LiTFSI-BEPyTFSI as an improved ionic liquid electrolyte for rechargeable lithium batteries

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Abstract

We report an electrochemical study of solutions of lithium bis(trifluoromethanesulfonyl)imide, LiTFSI, in a *N-n*-butyl-*N*-ethylpyrrolidinium bis(trifluoromethanesulfonyl)imide, BEPyTFSI. We show that these ionic liquid solutions have stability towards lithium metal electrode which allows various electrochemical tests, including impedance spectroscopy and voltammetry. The ionic conductivity and lithium transference number, of the order of 10^{-3} S cm^{-1} and 0.4, respectively, make these solutions suitable for application as electrolytes in advanced lithium batteries. A prototype of these batteries, having lithium iron phosphate as the cathode, showed good performance in terms of charge–discharge efficiency and rate capability. The results reported in this work, although preliminary, are encouraging in supporting the practical interest of this LiTFSI-BEPyTFSI class of lithium conducting ionic liquids.
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Keywords: Ionic liquids; Electrochemistry; Lithium; Batteries

1. Introduction

Ionic liquids, ILs, namely low temperature molten salts, have been attracting much attention in view of their potential applications as new types of solvents in synthetic chemistry and in electrochemistry [1,2]. This continuously growing interest is motivated by their unique properties such as non-volatility, non-flammability, wide temperature range of operation and high conductivity. These properties appear particularly appealing in view of the application of ILs as electrolytes in rechargeable lithium batteries [3,4]. The replacement of the conventional flammable and volatile organic solutions with ILs may in fact greatly reduce risks of thermal runaway and, eventually, fire accidents, thus finally improving the safety of the battery. The most common class of ILs is that formed by the combination of imidazolium-based cations, such as 1-ethyl-3-methyl imidazolium, EMI, and delocalized-charge anions, such as bis(trifluoromethanesulfonyl)imide, TFSI. However, EMI-TFSI, like most ILs, does not contain mobile Li$^+$ and

thus, to provide the electroactive species for the cell reaction it is necessary to add a lithium salt, most commonly lithium bis(trifluoromethanesulfonyl)imide, LiTFSI. Following the addition of the lithium salt, the conductivity decreases due to increase in viscosity and the interactions between Li$^+$ and anions. However, this is not a critical drawback since, although lower than that of the neat IL, the conductivity of the lithium salt solution is still sufficiently high for battery applications. For instance, the conductivity of LiTFSI-EMITFSI has been reported as 1.06×10^{-2} S cm^{-1} at 303 K [5] i.e. of the same order of magnitude of that of common organic solvent solutions.

The real problem is in the electrochemical stability of ILs, e.g., in the value of the reduction potential of the cation, which is generally too positive to allow lithium deposition. For instance, the cathodic limit of the EMI cation is ca. 1.0 V versus Li/Li$^+$ [6] and this obviously prevents the use of EMI-based electrolytes for lithium batteries. ILs also benefit by a wide flexibility in their molecular design associated with the large number of combinations of cations and anions available in IL chemistry. Thus, many authors have attempted to improve the electrochemical stability by suitable modifications of the IL structure [7–9]. However, the results are somewhat contradictory and some

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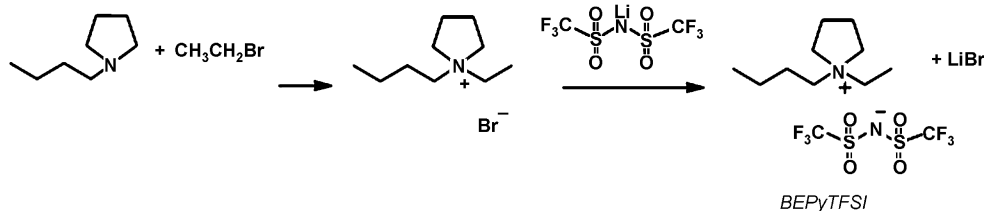
Scheme 1. Scheme of the synthesis procedure followed in this work for the preparation of the IL BEPyTFSI.

confusion still remains. In an attempt to clarify this aspect, as well as to improve the understanding of the IL electrochemistry, we report a study of *N-n*-butyl-*N*-ethylpyrrolidinium bis(trifluoromethanesulfonyl)imide, BEPyTFSI solutions of LiTFSI. Although a similar class of solutions has been already reported [10,11], the IL here selected differs from previous materials by the type of the side chains, which considerably affect the solution properties. The idea is to achieve new hydrogen-free structures having an enhanced electrochemical stability. The results reported in this work tend to confirm the validity of this approach.

