



New, ionic liquid-based membranes for lithium battery application

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ABSTRACT

New types of dimensionally stable, flexible gel-type electrolyte membranes with a relatively wide electrochemical stability, high lithium ion conductivity and other desirable properties have been prepared by immobilizing *N-n*-butyl-*N*-ethylpyrrolidinium *N,N*-bis(trifluoromethane)sulfonimide-lithium *N,N*-bis(trifluoromethane)sulfonimide (Py₂₄TFSI-LiTFSI), ionic liquid, IL, solutions in a poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVdF-HFP) matrix. The addition of a discrete amount of ethylene and propylene carbonate (EC-PC), solvent mixture to the membranes resulted in an improvement of the ionic conductivity and in a stabilization of the interface with the lithium electrode. These IL-based gel type membranes can operate without degradation up to a temperature of 110 °C where they reach conductivity values of the order of 10⁻² S cm⁻¹. All these properties make these polymer electrolyte membranes of interest for applications as separators in advanced lithium batteries.

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1. Introduction

Thanks to their unique properties, which include low vapor pressure, non-flammability, high ion conductivity as well as high thermal and electrochemical stability, room temperature ionic liquids (ILs) are considered as very promising electrolyte media for a variety of electrochemical devices [1–3]. For instance, great attention is currently directed to various derivatives of ILs formed by bulky organic cations and highly delocalized-charge inorganic anions as new electrolytes for lithium batteries, since these materials offer promises of reducing the safety hazards which still limit the range of application of these batteries [4–5]. Among the various ILs investigated, those based on the imidazolium (Im) or pyrrolidinium (Py) cations and the *N,N*-bis(trifluoromethane)sulfonimide (TFSI) anion are considered to be the most promising for lithium battery application [3–8].

Indeed, the 1-alkyl-3-alkyl-imidazolium-based ILs, in addition to a high ionic conductivity, have other favorable properties, which in principle make them very appealing electrolyte materials [6]. However, the use of these ILs is still prevented by a major drawback, namely a poor cathodic electrochemical stability, caused by attacks to hydrogen at C(2) carbon site. This issue can in part be controlled by alkyl substitutions at the C(2) carbon site; however, this results in a serious decay in the ionic conductivity which rules the ILs out from battery interest [6]. Thus, the challenge is to widen the cathodic limit such as to allow stability towards the lithium metal electrode

without sacrificing the ionic conductivity. Success has been recently obtained by using IL systems based on Py cations, e.g. 1-alkyl-1-methylpyrrolidinium cations [4,8–9].

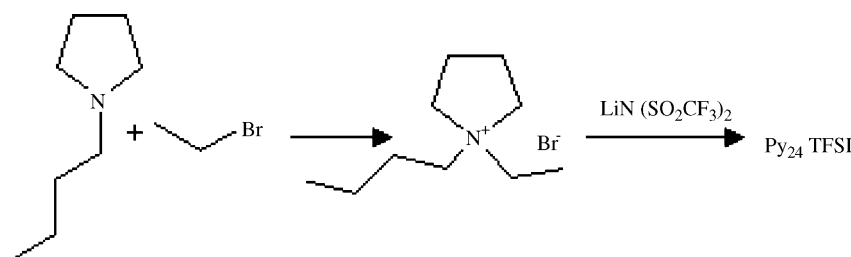
Indeed, recent electrochemical studies have demonstrated that solutions of lithium *N,N*-bis(trifluoromethane)sulfonimide in a *N-n*-butyl-*N*-ethylpyrrolidinium *N,N*-bis(trifluoromethane)sulfonimide (Py₂₄TFSI-LiTFSI) have a good compatibility with the lithium metal electrode still maintaining a high thermal stability and an acceptable ionic conductivity [5].

In view of the progress of the lithium battery technology, it is highly desirable to pass from a liquid to a polymer structure, since this design offers expectation of improvements in safety and reliability [10–11]. Consequently, it is of interest to extend this strategy also to the IL electrolyte cases by developing IL-containing membranes. This concept was originally exploited by Fuller et al. [12–13], who developed IL-polymer gel electrolytes (IPGEs) based on hydrophobic and hydrophilic imidazolium salts and poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVdF-HFP). Following this route, many works have been devoted to the development of imidazolium ILs-based, gel-type PVdF-HFP membranes [14–15]; however, these have only marginally included membranes based on Py. This is surprising considering that these cations have very favorable electrochemical properties.

