UV-cured polymer electrolytes encompassing hydrophobic room temperature ionic liquid for lithium batteries

C. Gerbaldi [a,*], J.R. Nair [a], Shahzada Ahmad [b], G. Meligrana [a], R. Bongiovanni [a], S. Bodoardo [a], N. Penazzi [a]

[a] Department of Materials Science and Chemical Engineering, Politecnico di Torino, C.so Duca degli Abruzzi 24, Turin 10129, Italy
[b] Electronic Materials Division, National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi 110012, India

ABSTRACT

We demonstrate herewith the application of in situ one-shot free radical photo-polymerisation (UV-curing) process to incorporate room temperature ionic liquids (RTILs) into polymer membranes which can be used as electrolytes for lithium-based batteries. The reactive formulation for the preparation of the polymer membranes was based on a dimethacrylic oligomer (BEMA). The polymer electrolyte membranes were synthesized by UV radiating a mixture of BEMA and a proper radical photo-initiator with different compositions of 1-ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide [EMIPFSI] and, additionally, LiTFSI as lithium source.

Stable and flexible polymer films with good mechanical integrity can easily be produced with varying the EMIPFSI content by using this method. Remarkable values of ionic conductivity were obtained even at ambient temperature. Galvanostatic charge/discharge cyclability tests were performed on the polymer electrolyte membranes by constructing a cell using LiFePO$_4$ as cathode and Li metal as anode. The preliminary results are interesting, exhibiting good reversibility and cyclability.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Recent years have witnessed more and more efforts devoted towards the improvement of specific properties of electrochemical devices, such as rechargeable lithium-based batteries, in view of their possible application in the automotive field and portable energy sources. Beyond the others, rechargeable lithium batteries, which are generally formed by a lithium metal anode, a separator containing the electrolyte and a metal oxide cathode capable of reversibly intercalating/de-intercalating Li$^+$ ions, represent an excellent choice for electrochemical power sources characterized by high energy and/or power density, good cyclability and reliability [1–3]. Recent advances in lithium cells concern the use of polymer electrolytes and ionic liquids.

An ionic liquid is a liquid that contains only ions. In the broad sense, the term represents all molten salts, for instance sodium chloride which is liquid at temperatures higher than 800 °C. Today, however, the term "ionic liquid" is commonly used for salts whose melting point is relatively low (below 100 °C). In particular, the salts that are liquid at room temperature are called room temperature ionic liquids (RTILs): they have arisen surge of interest as green solvents [4,5]. These novel class of liquids are being used as envi-

ronmental benign media in a plethora of applications, including the electrochemistry field. In recent years, RTILs with perfluoro alkyl groups and organic cations have been suggested for battery electrolyte applications due to their wide electrochemical stability window [6–9]. In some cases RTILs have conductivities of $\geq 10^{-2}$ S cm^{-1} at 25 °C with excellent electrochemical stability. Unlike conventional liquid solvents, RTILs have negligible vapour pressure. The absence of volatiles greatly improves the safety characteristics of a battery.

The use of ionic liquids, which are hydrophobic and non-volatile, will effectively help in putting an end to many problems associated with the current lithium-based battery systems, mainly due to the presence of water and to the volatile nature of the solvent. However, as Li-based battery requires Li$^+$ ions to be transported between the anode and the cathode, if ionic liquids are to be used as electrolytes, they must be further doped with a highly hygroscopic Li salt, so the preparation of such electrolytes remains a serious challenge. The RTILs doped with a suitable LiX salt, where X can be preferably of the same anion, may then be incorporated into a flexible, thin membrane to form a battery electrolyte [6,7,9].