2. Experimental

The IL here developed, i.e. *N-n*-butyl-*N*-ethylpyrrolidinium bis(trifluoromethanesulfonyl)imide (BEPyTFSI) was synthesized according to Scheme 1.

For this synthesis, 1-butylpyrrolidine and 1-bromoethane were mixed in acetonitrile and the resulting solution was stirred at 60 °C overnight. The solvent was evaporated, leaving a solid product (BEPyBr), which was then purified by recrystallization in a suitable mixture of ethylacetate and ethanol. Equimolar amounts of BEPyBr and LiTFSI were dissolved and mixed in distilled water under stirring at room temperature for 3 h. This step was followed by extraction with dichloromethane. The final BEPyTFSI product was obtained by evaporation of dichloromethane used as a solvent and finally dried under vacuum at room temperature for more than 24 h. The chemical structure and the purity of BEPyTFSI were confirmed by ^{1}H NMR (Varian Mercury-300) and DSC measurement (DSC 821 Mettler-Toledo). The melting point of BEPyTFSI was measured by DSC, scanning the temperature from −100 to 100 °C at 5 °C min^{-1}.

The BEPyTFSI IL was used for the preparation of the four LiTFSI-BEPyTFSI solutions analyzed in this work, having different concentrations, i.e. 0.1, 0.2, 0.3 and 0.4 mol kg^{-1}. All the manipulations were carried out in a dry box filled with argon.

The decomposition temperature of BEPyTFSI and of its LiTFSI solutions were investigated by TGA (TGA/SDTA 851 Mettler-Toledo), recording the weight loss experienced by the sample while raising the temperature from 25 up to 500 °C at 5 °C min^{-1}.

The ionic conductivity of BEPyTFSI and its LiTFSI solutions was measured by impedance spectroscopy, performed with a FRA 1255 Solartron on a two Pt-electrode cell.

The stability of BEPyTFSI against lithium was investigated by monitoring the time evolution of the impedance response of a symmetric Li/LiTFSI-BEPyTFSI/Li cell. A visual observation of the stability of lithium metal in LiTFSI-BEPyTFSI was also achieved by controlling the status of a lithium foil kept in contact for several days with the same solution used in the impedance cell.

The electrochemical window of the LiTFSI-BEPyTFSI solutions was determined by linear sweep voltammetry and cyclic voltammetry (PAR 362 Potentiostat) in two-electrode Teflon cells with platinum or copper, respectively, as the working electrode (surface area 1.13 cm^2), lithium as the counter electrode and a Whatman separator imbibed by the LiFTSI-BEPyTFSI solution as electrolyte.

The lithium transference number was determined by a dc polarization combined with impedance spectroscopy following the technique proposed by Bruce et al. [12]. 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 transport number, t_{Li^+}, is given by:

$$t_{Li^+} = \frac{I_{ss}(\Delta V - R_0 I_0)}{I_0(\Delta V - R_{ss} I_{ss})} \quad (1)$$

The Li/LiTFSI-BEPyTFSI/LiFePO$_4$ battery was assembled in a dry box by contacting in sequence a lithium foil anode, a 0.2 mol kg^{-1} LiTFSI-BEPyTFSI electrolyte solution soaked on
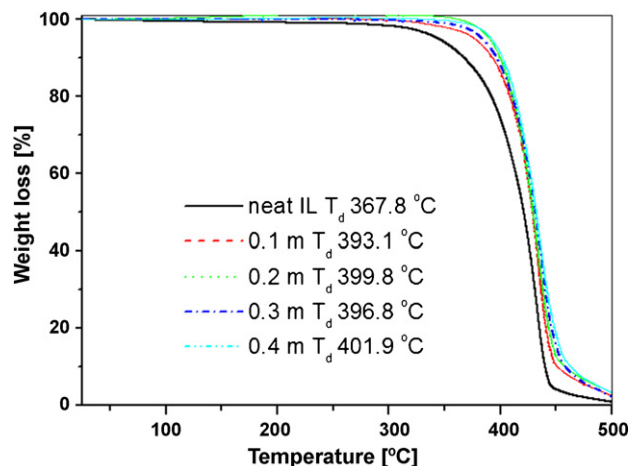
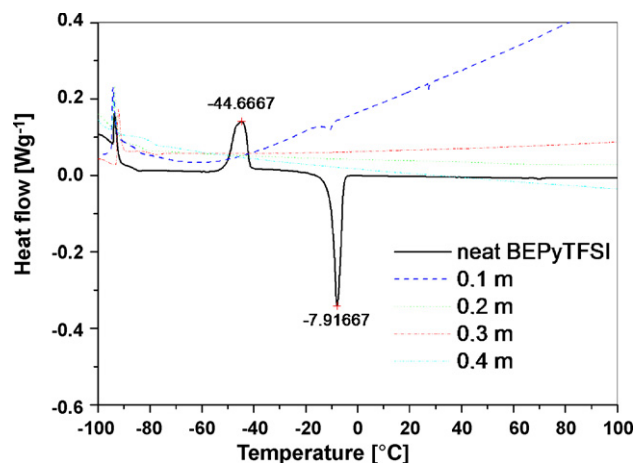Fig. 1. TGA curves of neat BEPyTFSI and 0.1, 0.2, 0.3, 0.4 mol kg^{-1} LiTFSI-BEPyTFSI solutions.