In this work we attempt to fill the gap, by reporting the preparation and the characterization of gel-type membranes formed by the immobilization of a LiTFSI-Py₂₄TFSI solutions in a PVdF-HFP matrix. Furthermore, also discrete amounts of ethylene carbonate-propylene carbonate (EC-PC) mixtures have been used as membrane additives. Following the original work of Ye et al. [16] we expect that, owing to their high dielectric constant and

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Scheme 1. Schematic illustration of synthesis reaction of Py₂₄TFSI.

relatively low viscosity, these organic carbonates can have a favorable effect on the overall properties of the membrane, especially in terms of ionic conductivity and of electrode compatibility. We will first report the properties of the neat LiTFSI-Py₂₄TFSI solution to then pass to describe those of the corresponding IPGEs.

2. Experimental

Scheme 1 illustrates the synthesis process adopted for the preparation of the Py₂₄TFSI ionic liquid. Details of this synthesis were reported in a previous work [5]. To assure lithium conduction, LiTFSI was added to Py₂₄TFSI, choosing 0.2 mol kg⁻¹ as the preferred concentration [5].

The IPGE membranes were prepared by solution casting. First, PVdF-HFP was dissolved in acetonitrile at a PVdF-HFP/acetonitrile weight ratio of 1/4. Thereafter, 0.2 m LiTFSI-Py₂₄TFSI, or, alternative, the mixture between the IL-salt solution and EC-PC, was added to the PVdF-HFP acetonitrile solution. The solution/PVdF-HFP weight ratio was set at 7/3. The mixture was vigorously stirred overnight at room temperature until homogeneity was reached. The resulting solution was then cast by heating at 75 °C and rapidly cooling down to room temperature by using an aluminum weight boat container. The heating-quenching process was repeated until free-standing membranes were obtained; the membranes were finally moved to an oven and dried at 70 °C overnight. All the procedures and material handlings were carried out in an argon-filled dry box.

Various membrane samples were prepared, including IL-free types with and without EC-PC. **Table 1** summarizes the compositions of all the membranes studied in this work. The average thickness of the electrolyte membranes is 500 μm.

The water content in the IL was carefully determined by using the standard Karl Fischer method (831 KF Coulometer, Metrohm).

The thermal properties of the IL solutions and the related membranes were determined by using thermal gravimetric analysis (TGA/SDTA 851 Mettler-Toledo) and differential scanning calorimetry (DSC 821 Mettler-Toledo). The TGA measurements were carried out at a scanning temperature rate of 5 °C min⁻¹. The DSC was run from 25 °C down to -120 °C with a cooling rate -10 °C min⁻¹ and subsequently up to 200 °C with a heating rate of 5 °C min⁻¹, followed by a cooling step down to 25 °C with -10 °C min⁻¹ rate.

The ionic conductivity of Py₂₄TFSI and of its LiTFSI solution was measured by impedance spectroscopy, performed with FRA 1255 Solartron on a two Pt-electrode cell. The conductivity of the membranes was determined by using cells formed by sandwiching the given membrane sample between two stainless steel blocking electrodes housed in Teflon containers.

Table 1
Composition of the membranes investigated in this work.

Sample	T _g (°C)	T _c (°C)	Mp (°C)	σ (10 ⁻³ S cm ⁻¹)
Py ₂₄ TFSI	-92.3	-38.5	-7.9	1.8
0.2 m LiTFSI-Py ₂₄ TFSI	-85.5			1.3

The electrochemical stability window of the Py₂₄TFSI IL, of the LiTFSI-Py₂₄TFSI solution and of the membranes was determined by linear sweep voltammetry and by cyclic voltammetry (PAR 362 potentiostat) using three-electrode cells for the solution and two-electrode cells for the membrane samples. The cells comprised a super P carbon-coated Al or Cu plate as the working electrode and lithium foil as the counter and the reference electrode.

The properties of the lithium metal electrode interface were evaluated by impedance spectroscopy analysis carried out by applying a 10 mV amplitude signal in the 100 kHz to 1 Hz frequency range on symmetrical lithium cells using a frequency response analyzer (FRA) Schlumberger Solartron model 1260. The sample surface area in contact with the electrodes is 1.13 cm².

3. Result and discussion

3.1. IL and its LiTFSI salt solution

By using the synthesis and purification procedures realized in this work, we obtained the Py₂₄TFSI ionic liquid with a very low water content, i.e. less than 20 ppm. This low water level is comparable to that accepted for Li battery grade electrolyte solutions [17]. We can then assume that our IL is suitable for lithium battery applications. The required lithium ion transport was assured by adding LiTFSI to Py₂₄TFSI to form a 0.2 mol kg⁻¹ solution, i.e. the concentration expected to give the most desirable transport properties [5]. **Table 2** summarizes the thermal and the conductivity values of the neat IL and of its LiTFSI solution. These values are in agreement with those previously reported for the same materials [5].

