



A binary ionic liquid system composed of *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide and lithium bis(trifluoromethanesulfonyl)imide: A new promising electrolyte for lithium batteries

S. Ferrari^a, E. Quartarone^a, P. Mustarelli^{a,*}, A. Magistris^a, S. Protti^b, S. Lazzaroni^b, M. Fagnoni^b, A. Albini^b

^a Department of Physical Chemistry, University of Pavia, and IENI-CNR, Via Taramelli 16, 27100 Pavia, Italy

^b Department of Organic Chemistry, Via Taramelli 12, 27100 Pavia, Italy

ARTICLE INFO

Article history:

Received 9 October 2008
Received in revised form
20 November 2008
Accepted 4 December 2008
Available online 9 December 2008

Keywords:

Lithium batteries
Electrolytes
Ionic liquids
Pyrrolidinium
LiTFSI

ABSTRACT

Room temperature ionic liquids are nowadays the most appealing research target in the field of liquid electrolytes for lithium batteries, due to their high thermal stability, ionic conductivity and wide electrochemical windows. The cation structure of such solvents strictly influences their physical and chemical properties, in particular the viscosity and conductivity.

In this paper we report on the preparation and characterization of a complete series of solutions between lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and the promising *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide (PY_{1,201}) ionic liquid. A wide molality range has been explored in order to identify the optimal compositions in terms of conductivity and electrochemical stability. Our thermal results show that the solutions are amorphous independently on the LiTFSI content. Up to salt concentration of 0.4 mol kg⁻¹ the solutions have a very low viscosity ($\eta \sim 36$ cP), a high ionic conductivity, even at temperatures below 0 °C, and a good electrochemical stability. Cations transport numbers ranging between 0.05 and 0.39 have been determined as a function of LiTFSI content. The combination of these properties makes the PY_{1,201}-based solutions potentially attractive liquid electrolytes for lithium batteries.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

In the last years, ionic liquids (ILs) have been widely investigated for their potential applications in numerous fields such as separation processes, catalysis, material science and electrochemistry. Their intrinsic properties, like negligible volatility even at elevated temperature, nonflammability, high chemical and thermal stability, combined to high ionic conductivity and electrochemical stability, make them very attractive candidates as electrolytes in rechargeable lithium batteries [1,2].

ILs are usually quaternary ammonium salts where the cation is mostly derived from a cyclic amine (pyridine, imidazole, piperidine, and pyrrolidine), and either an inorganic or an organic anion. A great variety of side chains can be connected to central N⁺, thus obtaining a number of cation structural modifications. By combining a wide

spectrum of available cations and anions, ionic liquids with very different physicochemical properties can be obtained.

Among the possible anions, [CF₃(SO₂)₂N]⁻ forms ionic liquids with low viscosity and melting point [3,4]. In particular, many studies on the pyrrolidinium-imide salts have shown high conductivity values, exceeding 1 mS cm⁻¹ at room temperature, and wide electrochemical windows [5,6]. Furthermore, several reports point out the influence of the alkyl-chain length on ILs properties [7,8]. For instance, the viscosity of the ionic liquid increases with the carbon atom number of the alkyl group with a consequent drop in conductivity [9].

However, scarce information is available on ether-functionalized ILs as potential solvents for liquid or polymer electrolytes in lithium batteries [10]. Alkylether functionalized imidazolium and pyrrolidinium salts with trifluoroborate and/or hexafluorophosphate anions have been reported. In both cases, it has been shown that the presence of extra-complexing units may improve the viscosity and ionic conductivity of the system, making them particularly appealing for electrochemical applications [11–13]. To date, pyrrolidinium imide salts with alkylether chains have been only marginally described in

* Corresponding author.

E-mail address: piercarlo.mustarelli@unipv.it (P. Mustarelli).

the literature [14], and no detailed data have been given on their solutions with LiTFSI.

In this work we report on the synthesis and characterization of *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide, and on the preparation and characterization of solutions with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). A wide range of solutions with molality ranging between 0 and 5.5 mol kg⁻¹ has been explored. Each solution has been carefully characterized as far as concerns density, viscosity, ionic transport. The electrochemical measurements have been performed on selected compositions.