Fig. 2. DSC curves of neat BEPyTFSI and of 0.1, 0.2, 0.3, 0.4 mol kg^{-1} LiTFSI-BEPyTFSI solutions.

Fig. 3. The value of ionic conductivity of neat BEPyTFSI and 0.1, 0.2, 0.3, 0.4 mol kg^{-1} LiTFSI-BEPyTFSI solutions at room temperature.

a separator and a lithium iron phosphate cathode. The latter was prepared as a composite film formed by a blend of LiFePO$_4$ (active material), super P carbon (electronic conducting additive) and PVdF (binder). The battery response was tested by galvanostatic charge–discharge cycles monitored and controlled by a Maccor Series 4000 Battery Tester.

3. Results and discussion

Fig. 1 compares the TGA response of the neat BEPyTFSI with those of LiTFSI-BEPyTFSI solutions having various LiTFSI concentrations. The figure confirms the expected high thermal stability of the neat IL, extending to 367.8 °C for 10% weight loss. Effectively, the thermal stability of the related solutions is even slightly higher than that of the neat IL. To account for this, interactions between lithium salt and the IL cannot be excluded and spectroscopic studies are underway to confirm this hypothesis.
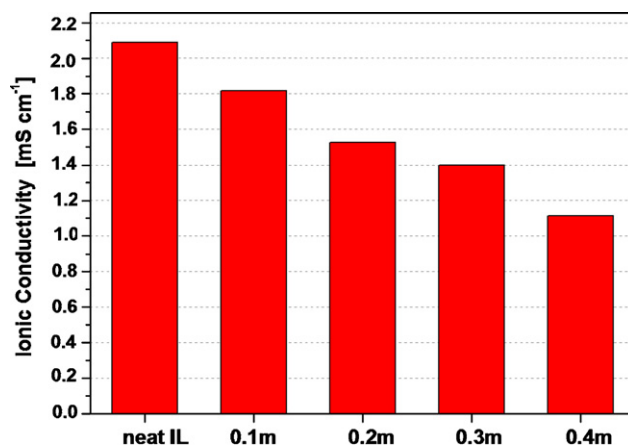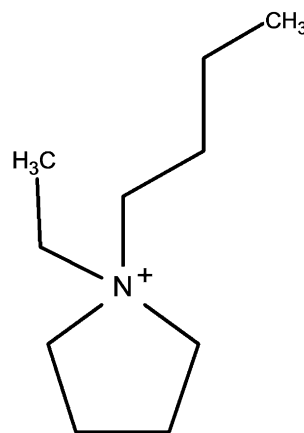

Fig. 4. Structure of the *N-n*-butyl-*N*-ethyl-pyrrolidinium, BEPy, cation produced and tested in this work.
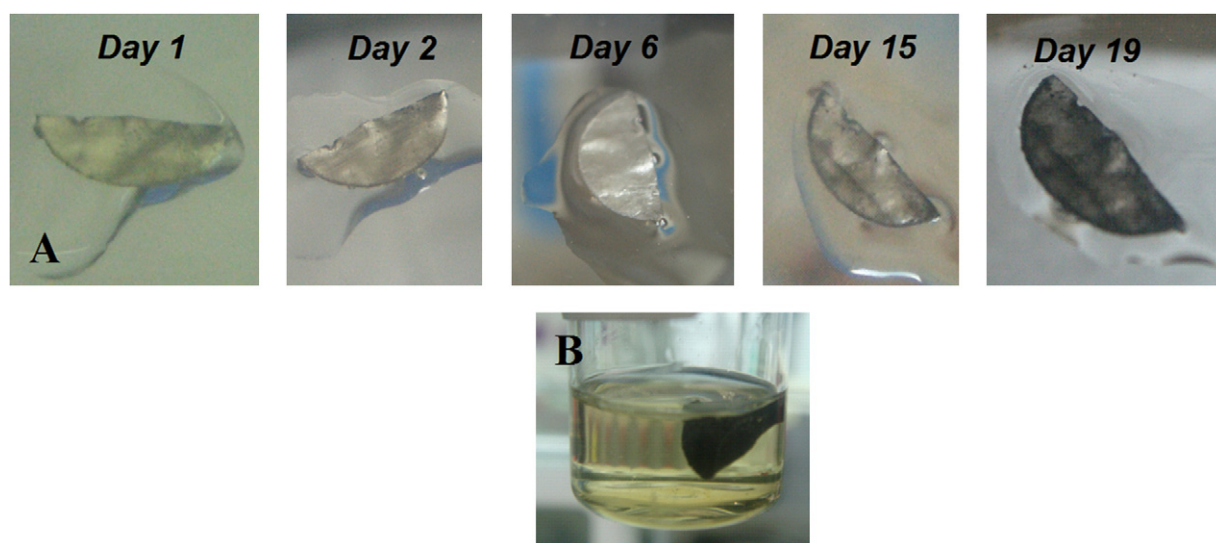