The electrochemical stability window, ESW, of the IL and the related decomposition phenomena are still matter of interpretation and occasionally, of controversial literature results [5]. Thus, we have devoted particular attention to this aspect. **Fig. 1** shows the anodic scans of the voltammetry of the neat Py₂₄TFSI and of its LiTFSI solution. We can observe that the value of the onset voltage, which is associated with the anodic decomposition limit of the ESW, increases passing from the neat IL to the solution. The higher stability of the latter may be accounted for by considering the strong coordination existing between the Li cations and the TFSI anions [18], which results in an enhancement of the over potential required for the oxidation of the TFSI anions.

More intriguing is the voltammetry response in the cathodic region. **Fig. 2**, which shows the cycled scans of the Py₂₄TFSI - LiTFSI solution, reveals the occurrence of various electrochemical events.

Table 2
Properties of Py₂₄TFSI and of its salt solution.

Sample	Composition (wt% = weight percent)
M-1	100 wt% PVdF-HFP
IL-M-2	30 wt% PVdF-HFP + 70 wt% IL-salt solution
IL-M-3	30 wt% PVdF-HFP + 56 wt% IL-salt solution + 14 wt% EC-PC mixture
M-4	30 wt% PVdF-HFP + 70 wt% EC-PC mixture

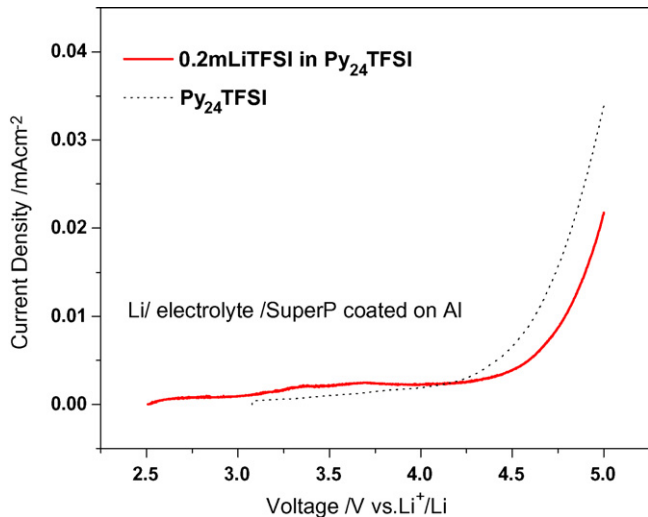


Fig. 1. Anodic sweep voltammograms of the neat $\text{Py}_{24}\text{TFSI}$ and of the 0.2 m $\text{LiTFSI-Py}_{24}\text{TFSI}$ solution. Room temperature. Super P carbon-coated Al plate working electrode. Lithium foil as the counter and the reference electrode.

Based on consisting literature results [19], we may reasonably associate the cathodic current onset around 1.5 V vs. Li/Li^+ with the reduction of TFSI. The following broad peak, ranging from 0.5 V to -0.05 V vs. Li/Li^+ , might be ascribed to a not yet clear decomposition process of the solution with the consequent formation of a solid electrolyte interface (SEI) film passivating the electrode surface. Indeed, the extension of this peak significantly decreases in the following scans, this confirming the occurrence of the film and its efficiency in kinetically prevent further decomposition of the solution. Finally, it cannot be excluded that the reproducible peak set around -0.05 V vs. Li/Li^+ is due to lithium deposition at the working Super P electrode (see Section 2 for details on the testing cell). This interpretation is apparently unsupported by the absence of a corresponding stripping peak in the following oxidation scan. On the other hand, this apparent contradiction can be accounted for considering that the structural and physico-chemical properties of Super P carbon are not favourable for assuring reversibility of the lithium deposition process.

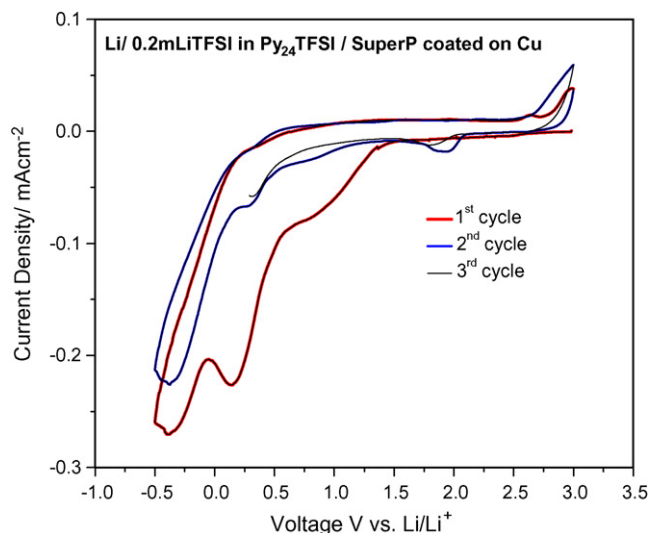


Fig. 2. Cathodic voltammogram of 0.2 m $\text{LiTFSI-Py}_{24}\text{TFSI}$ solution. Room temperature. Super P carbon-coated Cu plate working electrode. Lithium foil as the counter and the reference electrode.