2. Experimental

2.1. Synthesis of *N*-methoxyethyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PY_{1,201})

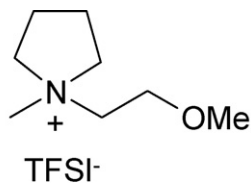
The ionic liquid PY_{1,201} (see Scheme 1) was synthesized by using a modification of the procedure introduced by Passerini et al. [15] for the synthesis of analogous derivatives. *N*-Methylpyrrolidine (60 g, 0.7 mol) and 1-iodo-2-methoxyethane 115 g (0.62 mol) in ethyl acetate (215 mL) were stirred overnight under a nitrogen flux. The solvent and excess pyrrolidine were then removed in vacuo to afford *N*-methoxyethyl-*N*-methylpyrrolidinium iodide (98 g, 58% yield) as a pale yellow solid. The iodide was suspended in ethyl acetate (20 mL) in a flask covered with an aluminum foil under nitrogen flux, and a deaerated (by nitrogen bubbling) water solution (100 mL) of lithium bis(trifluoromethanesulfonyl)imide (103.5 g, 0.36 mol) was then added.

The resulting suspension was vigorously stirred overnight. The organic phase was separated while the aqueous phase was extracted three times (20 mL each) with ethyl acetate. The resulting organic phases were collected and evaporated in vacuo. Crude PY_{1,201} was purified three times over an active coal (Darco® G-60, 100 mesh powder) column (ethyl acetate as the eluant), then dried by stirring in vacuo at 80 °C for 24 h, to afford 106 g of the title compound (PY_{1,201}, colorless, 69% yield). *N*-Methylpyrrolidine, lithium bis(trifluoromethanesulfonyl)imide, and ethyl acetate (purum for analysis) were commercially available. 1-Iodo-2-methoxyethane was synthesized from 1-methoxy-2-tosyl-ethane [16] by reaction with sodium iodide as previously reported [17].

¹H NMR (see Ref. [14]) (CDCl₃): 2.20–2.30 (br s, 4H), 3.10–3.20 (br s, 3H), 3.30–3.40 (br s, 3H), 3.50–3.60 (m, 6H), and 3.75–3.85 (br s, 2H). ¹³C NMR (δ, CDCl₃): 21.0 (CH₂), 48.6 (CH₃), 58.6 (CH₃), 63.2 (CH₂), 65.4 (CH₂), 66.0 (CH₂), and 115.0 (q, CF₃, *J* = 307 Hz). Anal. Calcd. for C₁₀H₁₈F₆N₂O₅S₂: C 28.30, H 4.28. Found: C 28.2, H 4.3.

2.2. Preparation of (1 - χ) PY_{1,201} - χ LiTFSI solutions

The lithium salt-ionic liquid solutions were prepared in a dry-box (MBRAUN O₂ < 1 ppm, H₂O < 1 ppm), under argon atmosphere,



The PY_{1,201} ionic liquid

Scheme 1. The PY_{1,201} ionic liquid.

Table 1
Salt molar fraction, χ, and molality, *m*, of the PY_{1,201}-LiTFSI solutions.

(1 - χ) PY _{1,201}	χ LiTFSI	<i>m</i> LiTFSI (mol kg ⁻¹)
1	0.00	0.00
0.95	0.05	0.12
0.90	0.10	0.26
0.85	0.15	0.41
0.75	0.25	0.78
0.60	0.40	1.57
0.50	0.50	2.36
0.375	0.625	3.93
0.30	0.70	5.50

by adding to PY_{1,201} proper amounts of LiTFSI previously dissolved in acetone. The solutions were dried at 70 °C in order to completely remove the solvent. The chosen salt concentrations, in terms of both molality and lithium molar fraction, are reported in Table 1.

2.3. Characterization

NMR spectra of PY_{1,201} were recorded on a 300 MHz spectrometer (Bruker). The attributions of the signals of the ¹H and ¹³C NMR spectra were supported by DEPT-135 experiments; chemical shifts are reported in ppm downfield from tetramethylsilane (TMS).

The DSC measurements were performed with a 2910 MDSC (TA Instruments) by using aluminium pans, at a rate of 5 °C min⁻¹ under nitrogen purge. TGA scans were recorded at 10 °C min⁻¹ under nitrogen flow with a 2950 TGA (TA Instruments).

The viscosity was measured at 20 ± 1 °C by means of a rotational viscosimeter (Rheotec, mod. RC20) with a cone-plate configuration, in control shear rate mode. The density was determined at 20 °C by a helium pycnometer (Micromeritics).

The ionic conductivity was measured by means of the impedance spectroscopy technique, using a frequency response analyser (FRA Solartron 1255), connected to an electrochemical interface (Solartron 1287), over the frequency range 1 Hz/1 MHz, by applying a voltage of 100 mV. The impedance scans were carried out in the temperature range between -28 and 70 °C, by using a two-probes liquid cell with silver electrodes and cell constant of 0.5 cm⁻¹. The stability of the pure IL and the solutions against lithium was investigated by monitoring the time evolution of the impedance response of a symmetric Li|electrolyte|Li cell.