Fig. 5. Photographs of lithium foil in contact with 0.1 mol kg^{-1} LiTFSI-BEPyTFSI solution, from day 1 to day 19 (A) and in contact for one night with 1 m LiTFSI-BMITFSI solution (B).

Fig. 7. Time evolution of the impedance response of a symmetrical Li/LiTFSI-BMITFSI/Li cell from day 3 to day 7 of storage.
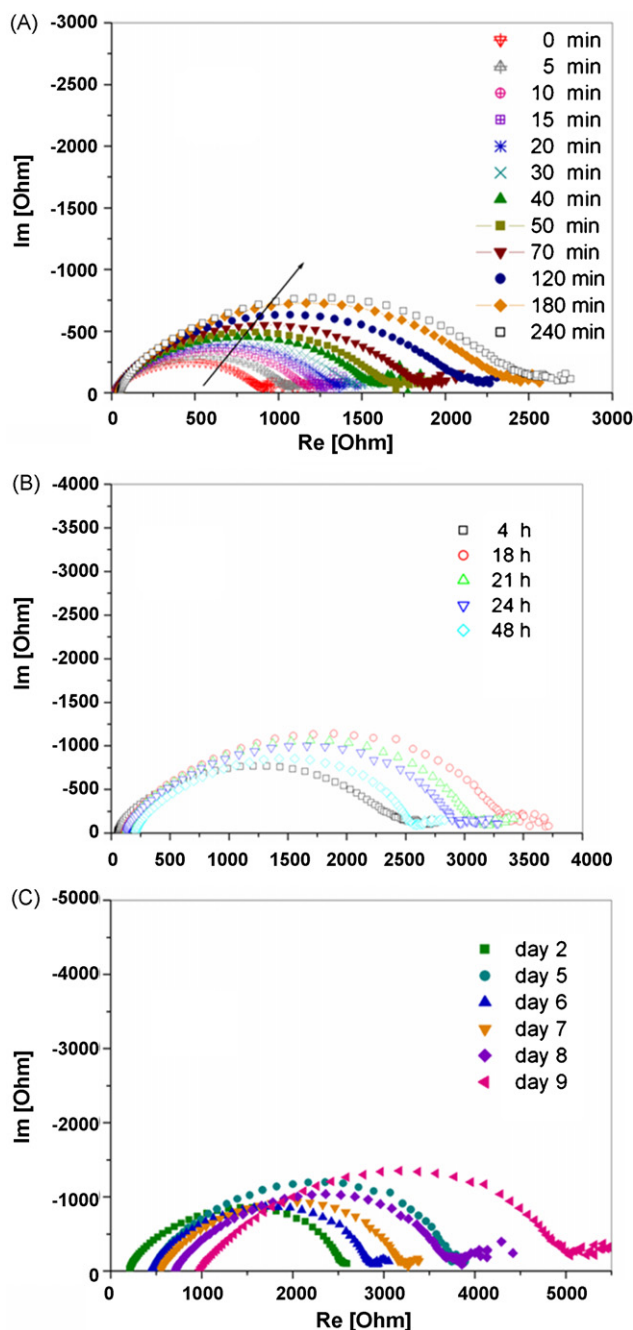

Fig. 6. Time evolution of the impedance response of a symmetrical Li/LiTFSI-BEPyTFSI/Li cell at progressively longer times of storage, i.e., 24 h (A), from 4 to 48 h (B) and from day 2 to day 9.