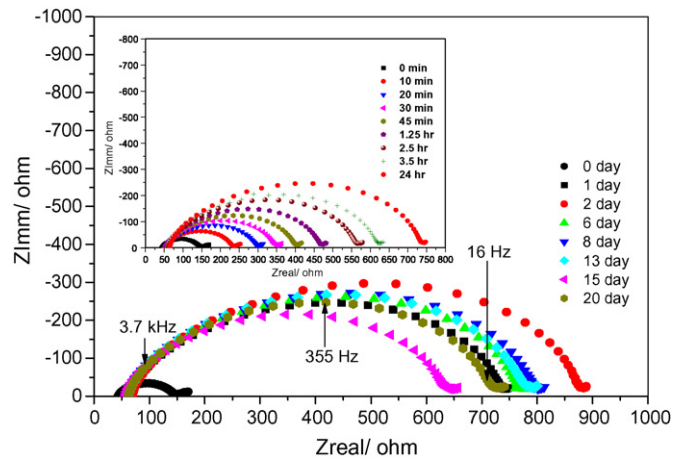


Fig. 3. Time evolution of impedance spectra of a $\text{Li}/0.2 \text{ m LiTFSI-Py}_{24}\text{TFSI}/\text{Li}$ symmetrical cell for 20 days and 24 h (inset). Room temperature. 1 Hz to 100 kHz frequency range.

On the basis of the results above described, we may assume that the $\text{LiTFSI-Py}_{24}\text{TFSI}$ solution here examined has a ESW extending from 1.5 V to around 4.5 V vs. Li/Li^+ . If this range certainly opens the use of high voltage cathodes, it does not necessarily exclude anodes operating below 1.5 V vs. Li/Li^+ since the occurrence of the SEI may kinetically extend the cathodic limit to allow electrode operation in voltage ranges well outside the thermodynamic window. It is in fact a situation of this kind that makes possible to use graphite anodes in classical lithium ion batteries [11].

It has then appeared to us of interest to investigate the characteristic of the SEI film with the aim of establishing its influence on the operation of a lithium metal electrode in the $\text{LiTFSI-Py}_{24}\text{TFSI}$ solution considered in this work. The investigation was carried out by determining the time evolution of the impedance response of a symmetrical $\text{Li}/\text{LiTFSI-Py}_{24}\text{TFSI}/\text{Li}$ cell kept under open circuit condition. Fig. 3 shows the results. The impedance evolves with the expected semicircle trend. The intercept of the high frequency semicircle with the real axis gives the value of the bulk electrolyte resistance, while the amplitude provides the resistance of the interface with the lithium electrode [20].

Fig. 4 shows how the two resistances change with time. A drastic increase is observed during the first day of storage of the cell; this being indicative of a very rapid, initial reaction between the IL-salt solution and the lithium metal electrode, quite likely associated with the formation of the SEI passivating film [21].

After one day storage, both the bulk and the interfacial resistances remain more or less stable oscillating around 10 and 300 Ω , respectively, this suggesting the completion of the SEI film in equilibrium with the IL-salt solution. The film however, being formed of species similar to those of the electrolyte components [19], may occasionally experience partial deformation and rebuild, this finally accounting for the observed oscillations in the course of the storage test.

3.2. $\text{LiTFSI-Py}_{24}\text{TFSI}/\text{PVdF-HFP}$ membranes

The availability of dimensionally stable and flexible electrolyte membranes is very desirable for the progress of lithium batteries. In this respect, particular interest is presently devoted to IPGE membranes as advanced electrolyte separators. Accordingly, in this work we have immobilized our $\text{LiTFSI-Py}_{24}\text{TFSI}$ lithium-conducting solution in a PVdF-HFP matrix to form a new type of IL-based membrane. The composition of this membrane, indicated with the acronym IL-M-2, is reported in Table 2. The investigation was