Both linear and cyclic voltammetry were performed by means of an Electrochemical Interface Solartron 1287 with a three electrodes cell, using lithium as both the counter and the reference electrodes, and nickel as the working one. A Whatman glass microfiber filter was used as the separator.

The lithium transference number, *T*_{Li}⁺, was determined by a dc polarization combined with impedance spectroscopy, as proposed by Bruce et al. and Evans et al. [18,19]. The method consists in applying a small dc pulse to a symmetrical Li|electrolyte|Li cell and measuring the initial, *I*₀, and the steady-state, *I*_{ss}, current which flow through the cell. The same cell was also monitored by impedance spectroscopy to detect the initial, *R*₀, and the final, *R*_{ss}, resistance of the two Li interfaces, this to account for the resistance of passivation layers and the eventual increase of this value upon the duration of the dc pulse. Under these circumstances, the lithium transference number, *T*_{Li}⁺, is given by:

$$T_{\text{Li}}^+ = \frac{I_{\text{ss}} \Delta V - I_0 R_0}{I_0 \Delta V - I_{\text{ss}} R_{\text{ss}}}$$

The limitations of this method when applied to ionic liquids will be addressed in Section 3.

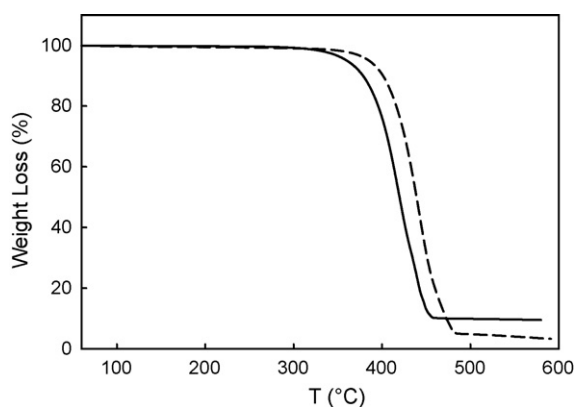


Fig. 1. TGA plots of the pure ionic liquid PY_{1,201} (solid line) and of the LiTFSI-based solution with molality $m = 5.5 \text{ mol kg}^{-1}$ (dashed line).

3. Results and discussions

3.1. Thermal properties, density and viscosity

Fig. 1 reports the TGA plots of the pure ionic liquid PY_{1,201} and of the 5.5 mol kg^{-1} LiTFSI-based solution. As expected, the pure IL is thermally stable up to about 350°C , and the addition of the salt does not affect this property, even in case of high salt concentration. In contrast, LiTFSI plays a role in determining the phase behavior of the solutions. Fig. 2 shows the DSC thermograms of the same samples described in Fig. 1. The pure ionic liquid does not show crystalline phases, at least within the DSC experimental conditions, but only a glass transition is detectable at -87°C in good agreement with the value of -91°C reported in Ref. [14], which was obtained at a DSC rate of $10^\circ\text{C min}^{-1}$. The absence of crystallization phenomena must likely be due to the presence of the ether oxygen which gives origin to polar electrostatic interactions inside the liquid. As a matter of fact, most of the oxygen-containing ionic liquids reported in Ref. [14] do not show any crystallization temperature. The same behavior observed for pure liquid is found for all the solutions. In fact, also in case of the highest salt molality the solution remains amorphous, but the glass transition temperature is remarkably shifted to higher values ($\sim -65^\circ\text{C}$). This effect is expected and it is likely due to the

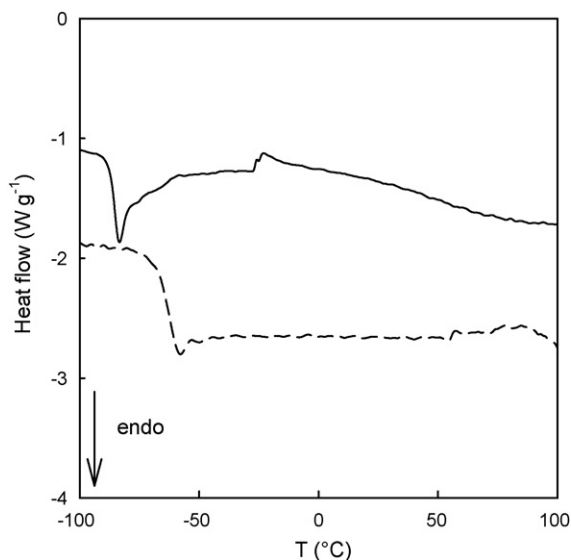


Fig. 2. DSC thermograms of the pure ionic liquid PY_{1,201} (solid line) and of the LiTFSI-based solution with molality $m = 5.5 \text{ mol kg}^{-1}$ (dashed line).