Fig. 2 compares the differential scanning calorimetry response of the solutions and that of the neat IL. The DSC trace of the BEPyTFSI clearly evidences the crystallization temperature ($-44.7\,^{\circ}$C) and the melting point ($-7.9\,^{\circ}$C) of the neat IL. As an effect of the LiTFSI salt mixing, all the traces relative to the solutions became peakless, apart from a small peak for the $0.1\,\mathrm{mol\,kg^{-1}}$ solution associated to its melting point.

By adding the LiTFSI salt to the IL, the viscosity and the formation of ionic couples progressively increase and thus, as expected, the value of the conductivity progressively decreases. However, an ionic conductivity hig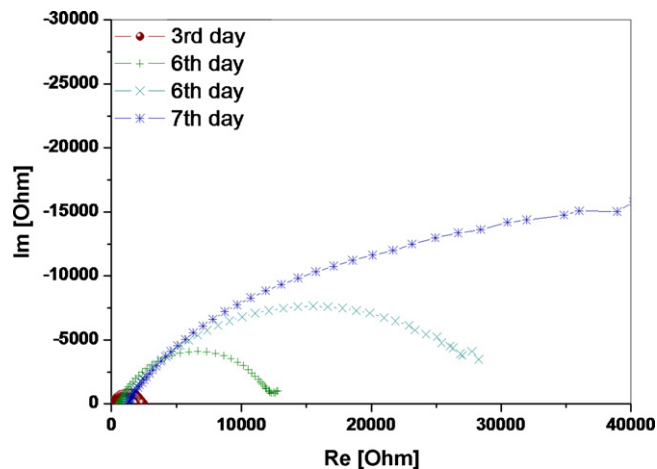her than $10^{-3}\,\mathrm{S\,cm^{-1}}$ was observed for all the LiTFSI concentrations here examined, see Fig. 3. This conductivity value, which is in agreement with that found by other authors for the general case of IL-based lithium solutions [3,5,8,9,11] is still sufficiently high for battery applications. It may be useful to recall here that the conductivity of the solutions most commonly used as electrolytes in lithium ion battery technology, e.g. the LiPF$_6$ 1 m in EC-DMC, ranges around 10^{-2} to $10^{-3}\,\mathrm{S\,cm^{-1}}$ [13].

However, it is important to point out that the value of the conductivity is not the only critical parameter for electrolytes addressed to lithium ion batteries. Since these batteries generally operate by lithium ion exchange between a graphite anode and a lithium metal oxide cathode, the value of the fraction of current transported by the lithium ions is of paramount importance. A low lithium ion transport number, $t_{\mathrm{Li^+}}$, leads to concentration polarizations, this greatly limiting the rate capability of the battery. Consequently, the knowledge of the $t_{\mathrm{Li^+}}$ value is crucial for the selection of lithium battery electrolytes.

To our knowledge, there are few reports, if any, on the value of this key parameter in IL-based solutions. A convenient way to determine $t_{\mathrm{Li^+}}$ in general has been developed and validated by Bruce et al. [12]. The method is based on a combination of dc and ac tests on a symmetrical lithium cell, see Section 2. Probably, the reason why this method was so far not successful for IL-based solutions is due to the fact that the most of ILs have an electrochemical stability window which is not compatible with the lithium electrode. For instance, the EMI cation, which is the component of the most common ILs, has a cathode reduction potential of 1 V versus Li/Li$^+$ [6], this obviously preventing its use in symmetrical lithium cells, and in general, as electrolyte in lithium batteries.

Therefore, it is important to search ILs having electrochemical windows more appropriate than that of EMI for not only practical purposes but also and specifically, for the definition of the electrochemical properties of related IL-based solutions. Various attempts to reach this goal have been reported. The most common strategy has been that of modifying the molecular conformation of the IL cation in order to prevent reduction
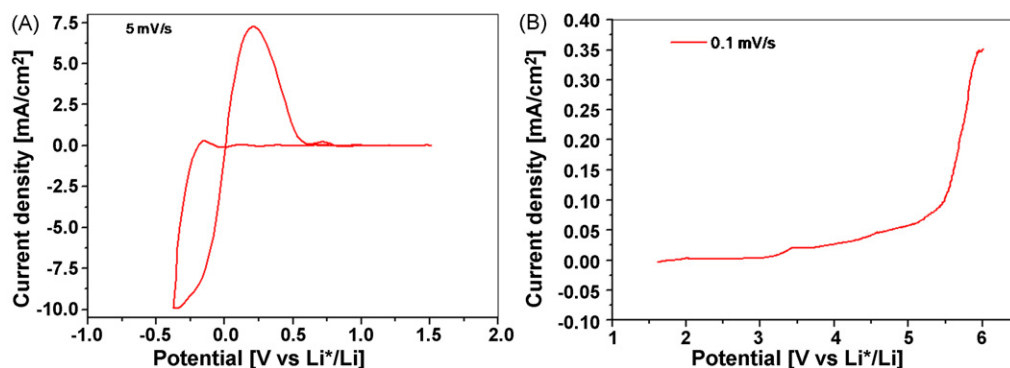
Fig. 8. Cyclic voltammetry of a copper foil electrode in a 0.2 mol kg^{-1} LiTFSI-BEPyTFSI solution (A) and sweep voltammetry of a platinum electrode in a 0.1 mol kg^{-1} LiTFSI-BEPyTFSI solution (B). Counter electrode: lithium foil. Room temperature.