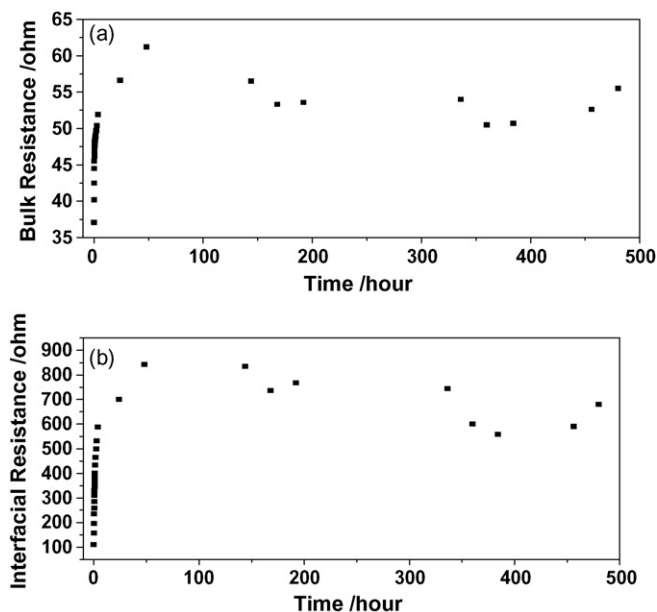


Fig. 4. Time dependence of (a) electrolyte and (b) interfacial resistance of the Li/0.2 m LiTFSI-Py₂₄TFSI/Li cell. Room temperature. Data derived from impedance spectroscopy.

extended to a membrane containing a discrete amount of an EC-PC mixture, indicated in Table 2 as IL-M-3. Finally, for sake of comparison, we have prepared a plain PVdF-HFP membrane (M-1 in Table 2), as well as a membrane containing EC-PC only (M-4 in Table 2). All these membranes, except the M-1 sample, showed comparable morphologies and similar mechanical properties with no evidence of liquid leakage during 4 months of storage time.

The thermal properties of the membranes were determined by TGA and DSC analyses. Fig. 5 shows the TGA response. The IL-containing membrane (IL-M-2) is stable up to 325 °C (see curve 3 in the figure) exhibiting a 70% weight loss over a 325–433 °C temperature range, this mainly reflecting the thermal behavior of the single IL based solution [5]. Then, a 30% weight loss, due to the decomposition of PVdF-HFP matrix (compare curve 4) follows. To be noticed that the percent of this weight loss corresponds to the actual membrane composition, compare Table 2. This result suggests that in the IL-M-2 membrane the IL-salt solution is physically adsorbed in

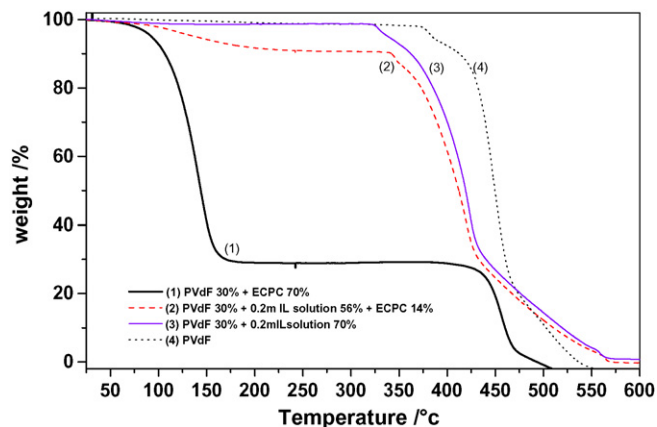


Fig. 5. TGA traces of membranes containing, PVdF-HFP (sample M-1), PVdF-HFP + EC-PC (sample M-4), PVdF-HFP + EC-PC + LiTFSI-IL solution (sample IL-M-3) and PVdF-HFP + LiTFSI-IL solution (sample IL-M-2). Scanning temperature rate: 5 °C min⁻¹. For sample composition see Table 2.

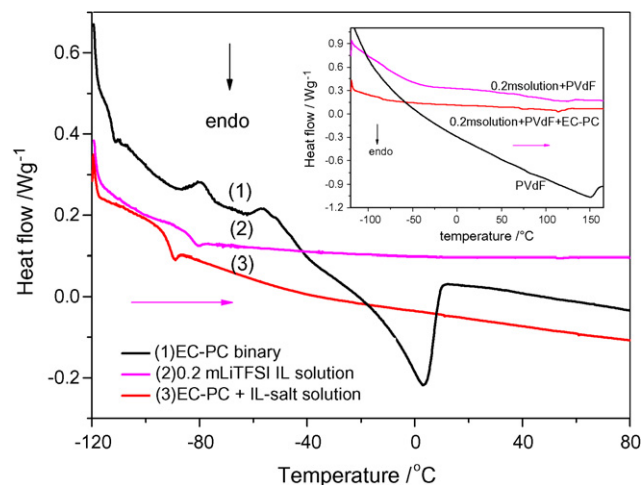


Fig. 6. DSC heating traces of the EC-PC mixture, IL-salt solution and the EC-PC/IL-salt solution mixture and the heating traces of the related membranes (inset). Scanning temperature rate: 5 °C min⁻¹.

the pores of the PVdF-HFP polymer matrix without any significant interaction with the matrix itself.