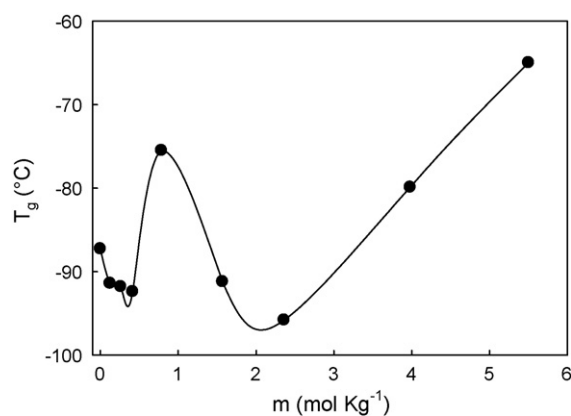


Fig. 3. Behavior of the glass transition temperatures, T_g vs. the molality, m , of the solutions PY_{1,201} TFSI-LiTFSI. The line is a guide for the eye. The symbols dimensions represent the error.

Li interactions with the TFSI anions. The behavior of the T_g vs. the LiTFSI concentration is reported in Fig. 3. A slight decrease of the glass transition temperature is observed for low salt contents, which is probably due to the plasticizing effect of the TFSI anion. The T_g values remain quite constant up to about 2 mol kg^{-1} ($\chi = 0.5$), as already observed in the case of PY-based solutions with alkyl substituents [5], with the notable exception of the solution 0.78 mol kg^{-1} ($\chi = 0.25$) where an anomalous maximum is found. The same anomaly is found in the behavior of the activation energy for conductivity (see below Fig. 7), and may be due to the formation of a complex. More detailed thermal and spectroscopic experiments, now under planning, are needed to clarify this point.

Fig. 4 shows the density and viscosity of the solutions vs. the LiTFSI concentration. The behaviors of these quantities are similar. The pure ionic liquid displays a density of 1.4 g cm^{-3} and a viscosity of 0.047 Pa s (47 cP), in reasonable agreement with Ref. [14]. The addition of salt up to a molality of 0.41 mol kg^{-1} does not affect notably the density, but it reduces the viscosity as low as 25 cP . The very low viscosity of the PY_{1,201}-LiTFSI solutions is expected to give positive effects on the ionic transport. Salt contents higher than 0.4 mol kg^{-1} make the solutions more viscous and dense. However, the behavior of both these quantities is not linear: a maximum of the viscosity (about 10 times higher than that one of the pure liquid) is observed at a salt concentration of 1.57 mol kg^{-1} , whereas a maximum of the density is observed at 2.36 mol kg^{-1} .

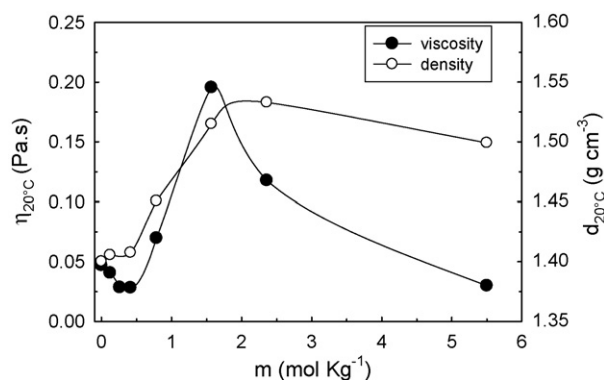


Fig. 4. Viscosity (filled circles) and density (open circles) of the solutions, measured at 20°C , the molality, m , of the solutions PY_{1,201} TFSI-LiTFSI. The lines are guides for the eye. The symbols dimensions represent the error.

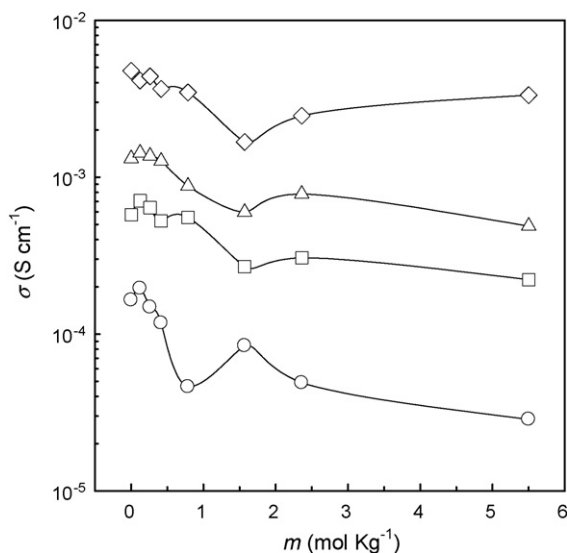


Fig. 5. Conductivity behavior of the PY_{1,201}-LiTFSI solutions vs. the molality, m , of the solutions PY_{1,201} TFSI-LiTFSI, measured at different temperatures: $T = -28$ °C (circles); $T = 0$ °C (squares); $T = 20$ °C (triangles); $T = 60$ °C (diamond). The lines are guides for the eye.