by decreasing the liability of the imidazolium ring protons. Since the protons in the C-2 position are more readily removed than those in C-4 or C-5 positions, the best results in terms of cathodic protection have been obtained for tetraalkylammonium cations [14,15]. There are various works which tend to confirm the validity of this strategy [7–9]. However, the results are contradictory and to our knowledge, a satisfactory material and the precise knowledge of its stability towards lithium, especially in terms of prolonged contact time, are not yet available.

In the attempt to shed more light in the field and with the main goal of improving the understanding of the IL electrochemistry, our strategy has been to achieve a suitable modification of the cation by adding side chains in order to obtain aliphatic and hydrogen-free structures, such as the *N-n*-butyl-*N*-ethyl-pyrrolidinium, BEPy, here considered, see Fig. 4.

Although a similar class of ILs has already been reported [10,11], the IL here selected differs from previous materials by the type of side chains, with the idea of exploiting the influence of the side chain of the cation moiety to promote enhanced lithium stability. This has been practically tested by direct visual control, as well as by a series of electrochemical techniques which include impedance spectroscopy, sweep voltammetry and cyclic voltammetry.

Fig. 5A illustrates the appearance of a small piece of lithium metal foil left in contact in a 0.1 mol kg^{-1} LiTFSI-BEPyTFSI solution for 2 weeks. Clearly, no significant damage of the

lithium foil was observed for the initial 6 days of contact. A part of the foil became slightly black only at day 15, to finally totally deteriorate after day 19. On the basis of this simple experiment we may then conclude that our IL-based solution is effectively stable with lithium at least within 1 week of contact.

This is an encouraging result especially when compared with that obtained with a more conventional IL-based solution, e.g. 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (BMITFSI). Fig. 5B shows the result of the same experiment carried out by monitoring the aspect of a lithium foil when in contact with a LiTFSI-BMITFSI solution: in this case lithium underwent total deterioration within only one night of contact.

The improvement in electrochemical stability of our LiTFSI-BEPyTFSI solution was further investigated by impedance spectroscopy. Fig. 6 shows the evolution of the impedance spectra of a symmetrical Li/LiTFSI-BEPyTFSI/Li cell at progressively longer times of storage under open-circuit conditions. The response may be basically interpreted in terms of two convoluted semicircles. Their amplitude, determined by the two intercepts with the real axis, may be associated to the impedance of the Li/electrolyte interfaces. Fig. 6A shows that this impedance continuously grows during the initial 240 min of contact, indicating the occurrence of a reaction between the lithium metal and the electrolyte with the formation and build-up of a solid electrolyte interface (SEI) layer. However, the figure also clearly shows that the width of the semicircles, and thus the
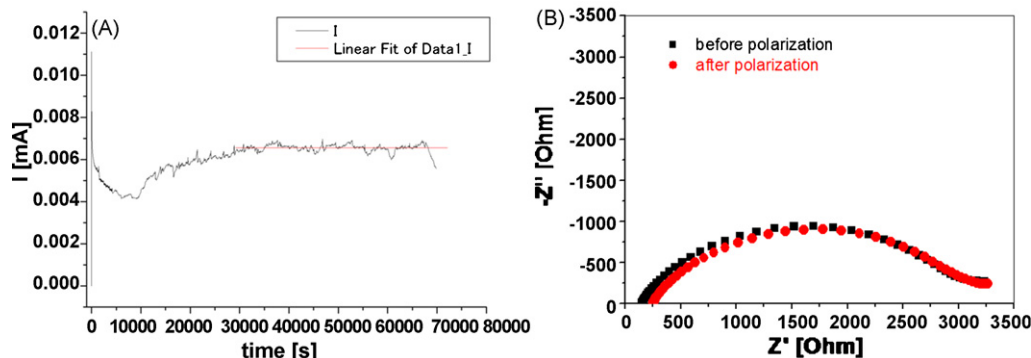