Curve (2) in Fig. 5 shows the TGA response of the membrane containing EC-PC, i.e. sample IL-M-3, see Table 2. The curve exhibits a 10% weight loss in a temperature range extending from 95 °C to 230 °C. This weight loss may be reasonably attributed to the evaporation of the EC-PC mixture; however, the amount of EC-PC detected by the TGA response is lower than that derivable from the membrane composition, i.e. 10% vs. 14% (see Table 2). In addition, the temperature range of evaporation is higher than that observed for the M-4 membrane containing EC-PC only, i.e. 95–230 °C vs. 70–180 °C, compare curve 1. These evidences strongly suggest the occurrence of interactions between the EC-PC mixture and the IL-salt solution. Interactions of this type can be important in influencing the electrochemical behavior of the membrane (see later).

A preliminary confirmation of the occurrence of interactions between EC-PC and the IL-salt solution can be provided by differential scanning calorimetry. Fig. 6 shows the DSC trace of the solution of LiTFSI-Py₂₄TFSI containing the EC-PC mixture (curve 3). For comparison purpose, the figure also reports the DSC traces of the two components, i.e. the neat LiTFSI-Py₂₄TFSI solution (curve 2) and the neat EC-PC mixture (curve 1). The large transition peak extending from -49 to 10 °C, clearly visible in the trace related to the EC-PC mixture, is absent in that related to the solution containing EC-PC in combination with LiTFSI-Py₂₄TFSI. This is convincing evidence that interactions between the IL solution and the carbonate mixture can indeed occur.

Interestingly, the DSC trace of the pure LiTFSI-Py₂₄TFSI solution is very similar to that of the solution in combination with the EC-PC mixture, compare curves 2 and 3 in Fig. 6. Considering the relatively high amount of IL-salt solution (80 wt%), one might tentatively assume that the PC-EC molecules are surrounded by this solution which then rules the DSC response. Thus, the quoted interactions between the two components could occur at the surrounding sites on the EC-PC molecules. However, this is a mere speculation and certainly more sophisticated studies, e.g. based on spectroscopic techniques, are required to verify this model. These studies are in progress in our laboratory.

The DSC analysis was extended to the IPGE membranes and the result is reported in the inset of Fig. 6. The combined plasticizing effect of the IL solution and of the EC-PC mixture is clearly evidenced by comparing the traces of the neat PVdF-HFP membrane with those of the EC-PC containing membrane: the endothermic

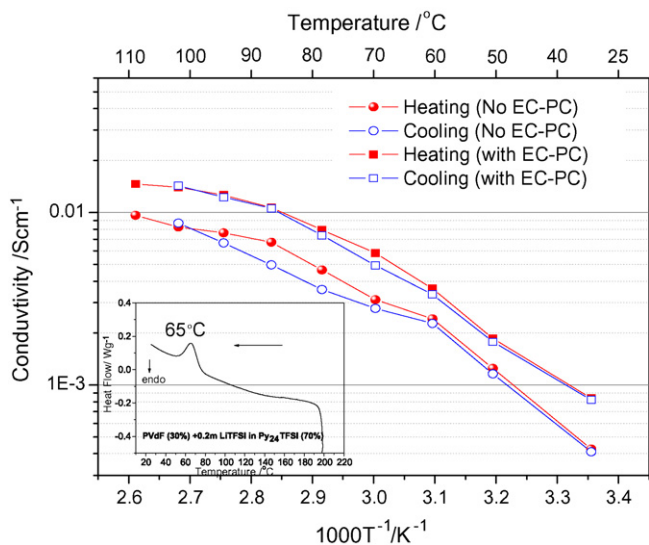


Fig. 7. Arrhenius conductivity plots of membranes containing IL-salt solution and the EC-PC/IL-salt solution mixture. The inset illustrates the DSC traces of the membrane containing IL-salt solution.

peak, corresponding to the melting of the polymer matrix, is shifted to a lower temperature and evolves with a much smaller area.

Fig. 7 compares the conductivity Arrhenius plots of the IL-M-2 membrane (no PC-EC) with that of the IL-M-3 membrane (with EC-PC addition). The room-temperature ionic conductivity value of the latter is $8.1 \times 10^{-4} \text{ S cm}^{-1}$ while that of the former is $3.7 \times 10^{-4} \text{ S cm}^{-1}$. It is important to point out that both the conductivity values are adequate for lithium battery applications. The increase of ionic conductivity for the IL-M-3 membrane is not surprising considering the high dielectric constant and the relatively low viscosity of the EC-PC binary mixture. The high dielectric constant assists in shielding cation-anion interaction [22] which, in this case, is the interaction between the TFSI⁻ and the lithium cations, this in turn enhancing the ionic dissociation of the LiTFSI salt in the IL solution and accordingly, the number of the free ions which contribute to the conduction.