3.2. Ionic conductivity

Fig. 5 shows the conductivity behavior of the PY_{1,201}-LiTFSI solutions as a function of the salt molality at four different temperatures, and namely $T = -28, 0, 20$ and 60 °C. At -28 °C, where the solutions are relatively near to the glass transition, the conductivity decreases with the increase of the LiTFSI concentration. As expected, a local minimum is found in correspondence of the maximum detected in the T_g s graph at 0.78 mol kg⁻¹. For $T \geq 0$ °C the behavior of conductivity vs. the salt content recalls that observed in the case of viscosity. Up to the salt concentration of 0.41 mol kg⁻¹ the conductivity remains nearly constant around the value of the pure ionic liquid, in contrast to what is generally observed in the case of pyrrolidinium-based systems with alkyl substituents, in which drops in conductivity occur even for small LiTFSI amounts [6,20]. Further enhancements of the molality cause a nonlinear behavior of the conductivity that reaches a minimum, well evidenced at 60 °C, which corresponds to the composition with the highest viscosity. We can conclude that at sub-ambient temperature the conductivity is chiefly related to the distance from the glass transition, whereas above 0 °C the rate limiting factor is given by the viscosity, whose relation with the T_g is evidently not trivial: as already stated, in fact, it may call for subtle phase changes.

Fig. 6 plots the conductivity vs. temperature between -28 and 70 °C for the pure ionic liquid and for the solutions with molality equal to 0.41 and 5.5 mol kg⁻¹. Values exceeding 1 mS cm⁻¹ are easily obtained at 20 °C in the case of salt concentration lower than 0.5 m, and another very promising aspect is that no dramatic conductivity losses are observed at sub-ambient temperatures. This is clearly due to the absence of crystallizations below 0 °C, which in contrast characterize the alkyl-pyrrolidinium ionic liquids, causing drops in conductivity from 10^{-3} to 10^{-9} S cm⁻¹ [5]. In the explored temperature range the conductivity plots of Fig. 6 show a quasi-Arrhenian behavior. Fig. 7 displays, vs. the salt concentration, the activation energies, E_a , calculated from the linear regression of the curves. Values ranging from 0.1 to 0.16 eV are obtained. Interestingly, the E_a behavior is very similar to that observed for the T_g (see Fig. 3) and not to that of the viscosity (Fig. 4). We stress that the conductivity behavior of standard lithium-based organic solutions [21] and ionic liquids [22] is often modeled in terms of the VTF approach ($\sigma(T) = A e^{-B/(T - T_0)}$). However, due to the relatively narrow range

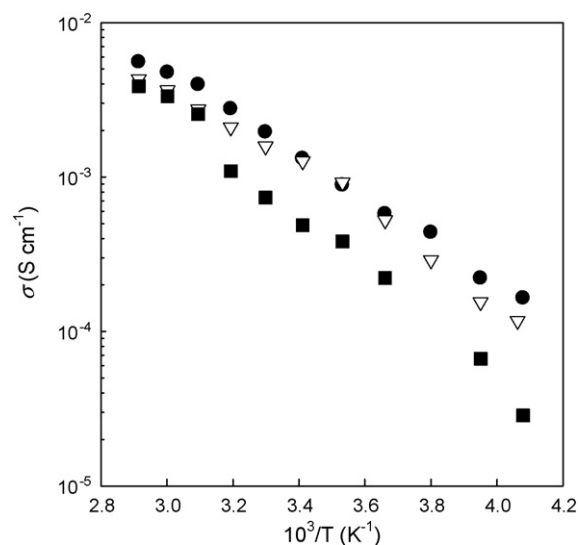


Fig. 6. Conductivity plots vs. reciprocal temperature of the pure PY_{1,201} (open triangles) and of two PY_{1,201}-LiTFSI solutions with $m = 0.41$ mol kg⁻¹ (filled circles) and $m = 5.5$ mol kg⁻¹ (filled squares).

of explored temperature, the Arrhenian fit is satisfactory in our case. In fact, we performed both Arrhenius and VTF linear best-fits that were characterized by similar quality factors. We also performed some sensitivity tests by considering T_0 as a parameter, and found that the quality of the fits does not change in a relevant way over large T_0 intervals.

