.5%), was kindly pro-

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vided by ENEA and stored in a glovebox. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, $\geq 99\%$) was purchased from Fluka. Potassium hexafluorophosphate (KPF₆, 98%), lithium tetrafluoroborate (LiBF₄, 98%), sodium dodecylbenzene sulfonate (NaDBSA), poly(diallyldimethylammonium) chloride solution (average M_w 400,000–500,000, 20 wt.% in H₂O) was obtained from Aldrich. Solvents were purchased from Panreac Quimica S.A. Trifluoromethanesulfonic acid lithium salt (LiCF₃SO₃, 95%) was a gift from 3M. Poly(ethylene oxide) (PEO, $\sim 100,000 M_w$) was obtained from Aldrich and poly(ethylene oxide)/diethylene glycol glycidyl methyl ether (P(EO/EM = 78/22)) was kindly supplied by Daiso Co., Ltd.

2.2. Synthesis of poly(diallyldimethylammonium)X⁻

Polymeric ionic liquid containing pyrrolidinium pendant units were synthesized by anion exchange reactions into the commercially available polymer poly(diallyldimethylammonium) chloride. The classical procedure for the anion exchange reaction follows: to prepare poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide, first a solution of 8.52 g (29.68 mmol) of bis(trifluoromethanesulfonyl)imide lithium salt in 10 ml of distilled water and a solution of 4 g (24.74 mmol of monomeric units) of poly(diallyldimethylammonium) chloride in 100 ml of distilled water were mixed in a 250-ml round bottom flask. After stirring for 5 min at room temperature, the resulting white solid was filtered and dried in a vacuum oven until constant weight (9.38 g, 93.5% yield). This simple procedure was used with the other salts, KPF₆, LiBF₄, NaDBSA and LiCF₃SO₃. Excepting those carried out with LiCF₃SO₃ that did not lead to polymer precipitation, in all the other cases new polymers were obtained following the anion exchange reaction.

2.3. Preparation of polymer electrolyte films

Poly(diallyldimethylammonium)TFSI, N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide and LiTFSI salt were each dissolved in acetone and then mixed in different proportions. The concentration of salt in the electrolytes is given by weight percent of salt in the polymer for binary mixtures and in the polymer plus ionic liquid for ternary mixtures. The concentration of ionic liquid is indicated in weight percent. For example, 50 wt.% of PYR₁₄TFSI means that the film contains 1 g of ionic liquid and 1 g of polymer. Free standing transparent polymer membranes were prepared by casting onto glass slides and the films were subsequently dried at 90 °C under vacuum for 16 h before each conductivity measurement and electrochemical window experiment.

2.4. Characterization methods

Infrared spectroscopy was performed in Avatar 360 FT-IR Thermo Nicolet equipment and NMR experiments were carried out with a Bruker AM 250 (250 MHz). Thermal gravimetric anal-

ysis (TGA) was obtained using a Q500 analyser manufactured by TA instruments. The experiments were conducted under N₂ at a heating rate of 10 °C min⁻¹.

Conductivity measurements of the polymer electrolytes were carried out by the impedance spectroscopy technique, using a potentiostat/galvanostat Autolab PGSTAT30 (Eco Chemie) equipped with a FRA2, at frequencies between 1 MHz and 1 Hz and an amplitude of 5 mV. The experiments were carried out in a Teflon conductivity cell with two platinum electrodes where a piece of polymer electrolyte (0.5 cm width and 1.0 cm length) was set. The thickness was evaluated with a micrometer.