Lithium is an undisputed choice as an anode, but when used with liquid electrolytes, the metal is unevenly redeposited in the form of dendrites, leading to inherently unsafe cells with a short lifetime [1]. This is mainly due to current non-homogeneities induced by the passivation layer present on the surface of lithium metal. The use of dry/solid polymer electrolytes is a straightforward approach to

* Corresponding author. Tel.: +39 011 5644638; fax: +39 011 5644699.
E-mail address: claudio.gerbaldi@polito.it (C. Gerbaldi).

overcome this problem, and UV-curing is a facile method to obtain polymer electrolyte membranes.

Free radical photo-polymerisation (UV-curing) is a well-established polymerisation technique, taking place at room temperature under UV-radiation. This technique has an edge over conventional routes as it gives freedom to polymer chemists to design polymeric networks and to tune their final properties [10]. It is versatile, easy to use, fast and environmentally friendly, as energy consumption is low and there is no emission of volatile organic compounds, as the use of solvent is almost avoided. In fact, highly cross-linked polymers are readily synthesized by the irradiation of appropriate formulations of mono and multifunctional monomers, namely dimethacrylates, in the presence of a proper free radical photo-initiator [11–13].

In our previous articles, we have illustrated and discussed about the application of free radical photo-polymerisation to prepare methacrylic-based polymer electrolyte membranes which can be used as electrolytes for lithium battery application [12–14]. In the present communication, ionic conductivity and safety aspects of these highly cured methacrylic-based 3D network polymer electrolytes have been optimised by replacing the conventional electrolyte solvents (e.g., ethylene carbonate, propylene carbonate, diethyl carbonate, etc.) by the EMIPFSI room temperature ionic liquid (RTIL). Moreover, the promising perspectives of such kind of polymer electrolyte membranes in the field of lithium-based batteries are illustrated by the experimental data reported on the electrochemical response of a laboratory-scale lithium polymer cell.

2. Experimental

2.1. Synthesis

The room temperature ionic liquid 1-ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide [EMIPFSI] was prepared by using a previously reported method and it was obtained as a transparent liquid [15,16]. 1-Methylimidazole was obtained from HiMedia (India) while ethyl bromide and cyclohexane used were of reagent grade; ethyl acetate and isopropyl alcohol were used as received from Merck India Ltd. Lithium bis(perfluoroethylsulfonylimide) [LiPFSI] salt, kindly supplied by 3M (USA), was dried under vacuum at 120 °C overnight before use. 1-Ethyl-3-methyl imidazolium bromide [EMIBr] was first prepared by a metathesis reaction, reacting 1-methylimidazole with ethyl bromide at 80 °C for 24 h, and it was recrystallised twice. Metathesis is a bimolecular process involving the exchange of bonds between the two reacting chemical species, which results in the creation of products with similar or identical bonding affiliations [17]. Finally, the anion exchange reaction was carried out, from Br^- to bis(perfluoroethylsulfonyl)imide, by heating an equimolar mixture of EMIBr and LiPFSI salt and, finally, filtered through activated alumina to give an anhydrous, highly pure, colourless liquid of EMIPFSI.

The reactive formulation for the preparation of the polymer membranes was based on a dimethacrylic monomer, i.e. Bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA, average $M_n = 1700$, Aldrich). The polymer electrolyte membranes were synthesized by mixing BEMA and a proper radical photo-initiator (i.e., 2-hydroxy-2-methyl-1-phenyl-1-propanone, Darocur 1173, Ciba Specialty Chemicals) with the EMIPFSI as RTILs and using lithium bis(trifluoromethane) sulfonimide (LiTFSI, Ferro Corp., USA, battery grade) as an additional ions (lithium) source. The mixture was later drawn into a film and exposed to UV-radiation for approx. 3 min, consisting of 2 steps each of 90 s. The final thickness of the film was about 200 μm (measured with a Vernier digital calibre). The photo-

Table 1
Description of the polymer electrolyte membranes containing different proportions of RTILs. In all cases, the percentage of radical photo-initiator added was 3 wt.%.