3.3. Electrochemical stability

As stated in Section 2, the stability of the solutions against metallic lithium, and the formation of passivation layers, have been studied by monitoring the behavior with time of the interfacial resistance, R_{ct} , in a symmetric Li|electrolyte|Li cell [6]. Fig. 8 shows the R_{ct} values vs. time for the 0.41 and 5.5 m solutions. The values of the pure IL are reported for the sake of the comparison. The solution with lower molality appears less reactive against the lithium electrode with respect to the higher concentration solution. In this latter case, in fact, the passivation layer grows rapidly, and an increase up to 60 times of the charge transfer resistance may be observed already after 1 day of storage. A similar behavior has been reported for PY_{1,4}TFSI-LiTFSI solutions [6].

The electrochemical behavior of the electrolyte has been investigated by linear and cyclic voltammetry. Fig. 9a compares the

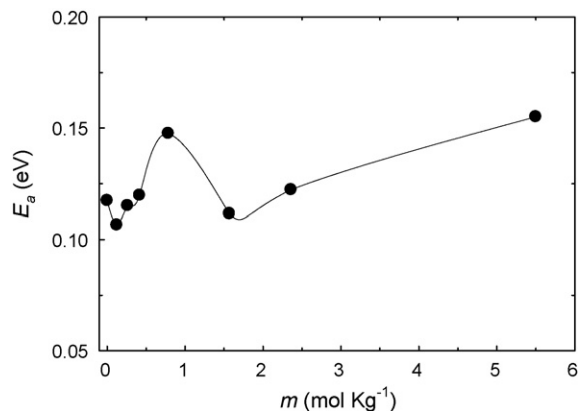


Fig. 7. Activation energy values for the PY_{1,201}-LiTFSI solutions vs. the solution molality. The line is a guide for the eye. The symbols dimensions represent the error.

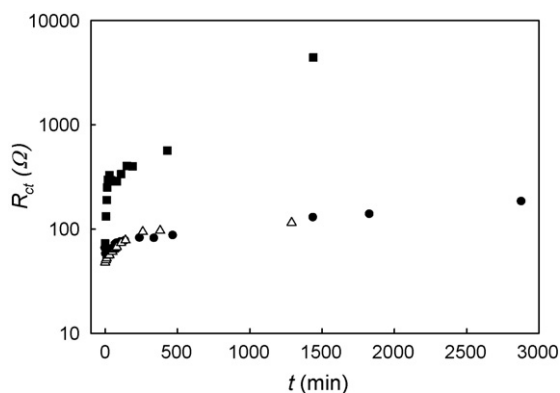


Fig. 8. Changes of the charge transfer resistance, R_{ct} , vs. time for pure $PY_{1,201}$ (open triangles) and for two solutions with $m=0.41 \text{ mol kg}^{-1}$ (filled circles) and $m=5.5 \text{ mol kg}^{-1}$ (filled squares). Cell: $\text{Li}|\text{electrolyte}|\text{Li}$.

linear voltammetry of the pure ionic liquid with those of the solutions containing 0.41 and 5.5 mol kg^{-1} of LiTFSI , respectively. From the analysis of the plot, we can see that the presence of salt in ionic liquid does not remarkably affect the pure $PY_{1,201}$ breakdown voltage, which exceeds 4 V in all the cases. In contrast, the deposition/dissolution processes of the lithium electrode seem to be remarkably influenced by the salt concentration. Fig. 9b, in