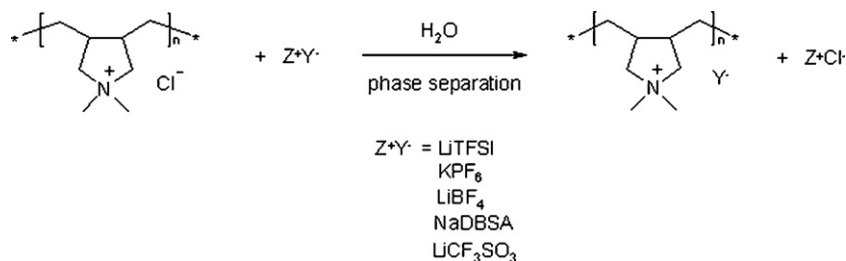
The electrochemical stability window (ESW) of the polymer electrolytes and the PYR₁₄TFSI–lithium salt mixture were obtained by linear sweep voltammetry (LSV, 10 mV s⁻¹), in a lithium/electrolyte/SS (stainless steel, 0.5 cm²) cell at room temperature with Li as reference electrode. Since the IL–salt mixture was liquid, it was absorbed in a glass microfibre sheet before measurement. LSV tests were performed using a Biologic MPG multichannel potentiostat–galvanostat.

3. Results and discussion

3.1. Synthesis and characterization of polymeric ionic liquids based on poly(diallyldimethylammonium)X⁻

Two main strategies have been followed in the literature to synthesize polymeric ionic liquids. The first one consists of synthesizing a range of monomers containing different anions and then obtaining a range of different polymeric ionic liquids after polymerization [15,16]. The second one proposes to carry out the anion exchange reaction into the water soluble polycations containing halide anions. The anion exchange reaction, which is frequently used in the synthesis of ionic liquids, is typically accompanied by phase separation due to the hydrophobic character of the formed ionic liquid. In the case of polymeric ionic liquids this reaction is translated into precipitation of the new polymer because of their insolubility in water. This strategy has the advantage of obtaining a range of polymeric ionic liquids from the same initial polymer precursor and thus, only a simple purification step by filtration was required to obtain very pure polymers. In previous studies, we reported the synthesis of imidazolium-, pyridinium- and tetralkylammonium-based polymeric ionic liquids [17,18] via anion exchange reaction and we demonstrated that the anion exchange reaction is quantitative when is carried out into polymeric backbones.

In this work, we applied the anion exchange method to a commercially available pyrrolidinium-based polymer, poly(diallyldimethylammonium) chloride. Scheme 1 shows the synthetic procedure for new polymeric ionic liquids containing pyrrolidinium pendant groups. The simple anion exchange procedure was applied to poly(diallyldimethylammonium) chloride using different salts such as LiTFSI, KPF₆, LiBF₄, NaDBSA and LiCF₃SO₃. In all these cases with the exception of LiCF₃SO₃, the new formed polymer becomes hydrophobic and precipitates



Scheme 1.

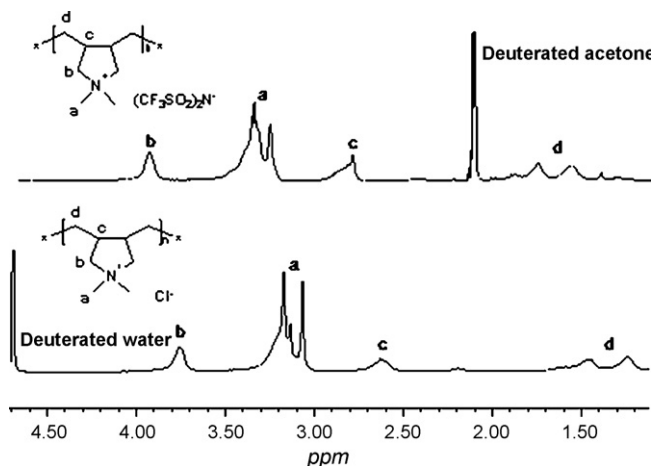


Fig. 1. 250 MHz ^1H NMR spectra of poly(diallyldimethylammonium) chloride and poly(diallyldimethylammonium)TFSI.

quantitatively in the aqueous media. The obtained polymers were washed, filtered and dried until constant weight.