Fig. 9. Chronoamperometric curve of a Li/0.1 mol kg^{-1} LiTFSI-BEPyTFSI/Li cell after a 80 mV dc pulse (A) and impedance response of the same cell before and after the dc polarization (B). Room temperature.
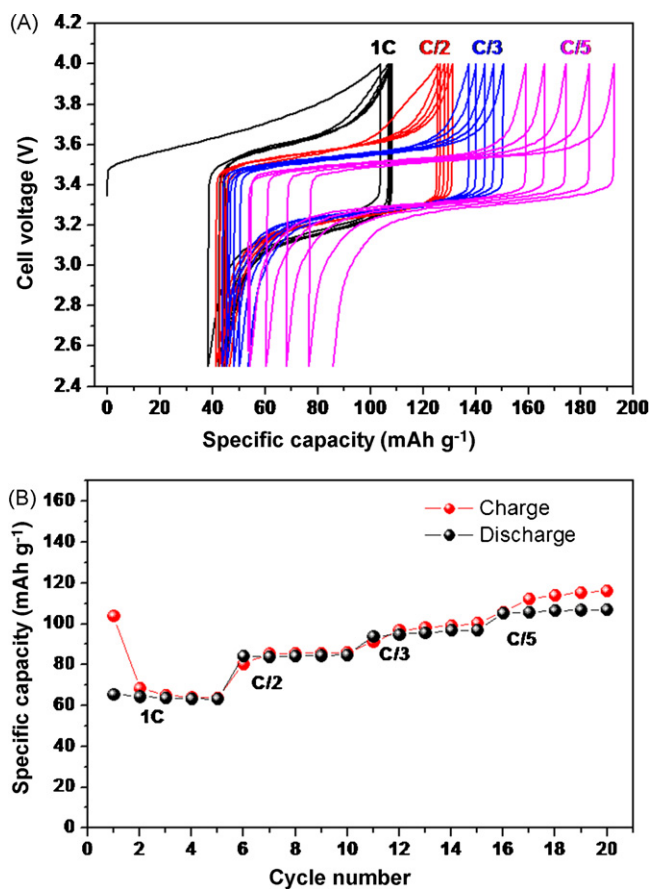
Fig. 10. Typical voltage profiles of charge–discharge cycles (A) and capacity vs. cycle number (B) of the Li/LiTFSI-BEPyTFSI/LiFePO$_4$ battery at various rates and at room temperature.

value of the interface resistance remain more or less constant on the value of 300 Ω for 8 days to then expand after 9 days of contact, see Fig. 6B and C. Notice in Fig. 6C, that the highest frequency-intercept shifts upon the time of the measurements to reach the value of ca. 1000 Ω. This indicates that lithium reacts with the electrolyte; however, the reaction is expected to be eventually prevented by the formation of a passivating layer (see below).

The same impedance analysis was run on a cell using a conventional LiTFSI-BMITFSI electrolyte solution as a reference. A much faster growth of the interfacial impedance was detected, from an initial value of ca. 3000 Ω to several thousand ohms within a week of storage, see Fig. 7.

The electrochemical behavior of the LiTFSI-BEPyTFSI electrolyte was further investigated by voltammetry. Fig. 8A shows the cyclic voltammetry of a copper electrode in a cell using the 0.2 mol kg^{-1} LiTFSI-BEPyTFSI solution as electrolyte and a lithium metal counter electrode. The figure illustrates a cathodic scan starting from the open-circuit voltage and extending down to the lithium deposition range, i.e. to −0.3 V versus Li. The lithium deposition–lithium stripping peaks on and from the copper substrate are clearly visible. The coulombic efficiency is ca. 90%, this confirming the reversibility of the process and, ultimately the compatibility of the electrolyte with the lithium metal electrode. Fig. 8B shows the sweep voltammetry of a

platinum electrode in 0.1 mol kg^{-1} LiTFSI-BEPyTFSI solution, extended to the anodic side. In this case, the onset of the current is associated to the decomposition of the electrolyte. These results demonstrate that the LiTFSI-BEPyTFSI electrolyte has a stability window extending from about 0–5 V versus Li, this confirming its feasibility for application in lithium ion batteries.

In summary, the impedance and the voltammetry results support the conclusion drove on the basis of the visual experiments reported in Fig. 5, namely that the passage from the labile BMI cation to the BEPy cation, indeed resulted in a consistent improvement of the stability toward lithium, at least in terms of reaction kinetics. Although kinetically limited, the stability of the LiTFSI-BEPyTFSI electrolyte is certainly sufficient to allow the test for the determination of the lithium transport number.