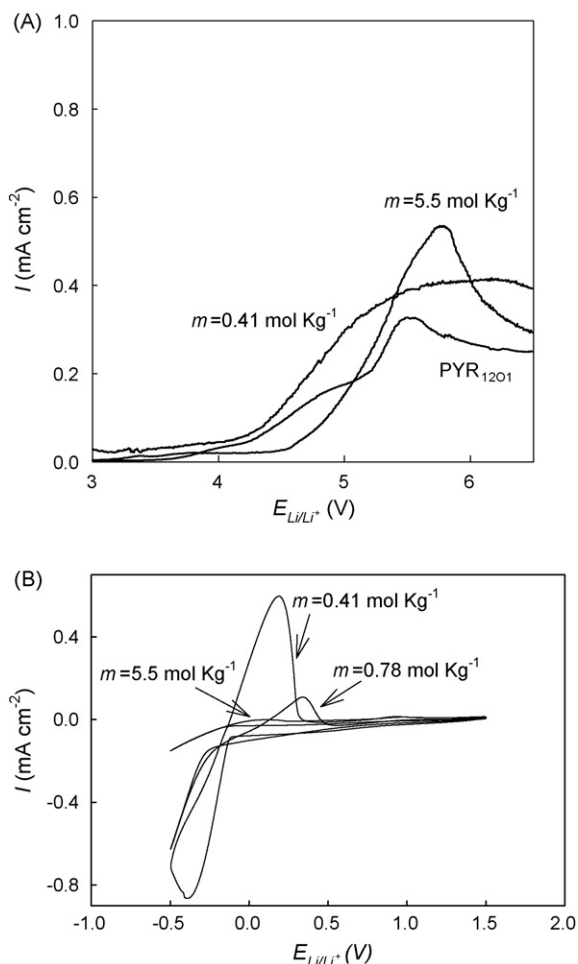


Fig. 9. (A) Linear voltammetry plots of two $PY_{1,201}$ - LiTFSI solutions with $m=0.41$ and 5.5 mol kg^{-1} . The curve of pure $PY_{1,201}$ is also reported as a comparison. Scan rate: 0.2 mV s^{-1} . (B) Cyclic voltammetry curves (5th cycle) of three $PY_{1,201}$ - LiTFSI solutions with different molality. Scan rate: 5 mV s^{-1} .

Table 2

Results of the dc polarization experiments to determine the lithium transference numbers. See Section 2 for the details.

χ	I_0 (μA)	I_{ss} (μA)	R_0 (Ω)	R_{ss} (Ω)	ΔV (mV)	T^+
0.05	42	13.7	1606	1828	70	0.02
0.15	22	8.5	138	183	6	0.26
0.70	6.3	3.4	593	855	6	0.39

fact, reports the cyclic voltammetry of three solutions of increasing molality, 0.41 , 0.78 and 5.5 mol kg^{-1} . The 0.41 m sample shows the typical stripping and plating peaks between -0.5 and 0.5 V , whereas at higher salt contents the cycling efficiency is remarkably suppressed, in particular for what concerns the reduction step. This phenomenon is likely related to the formation of different passivation layers at the electrode interface, which may favor the oxidation and reduction of other ionic species, coming from the decomposition of the salt [2]. It has been stressed in the literature that the comparison of the electrochemical data on ionic liquids is difficult because the reference systems are different and in some cases not strictly electrochemically defined [1]. Moreover, the use of the $\text{Li}|\text{Li}^+$ as the reference couple is criticized because of the possible reactivity of lithium with the ionic liquid [14]. A good suggestion to overcome this problem is to use the couple ferrocene/ferrocinium ($\text{Fc}|\text{Fc}^+$) as the external reference. However, the knowledge of the electrochemical behavior having Li as the reference may be also of relevance, in order to have a better understanding of the behavior of the ionic liquid under operating conditions. Another point to be addressed in the potential reactivity of the $PY_{1,201}$ - LiTFSI electrolyte with the aluminium parts of the battery.

3.4. The cation transference number, T^+

Table 2 reports the currents, the resistances and the cation transference numbers for three $PY_{1,201}$ -based solutions with different salt concentrations. We stress that the employed method is valid for the electrochemical systems in which the charge transfer reaction is not the limiting step in the cell [18]. Indeed, this cannot be the case of these ionic liquids. This problem may be overcome by a proper choice of the polarization voltages, as deeply discussed by Abraham and co-workers for both liquid and polymer electrolytes [23,24]. In fact, in the case of the solution with lowest molality high dc sweeps (70 mV) have been necessary in order to balance the iR drops due to the larger resistances of the passivation layers on lithium electrode. From the analysis of Table 2 we can note that the increase of salt content moderately improves the lithium transference number. T^+ ranging from 0.02 to ~ 0.4 have been obtained between 0.41 and 5.5 mol kg^{-1} , which are in fair agreement with what reported in literature for similar systems [6]. However, to check these results NMR measurements of self-diffusion coefficients are now in progress and will be the object of a future paper.