It is well known that the nature of the anion influences the final properties of the ionic liquid such as solubility, viscosity, and thermal stability. Furthermore, it was demonstrated that the properties of the polymeric anionic liquids also depend on the nature of the counter-anion. For example, anion exchange into imidazolium polymeric ionic liquids leads to hydrophobic polymers, insoluble in water but soluble in organic solvents such as acetone, tetrahydrofuran, and dichloromethane [17]. The same behavior was observed in the new family of pyrrolidinium-based polymeric ionic liquids reported here. As an example, one of the obtained polymers, poly(diallyldimethylammonium)TFSI was not soluble in very polar solvents such as water and methanol or apolar solvents like toluene but becomes soluble in medium polar solvents such as acetone and dimethyl formamide.

The synthesized polymers were characterized by nuclear magnetic resonance (NMR) and FT-infrared spectroscopy. Fig. 1 presents the ^1H NMR spectra of poly(diallyldimethylammonium) chloride and poly(diallyldimethylammonium)TFSI in deuterated water and acetone, respectively. The spectrum of commercially available poly(diallyldimethylammonium) chloride is similar to the reported in the literature [19]. We observed the same peaks in the spectra of poly(diallyldimethylammonium)TFSI, with a shifting of 0.21–0.25 ppm for all peaks probably due to the different influence of the new anion. The presence of the peaks in the spectrum confirmed that the structure of the polymer backbone was maintained after the anion exchange reaction. Fig. 2 shows the FT-IR spectra of the initial polymer and the obtained polymers having TFSI, PF_6 , BF_4 and DBSA counter-anions. The bands corresponding to the poly(diallyldimethylammonium) cation, were found between 2900 and 3100 cm^{-1} , at 1640 and at 1476 cm^{-1} in all spectra. The band corresponding to the initial polymer having a chloride anion was observed at 3391 cm^{-1} and disappeared after anion exchange reaction. Correspondingly, new bands appeared attributed to the new different anions such as TFSI anion (1354, 1194, 1136 and 1053 cm^{-1}), hexafluorophosphate anion (835.5 cm^{-1}), tetrafluoroborate anion (1085 cm^{-1}) and dodecylbenzene sulfonate anion (3450, 2949, 2923, 2846, 1399, 1367, 1094, 1027 and 1008 cm^{-1}). The FT-IR spectra constitute an indication of the anion exchange but it is not a quantitative technique. In order to evaluate if the reaction was quantitative a simple precipitation titration test with AgNO_3 was carried out. The titration test consisted of the addition of AgNO_3 to a solution of the new polymer in acetone. The test confirmed that no Cl^- anions remained in the polymeric ionic

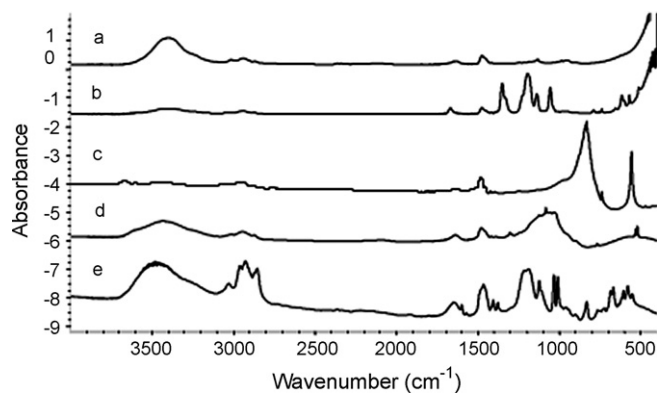


Fig. 2. FT-infrared spectra of poly(diallyldimethylammonium) X^- (where X is (a) Cl^- , (b) TFSI $^-$, (c) PF_6^- , (d) BF_4^- and (e) DBSA $^-$).

liquid because no precipitation of AgCl occurred. This result in combination with FT-IR and NMR observations proved that the anion exchange reaction was quantitative.