Both Arrhenius plots of Fig. 7 evidence a smooth variation of the conductivity with the absence of abrupt decays in the entire temperature range of investigation, i.e. from 25 to 110 °C, confirming the thermal stability of the membranes. The change in slope, observed at a temperature around $55 \pm 5 \text{ °C}$, quite likely corresponds to the amorphous-to-crystalline phase transition of the polymer membrane, as also suggested by the related DSC curves (see inset of Fig. 7).

Remembering that electrochemical stability is one of the aspects of concern for the electrochemical applications of IL-based systems, it has appeared to us important to evaluate the stability window of the membranes and compare it with that of the neat IL solution. It is also interesting to determine whether the EC-PC component may have a role in influencing the properties of the interface with the lithium electrode.

The anodic scans of the sweep voltammetry test show that the onset of anodic current for both the investigated membranes occurs around 4.2 V (data not shown). This result indicates that the anodic stability of the membranes is comparable with that of the IL solution (compare Fig. 1) and that the addition of EC-PC does not modify this situation. To be noticed that the anodic decomposition voltage for the PVdF-HFP matrix alone has been reported to be around 4.8 V [23]. Although the experimental condition is here slightly different, it is nevertheless reasonable to exclude that the decomposition of PVdF-HFP could occur at a voltage as low as 4.2 V, this finally

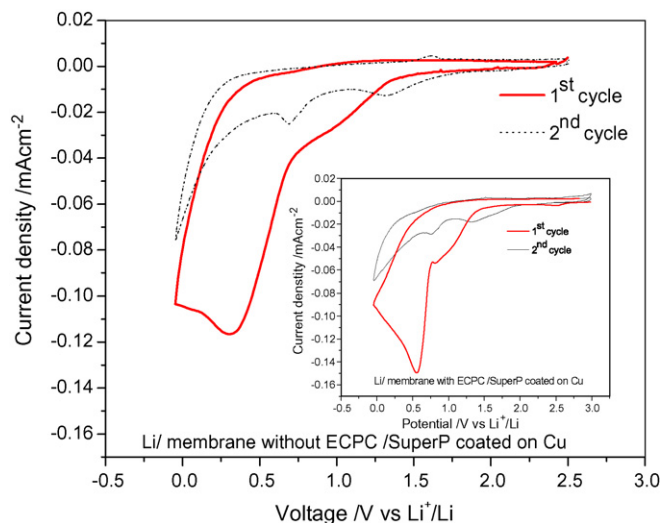


Fig. 8. Cyclic voltammogram of the membrane containing IL-salt solution. The inset illustrates the voltammetry of the membrane containing IL-salt solution with EC-PC addition (sample IL-M-3) For sample composition see Table 2.

demonstrating that the anodic limit of the ESW of the membrane is due to the oxidation of the IL-salt solution.

The cathodic scan of the voltammetry of the membranes reveals a multi-peak response which is similar to that observed with the neat IL solution (compare Fig. 2). Fig. 8 shows the response for the IL-M-2 membrane (IL-salt solution) and for the IL-M-3 membrane (IL-salt solution with EC-PC addition), see inset of Fig. 8. The onset of cathodic current around 1.5 V can be observed in the first cycle of both membranes. This result suggests that the EC-PC additive does not play a role in influencing the cathodic stability of the IL solution. The following broad peak in the reduction scan of both membranes is assumed to be representative of a passivating film formation possibly overlapping with a lithium intercalation process in the Super P working electrode (see discussion in Section 3.1). However, the difference with the behavior of the neat IL solution is in the fact that both the height and the extension of the peak greatly decrease in the following cycles and this is a convincing indication of the efficiency of the passivating film in protecting from further decomposition of the IL-based membranes.

The above results suggest that the membranes may be suitable electrolyte media in combination with a lithium metal electrode in advanced battery configurations. This was effectively confirmed by running impedance analyses of symmetrical lithium cells based on the two membranes, respectively, as electrolytes. Fig. 9 reports the time evolution of the bulk and interfacial resistances of these cells.

The first evidence resulting from these impedance tests is that the bulk resistance of the EC-PC-containing membrane after an initial decay, probably due to dimensional changes following the applied pressure during the cell construction, stabilizes at a value much lower than that of the membrane without EC-PC, see Fig. 9(a). This difference is associated with the high dielectric constant and the relatively low viscosity of EC-PC, two conditions which are expected to induce a beneficial effect on the transport properties.