4. Conclusions

A number of solutions of LiTFSI in N -methoxyethyl- N -methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($PY_{1,201}$) have been prepared by varying the salt concentration in the range 0 and 5.5 mol kg^{-1} . Contrary to what observed in the case of pyrrolidinium-based systems with alkyl substituent, the $PY_{1,201}$ solutions are amorphous over the whole explored molality range with values of T_g which depend on the salt content. This important feature is likely related to the presence of the ether moiety. Very low viscosities (down to 25 cP) has been measured at 20°C up to molality of 0.4 mol kg^{-1} , in contrast to what generally observed for other types of ionic liquids. The room temperature conductivity of the pure $PY_{1,201}$ remains constant at about 1 mS cm^{-1} for a wide

range of salt content. High conductivity values are also observed at sub-ambient temperatures, due to the absence of crystallization processes. Cation transference numbers, T^+ , between 0.05 and 0.39 have been obtained as a function of the salt concentration. The increase of salt concentration causes a nonlinear behavior of bulk quantities like T_g , density and viscosity which calls for complex interactions between the salt and the ionic liquid. This topic deserves further spectroscopic studies now in progress.

Acknowledgement

We gratefully acknowledge funding from CARIPLO Foundation (Project 2006.0688/10.8485 “Nuove membrane elettrolitiche nanocomposite a base di liquidi ionici”).

References

- [1] M. Galiński, A. Lewandowski, I. Stępnik, *Electrochim. Acta* 51 (2006) 5567–5580.
- [2] D.R. MacFarlane, M. Forsyth, P.C. Howlett, J.M. Pringle, J. Sun, G. Annat, W. Neil, E.I. Izgorodina, *Acc. Chem. Res.* 40 (2007) 1165–1173.
- [3] H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Hishiko, M. Kono, *J. Power Sources* 160 (2006) 1308–1313.
- [4] W.A. Henderson, M. Herstedt, V.G. Young Jr., S. Passerini, H.C. De Long, P.C. Truelove, *Inorg. Chem.* 45 (2006) 1412–1414.
- [5] M. Forsyth, J. Huang, D.R. MacFarlane, *J. Mater. Chem.* 10 (2000) 2259–2265.
- [6] A. Fericola, F. Croce, B. Scrosati, T. Watanabe, H. Ohno, *J. Power Sources* 174 (2007) 342–348.
- [7] D.R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, *J. Phys. Chem. B* 103 (1999) 4164–4170.
- [8] J. Salminen, N. Papaiconomou, R. Kumar, J.-M. Lee, J. Kerr, J. Newman, J.M. Prausnitz, *Fluid Phase Equilib.* 261 (2007) 421–426.
- [9] H. Tokuda, K. Hayamizu, K. Ishii, M.A.B.H. Susan, M. Watanabe, *J. Phys. Chem. B* 109 (2005) 6103–6110.
- [10] D.M. Tigelaar, M.A.B. Meador, W.R. Bennett, *Macromolecules* 40 (2007) 4159–4164.
- [11] L.C. Branco, J.N. Rosa, J.J.M. Ramos, C.A.M. Afonso, *Chem. Eur. J.* 8 (2002) 3671–3677.
- [12] Z. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Lett.* 33 (2004) 1636–1637.
- [13] H.S. Schrekker, M.P. Stracke, C.M.L. Schrekker, J. Dupont, *Ind. Eng. Chem. Res.* 46 (2007) 7389–7392.
- [14] Z.-B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Eur. J.* 12 (2006) 2196–2212.
- [15] G.B. Appetecchi, S. Scaccia, C. Tizzoni, F. Alessandrini, S. Passerini, *J. Electrochem. Soc.* 153 (2006) A1685–1691.
- [16] R. Heathcote, J.A.S. Howell, N. Jennings, D. Cartledge, L. Cobden, S. Coles, M. Hursthouse, *Dalton Trans.* (2007) 1309–1315.
- [17] D. Werner, H. Brunar, C.R. Noe, *Pharm. Acta Helv.* 73 (1998) 3–10.
- [18] P.G. Bruce, J. Evans, C.A. Vincent, *Solid State Ionics* 28–30 (1988) 918–922.
- [19] J. Evans, C.A. Vincent, P.G. Bruce, *Polymer* 28 (1987) 2324–2328.
- [20] I. Nicotera, C. Oliviero, W.A. Henderson, G.B. Appetecchi, S. Passerini, *J. Phys. Chem. B* 109 (2005) 22814–22819.
- [21] G.Y. Gu, R. Laura, K.M. Abraham, *Electrochem. Solid State Lett.* 2 (1999) 486.
- [22] A.B. McEwen, H.L. Ngo, K. LeCompte, J.L. Goldman, *J. Electrochem. Soc.* 146 (1999) 1687.
- [23] K.M. Abraham, Z. Jiang, B. Carroll, *Chem. Mater.* 9 (1997) 1978–1988.
- [24] H.S. Choe, B.G. Carroll, D.M. Pasquariello, K.M. Abraham, *Chem. Mater.* 9 (1997) 369–379.