The synthesized polymers were then characterized by thermogravimetric analysis (TGA). The results are shown in Fig. 3. It appears clearly that obtained polymers presented different thermal behaviors proving that thermal stability strongly depends on the anion. The initial polymer, poly(diallyldimethylammonium) chloride, is highly hygroscopic, decomposes in two steps and presented the lower thermal stability. Poly(diallyldimethylammonium) BF_4 , and poly(diallyldimethylammonium) PF_6 , decomposed also in two steps but the other ones decomposed in one step. The best thermal stability is obtained with the poly(diallyldimethylammonium)TFSI which decomposed between 400 and 500 $^\circ\text{C}$.

3.2. Design and electrochemical characterization of polymer electrolytes based on poly(diallyldimethylammonium)TFSI

The obtained poly(diallyldimethylammonium)TFSI presents a chemical structure similar to the one of pyrrolidinium ionic liquid N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide $\text{PYR}_{14}\text{TFSI}$, which is one of the most promising ionic liquids to be used in lithium batteries. This analogous chemical structure and the good thermal properties make this polymer an ideal matrix for designing polymer electrolytes based on blends between the polymer, the ionic liquid and a lithium salt.

In this work, polymer electrolytes with different ratios of PIL:IL:Li salt were prepared by casting from acetone, which is a good solvent for the three components. After casting, transparent and free standing films were obtained with the exception of

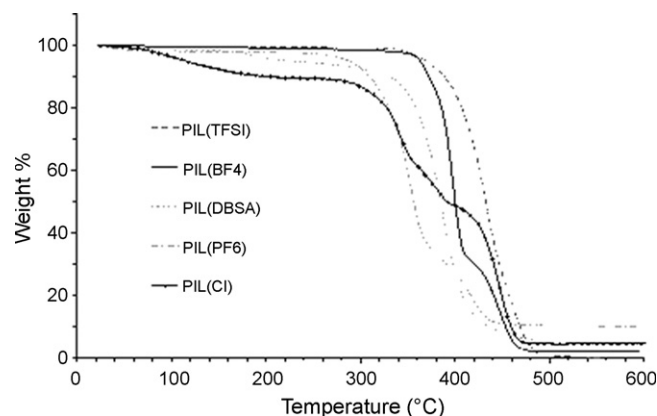


Fig. 3. TGA profiles of the initial polymer, poly(diallyldimethylammonium) chloride, and of the different PILs synthesized by anion exchange reaction.

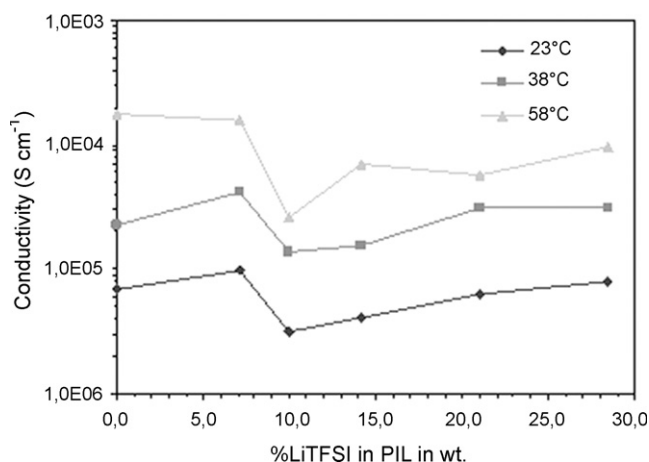


Fig. 4. Ionic conductivity of membranes of poly(diallyldimethylammonium)TFSI containing different amounts of LiTFSI at different temperatures: 23, 38 and 58 °C.