Fig. 9A shows the chronoamperometric curve of a Li/0.1 mol kg^{-1} LiTFSI-BEPyTFSI/Li cell after a 80 mV dc pulse. The current flow through the cell initially decays, probably due to the already cited initial reaction with lithium. The current, however, soon stabilizes, this being an additional confirmation of the occurrence of a stable passivating layer on the lithium surface. By fitting the curve, one obtains the values of the current at the initial polarization time, I_0 and under steady-state conditions, I_{ss}. Fig. 9B shows the impedance of the cell before and after polarization. The two curves practically overlap, this indicating that there is no great difference between the initial R_0 and the final resistance R_{ss} of the two Li interfaces, this being an additional confirmation of the stability of the lithium electrode in the IL-based electrolyte. By inserting the values of I_0, I_{ss}, R_0 and R_{ss} in Eq. (1), the lithium transference number results to be 0.4, i.e. a reasonable value for practical application in lithium batteries.

To confirm this, we have assembled and tested a battery formed by a lithium anode, a lithium iron phosphate cathode and our IL as the electrolyte:

$$\text{Li/LiTFSI-BEPyTFSI/LiFePO}_4 \qquad (2)$$

The electrochemical process of this battery is the reversible removal-uptake of lithium from and to lithium iron phosphate:

$$\text{Li} + \text{LiFePO}_4 \leftrightharpoons \text{Li}_{(1+x)} + \text{Li}_{(1-x)}\text{FePO}_4 \qquad (3)$$
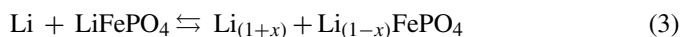
which is expected to develop along a 3.5 V flat plateau for a total specific capacity of 170 mAh g^{-1}.

Fig. 10A shows some typical charge (lithium removal)-discharge (lithium uptake) cycles of the battery and Fig. 10B the capacity versus cycle number. The battery operates with the expected voltage profiles delivering a good fraction of the theoretical capacity even at rates as high as 1 C. The cycle response is also encouraging since no decay in capacity is shown during this initial test and the charge–discharge efficiency following the first cycle, where rearrangements in the structure of the electrode take place, approaches 100%.

Obviously, the life of this particular battery is expected to be limited by the time-dependent stability of the electrolyte towards the lithium electrode, see Figs. 5 and 6. However, the results above discussed, although preliminary, demonstrate the basic feasibility of the IL solutions as electrolytes for lithium batteries.

A. Fernicola et al. / Journal of Power Sources 174 (2007) 342–348

4. Conclusion

The results reported in this work demonstrate that, taking advantage of the ILs' property of offering a wide flexibility in molecular design, one may properly modify their structure to consistently widen the electrochemical window, such as to obtain electrolyte solutions having long-time stability towards lithium metal electrodes. We have shown that this strategy applies to the LiTFSI-BEPyTFSI solutions which have been proved to be much more stable than conventional BMI-based solutions. Obviously, this is not a conclusive result since the stability is kinetically controlled and extends only for a few days. However, in our opinion the result is encouraging in demonstrating the validity of the strategy.

A first positive effect is that the stability of our solution is long enough to allow the determination of the lithium transport number, providing data that to our knowledge has been rarely reported. The value of t_{Li^+}, combined with that of the cathodic and anodic stability, appear suitable for allowing a preliminary test of the LiTFSI-BEPyTFSI solution as an electrolyte in advanced lithium batteries, with encouraging results.

The next important step along the line of this work is to enhance the stability of the LiTFSI-BEPyTFSI, or of other related solutions, to practical values. There are various strategies that can be exploited to reach this goal. One is the optimization of the type of the side chain to further improve the resistance of the ring towards reduction. Alternatively, or even in addition, one may add the IL solution with a SEI forming component, such as ethylene carbonate, EC, or even better, vinylene carbonate, VC. This strategy has been used with some success for other types of IL-based electrolytes [16]. Finally, if all these strategies fail, one may consider switching to anodes operating at potentials sufficiently high to fall within the stability window of the electrolyte but still sufficiently low to give a reasonable voltage when coupled with cathodes such as LiFePO$_4$ or LiCoO$_2$. One of these alternative anodes is lithium titanate, Li$_4$Ti$_5$O$_{12}$ [17] which operates at 1.5 V versus Li and thus, if coupled with LiFePO$_4$ may give a 2 V battery.

All these strategies will be considered and evaluated in our laboratory and the results will be reported in future papers.

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