More relevant are the differences between the interfacial resistances of two membranes. Fig. 9 (b) shows that the resistance of the EC-PC-containing membrane is much lower than that of the membrane without the additive. In addition, both bulk and interfacial resistance of the former appear to be more stable with time than those of the latter. These differences strongly suggest that the passivating films occurring in the two membranes may have a different chemical composition and that the presence of EC-PC

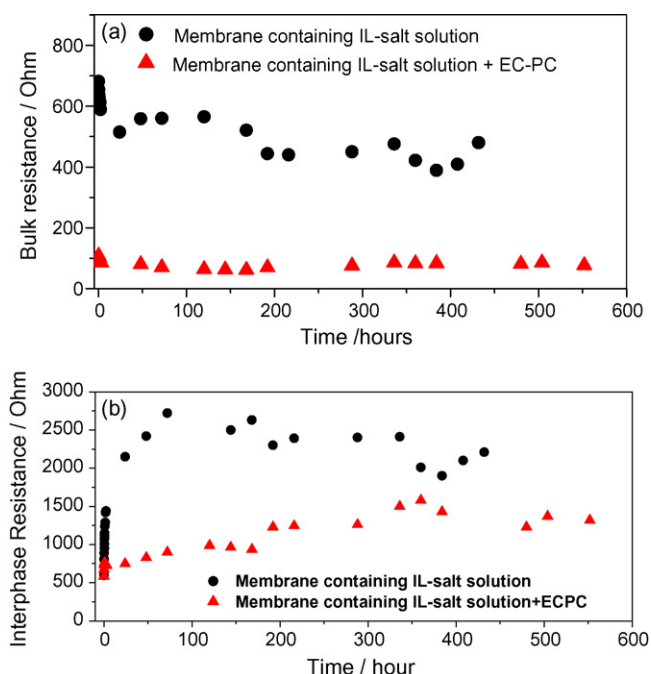


Fig. 9. (a) Time dependence of the bulk resistance of the membrane containing the IL salt solution (sample IL-M-2, circles) and of the membrane containing IL-salt solution with EC-PC addition (sample IL-M-3, triangles). (b) Lithium interfacial resistance of the membrane containing the IL salt solution (sample IL-M-2, circles) and of the membrane containing IL-salt solution with EC-PC addition (sample IL-M-3, triangles). Room temperature. Data obtained from impedance spectroscopy. For sample composition see Table 2.

enforces the protective role of the SEI film on the lithium metal electrode surface. In synthesis, the presence of a discrete content of the organic additive may kinetically lead to an electrode stability, which is not obtainable with the sole IL solution. Thus, the membranes containing the additive appear as the electrolytes of choice for the development of stable, advanced lithium batteries. Spectroscopy studies are in progress in our laboratory to confirm this expectation, as well as the study of the reversibility of the Li deposition/stripping process, and tests in lithium metal batteries using cathode materials compatible with the electrochemical window of the membranes studied in this work, such as LiFePO_4 or LiCoO_2 . The aim of further research is to reach a more comprehensive understanding of the interfacial phenomena and the SEI compositions for these membranes.

4. Conclusion

The results obtained in this work confirm the value of ILs as new electrolyte media for lithium battery applications. We have shown that our selected $\text{Py}_{24}\text{TFSI-LiTFSI}$ solution has a high thermal stability and a promising electrochemical behavior and that these favorable properties are enhanced by trapping this solution in a PVdF-HFP polymer matrix. The resulting membranes are freestanding, transparent, flexible and have a room temperature conductivity ranging from 3.4 to $9.4 \times 10^{-4} \text{ S cm}^{-1}$. In addition they do not show evidence of IL leakage even during 4 months of storage time and

can operate up to 110°C without degradation, reaching conductivity values as high as $10^{-2} \text{ S cm}^{-1}$. Even more importantly, these membranes, due to the formation of a stable, protective SEI film, exhibit sufficient interfacial properties with the lithium metal electrode.

We confirm the beneficial role of the addition of discrete amount of carbonate mixtures, such as the EC-PC mixture, both on the transport and interfacial properties of the membranes. This effect, originally demonstrated in similar IL-based electrolyte membranes by Ye et al. [16], is here further substantiated by thermal and impedance studies of IPGE membranes. The presence of the carbonate solvent mixture enhances the conductivity of the membranes, which reaches values of the order of $8 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature, and improves the stability of the interface with a lithium metal electrode by forming a highly protective SEI film.

Interestingly, TGA and DSC data revealed the occurrence of definite interactions between the IL-salt solution and the EC-PC mixture. These interactions result in an improvement of the thermal stability in the EC-PC containing membrane. Nonetheless, the addition of EC-PC clearly decreases the thermal stability of the membranes when compared with that additive-free ones. However, this drawback is counterbalanced by the improvements in ionic conductivity and, particularly in interfacial stability towards the lithium electrode.

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