IL compositions higher than 50% where sticky gels were obtained. In a first stage we studied binary mixtures composed of polymeric ionic liquid and lithium salt (binary mixture 1) and composed of polymeric ionic liquid and ionic liquid (binary mixture 2). Next, we optimized ternary compositions (polymeric ionic liquid, ionic liquid and lithium salt) in order to obtain polymer electrolyte films with good mechanical properties and high ionic conductivity to be used in lithium batteries. Ionic conductivity measurements were performed by the classic ac impedance method for all polymeric electrolytes.

Fig. 4 shows the conductivity measurements for binary mixture 1 (polymeric ionic liquid plus lithium salt) at three different temperatures. At 23 °C, whatever was the quantity of salt in the poly(diallyldimethylammonium)TFSI matrix, the ionic conductivity of the electrolyte was between 3.15×10^{-6} and $9.8 \times 10^{-6} \text{ S cm}^{-1}$. No clear trend in the ionic conductivity with the percentage of LiTFSI salt in the polymer matrix was observed. However, a slight increase of the ionic conductivity was observed for a content of 7.1% of LiTFSI, followed by a decrease at 10% of salt in the polymer matrix. After this point, the conductivity increases slowly. At 58 °C, the ionic conductivity varies from 3×10^{-5} to $1.8 \times 10^{-4} \text{ S cm}^{-1}$ depending on the salt concentration in the polymer. These values are similar to the ones reported by Ohno and co-workers [13] for polymerized ionic liquid having an organoboron unit (between 1.93×10^{-5} and $3.74 \times 10^{-5} \text{ S cm}^{-1}$ at 50 °C). For this type of binary mixtures made of polymer and salt, the mechanical stability of the films was not completely satisfactory. The membranes were usually rigid and fragile at high salt content.

Fig. 5 shows the variation of ionic conductivity for binary mixtures composed of poly(diallyldimethylammonium)TFSI and ionic liquid (PYR₁₄TFSI) (binary mixture 2). As shown before with other polymer matrices, the ionic conductivity of the polymer electrolyte increased with the percentage of ionic liquid in the mixture. For instance, the addition of 50% of PYR₁₄TFSI raised the conductivity by almost two orders of magnitude reaching about $1.5 \times 10^{-3} \text{ S cm}^{-1}$ at 57 °C. All membranes showed good compatibility and no phase separation or ionic liquid segregation was observed. The flexibility of the membranes increases with the enhancement of ionic liquid content and completely transparent and free standing films were obtained. However, membranes containing more than 50% of PYR₁₄TFSI were very sticky and quite difficult to handle. The temperature is directly related to the viscosity of the material and to the mobility of ions in the electrolyte. As expected, an increase in the conductivity of the electrolytes was observed when the temperature increased.

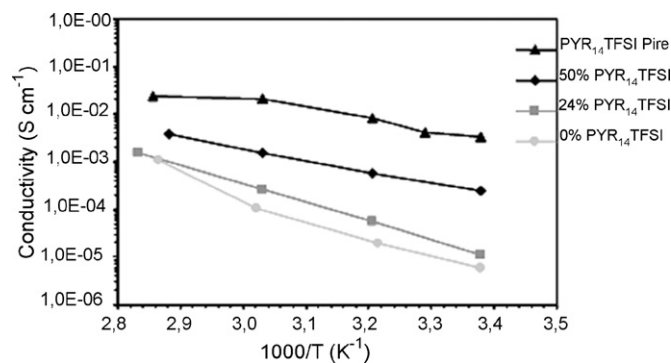


Fig. 5. Ionic conductivity versus temperature of membranes of poly(diallyldimethylammonium)TFSI containing different amounts of PYR₁₄TFSI ionic liquid.

Finally, we studied ternary mixtures composed of the polymer, ionic liquid and lithium salt. First, we fixed a percentage of 50% of ionic liquid into the polymer due to the good compromise between mechanical stability and ionic conductivity observed before for this composition. Then, we varied the percentage of LiTFSI salt in the mixture. The results are presented in Fig. 6a. Comparing with the values collected in Fig. 4 the ionic conductivity is enhanced by almost two orders of magnitude by the presence of ionic liquid. These results are similar to the previously observed case of the binary polymer/ionic liquid blends. In this case, we observed a clear diminution of the ionic conductivity when the membrane reaches a content of 28% of LiTFSI salt. At 23 °C, the optimized ionic conductivity for a polymer electrolyte containing 10% of LiTFSI

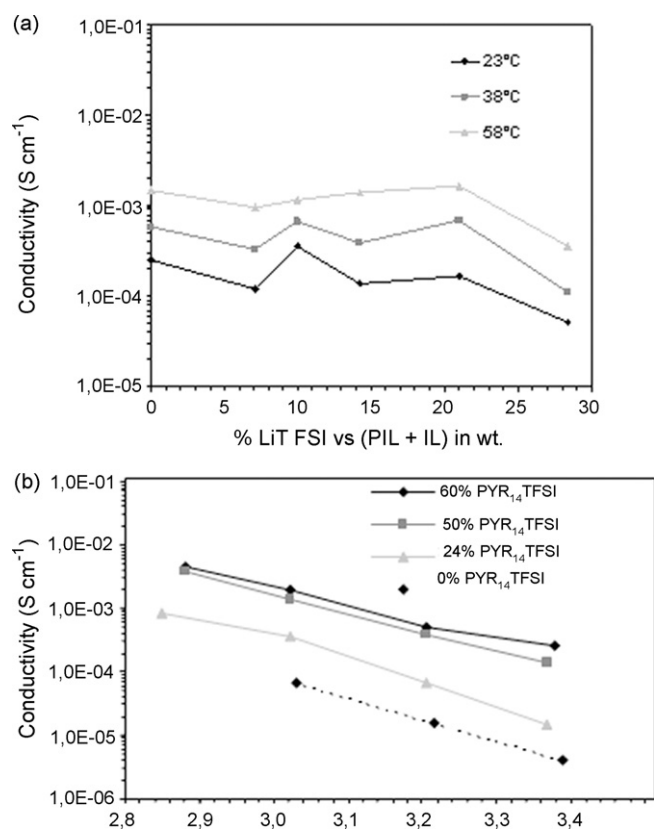


Fig. 6. (a) Ionic conductivity as a function of LiTFSI content for ternary polymer membranes containing a fixed 50% of PYR₁₄TFSI at different temperatures: 23, 38 and 58 °C. (b) Ionic conductivity versus temperature of membranes of poly(diallyldimethylammonium)TFSI containing 14.2% of LiTFSI and different amounts of PYR₁₄TFSI.

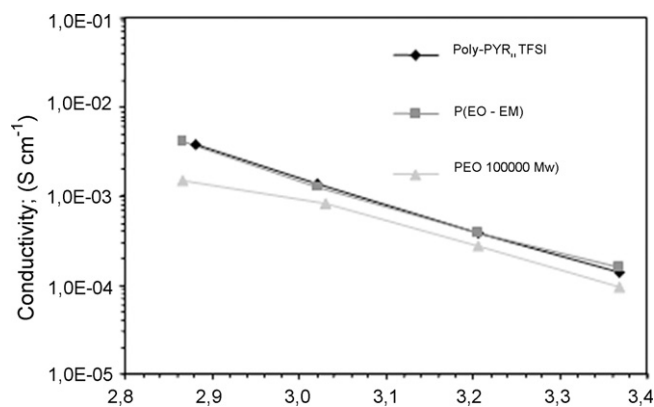


Fig. 7. Ionic conductivity versus temperature of ternary membranes containing 50% of PYR₁₄TFSI and 14.2% of LiTFSI with different polymer matrices: poly(diallyldimethylammonium)TFSI, P(EO-EM) and PEO.

is about $3.6 \times 10^{-4} \text{ S cm}^{-1}$. On the other hand, Fig. 6b shows the ionic conductivity for ternary mixture fixing a 14.2% of LiTFSI salt in the polymer and changing the percentage of ionic liquid. As observed before, the addition of 50% of ionic liquid to the membrane enhanced the ionic conductivity by two orders of magnitude. At 24 °C, conductivity of $1.4 \times 10^{-4} \text{ S cm}^{-1}$ was reported for self-standing and flexible polymer electrolytes. The addition of 60% of ionic liquid to the polymer electrolyte does not contribute significantly to the enhancement of the conductivity but again results in sticky films, difficult to handle.

In order to compare with matrices commonly used in polymer electrolytes, we prepared and characterized membranes with similar amount of ionic liquid and lithium salt but based on commercial poly(ethylene oxide) and poly(ethylene oxide/diethylene glycol glycidyl methyl ether) (P(EO-EM)) matrices. As shown in Fig. 7, we obtained very similar results between mixtures made with P(EO-EM) (amorphous PEO) and poly(diallyldimethylammonium)TFSI. Concerning the polymer electrolytes based on commercial PEO (semicrystalline), the ionic conductivity is a little bit lower than the other two membranes. Interestingly, the polymer electrolyte membranes based on poly(diallyldimethylammonium)TFSI presented an improved mechanical stability compared with the very sticky membrane electrolytes formed with PEO and P(EO-EM) and free standing films were handled without any difficulty (see Fig. 8).

Besides ionic conductivity, the electrochemical stability of these polymer electrolytes is another important property that must be taken into account in order to consider these electrolytes as candidates for lithium batteries. Linear sweep voltammetry curves of different polymer electrolytes were measured to evaluate their electrochemical stability at room temperature. Separate experi-

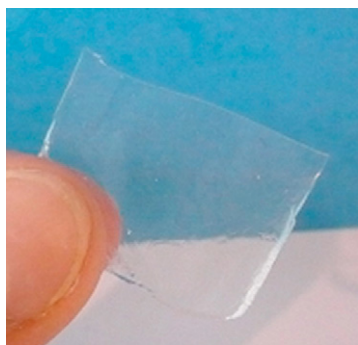


Fig. 8. Polymer electrolyte containing poly(diallyldimethylammonium)TFSI as polymer matrix, 50% of PYR₁₄TFSI and 14.2% of LiTFSI. Free standing and transparent film.

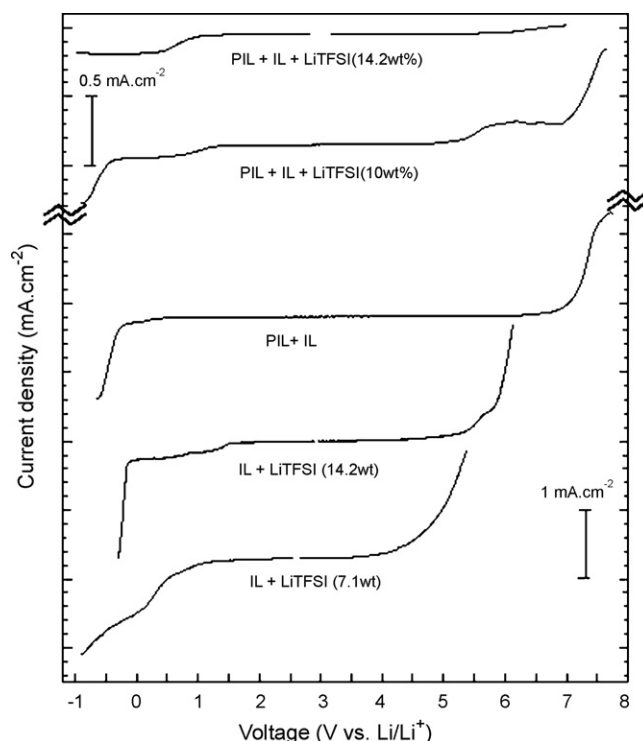


Fig. 9. Linear sweep voltammograms of PYR₁₄TFSI + 14.2% of LiTFSI, poly(diallyldimethylammonium)TFSI + PYR₁₄TFSI (50%) and two ternary mixtures poly(diallyldimethylammonium)TFSI + PYR₁₄TFSI (50%) + X% LiTFSI (X = 10 and 14.2) at 21 °C. Scan rate 10 mV s⁻¹.

ments were conducted for the cathodic and anodic electrochemical stability measurements by scanning from open-circuit potential to negative (cathodic) or positive (anodic) voltages, with clean electrodes and a fresh sample in each case. Fig. 9 shows the electrochemical stability window of the following membranes: a binary mixture of poly(diallyldimethylammonium)TFSI and PYR₁₄TFSI (50 wt.%) and two ternary mixtures. Both ternary mixtures contain 50% of PYR₁₄TFSI, with one of them containing 10% of lithium salt and the other 14.2% of LiTFSI. Ionic liquid, PYR₁₄TFSI, with LiTFSI lithium salt (7.1 and 14.2 wt.%) was also measured for comparative purposes.

The ESW of the materials is determined by the rapid increase of current that, using IL + salt as reference, probably corresponds to the oxidation of TFSI⁻ anion in the anodic sweep and reduction of either PYR₁₄⁺ or Li⁺ cation in the cathodic scan [10]. The cathodic stability of the polymeric membranes does not change significantly compared to the IL + salt electrolyte, probably due to the similar chemical nature of poly(diallyldimethylammonium)⁺ and PYR₁₄⁺ cations. It is already known that the cathodic stability of pure PYR₁₄TFSI is improved by LiTFSI addition [20]. These results show an increase of not only cathodic but also anodic stability limits with higher lithium salt content, both for binary and ternary mixtures. Nevertheless, it is noteworthy that the polymeric ionic liquid is further enhancing stability towards reduction by itself as evidenced by comparison between IL + salt and polymeric binary and ternary mixtures. This feature was previously observed to some extent for PEO + IL polymer electrolytes [10]. The cathodic current near 0V versus Li/Li⁺ in the samples containing LiTFSI may be related to the plating of Li metal. Some current flow is also observed at about 1.0V versus Li/Li⁺ for IL + LiTFSI. In the case of 14.2 wt.% sample, the first feature appearing at 1.0–1.5V might be due to water uptake during the preparation in non-dry conditions, aided by the high content of hygroscopic LiTFSI. The absence of this feature in the scans of the polymeric membranes (also prepared in non-dry con-

ditions) might indicate their less sensibility to water, thus easing the processing conditions. However, the phenomenon at 0.5–1.0 V may be related to an initial cathodic reduction of $\text{PYR}_{14}\text{TFSI}$ and it can be found both in IL + LiTFSI mixtures and polymeric membranes, although the reaction is limited in the case of the membranes. The reversible nature of this feature has been observed by cyclic voltammetry experiments on a PIL + IL + LiTFSI (14.2 wt.%) film in the range –0.5 to 3 V. All in all, the high conductivity ternary mixtures, and especially the composition with 14.2 wt.% salt, showed a wide ESW (near to 7.0 V), stable both towards lithium and at high voltage, which makes them good candidate electrolytes for lithium batteries.

4. Conclusion

A new family of polymeric ionic liquids having pyrrolidinium cation pendant units was synthesized and characterized. These polymeric ionic liquids showed excellent performance as polymer matrices for polymer electrolytes compositions together with pyrrolidinium ionic liquids and lithium salts. Free standing mechanically stable transparent polymer films showing an ionic conductivity higher than a $10^{-4} \text{ S cm}^{-1}$ at room temperature could be obtained. Furthermore, the polymer electrolytes showed an electrochemical window ever wider (near to 7.0 V) than the one of pyrrolidinium ionic liquids which makes them interesting candidates for all solid-state lithium batteries. Current experiments are being carried out in this direction together with an investigation of the lithium transport properties of these polymer electrolytes.

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