Sample	BEMA	EMIPFSI	LiTFSI
ILBM-50	40	50	10
ILBM-60	30	60	10
ILBM-70	20	70	10

chemical curing was performed by using a medium vapour pressure Hg UV lamp (Helios Italquartz, Italy), with a radiation intensity on the surface of the sample of 28 mW cm^{-2}. For this process, the samples were held under a pure N_2 atmosphere in small sealed boxes equipped with a quartz window. These conditions assured maximum curing (disappearance of the methacrylic double bonds, checked by FT-IR). This method is facile and reproducible: stable, flexible, transparent polymer films of varying RTILs content can easily be obtained.

In this work we are reporting our preliminary results on three different polymer electrolyte membranes prepared by mixing BEMA with different compositions of EMIPFSI, while the percentage of LiTFSI was fixed at 10 wt.%. The different compositions used for producing the membranes are described in Table 1. The radical photo-initiator was added to any formulation at 3 wt.%.

2.2. Analyses and membrane characterisation techniques

The kinetics of the photo-polymerisation process was investigated by using FT-IR spectroscopy (NICOLET-5700 Real-Time FT-IR instrument, which collects the spectra in real time, while the sample is irradiated by UV light), following the decrease in the area of the band attributable to the acrylic/methacrylic groups at 1630 cm^{-1}. The tests were carried out at ambient temperature on a UV transparent SiC wafer by irradiating the mixtures of monomers for 3 min. The UV lamp used was Lightning curve LC-8 with an intensity of 15–16 mW cm^{-2}. The intensity of UV lamp was measured using a ORIEL photometer. Differential scanning calorimetry (DSC) measurements were used to determine the glass transition temperature (T_g) of the polymer membranes; they were performed on a METTLER-DSC30 (Greifensee, Switzerland) instrument equipped with a low temperature probe in the range of −140 to 100 °C, at a heating rate of 10 °C min^{-1}. The thermal stability of the samples was tested in the temperature range of 25–600 °C by thermo-gravimetric analysis using a TGA/SDTA-851 instrument (METTLER, Switzerland) under N_2 flux at a heating rate of 10 °C min^{-1}.

2.3. Electrochemical characterisation techniques

The ionic conductivity of the polymer electrolyte membranes at various temperatures was determined by electrochemical impedance spectroscopy (EIS) analysis of test cells formed by sandwiching discs of 0.785 cm^2 of the given membrane between two stainless-steel 316 (SS-316) blocking electrodes. The cells, at open circuit, were housed in a temperature controlled oven. A PARSTAT-2273 potentiostat/galvanostat/F.R.A. (Frequency Response Analyser) instrument (Princeton Applied Research, USA) was employed for measurements over a 1 Hz to 100 kHz frequency range. The resistance of the electrolyte was given by the high-frequency intercept determined by analysing the impedance response using a fitting program provided with the Electrochemistry PowerSUITE® software (version 2.58, Princeton Applied Research, USA).

The polymer electrolyte membranes were tested for interfacial stability with the lithium metal electrode by monitoring the evolution in time of the impedance response of a symmetrical Li/polymer
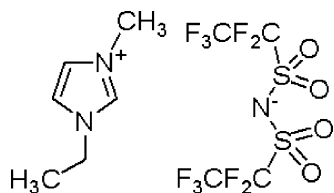
Fig. 1. Structure of 1-ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide [EMIPFSI] room temperature ionic liquid.

electrolyte membrane/Li cell at open circuit potential and room temperature.

The anodic breakdown voltage was evaluated by running a sweep voltammetry in a 2-electrodes Teflon-made Swagelok cell. Acetylene black on Al current collector and Li metal as working and counter electrodes, respectively, and the given membrane as electrolyte was the cell configuration adopted (potential scan range from O.C.V to 5.5 V vs. Li; potential scan rate used was 0.100 mV s^{-1}). Under these conditions, the onset of the current was assumed to indicate the decomposition voltage of the electrolyte [18].

A lithium polymer cell was assembled by using a lithium metal disk anode, a layer of the polymer electrolyte membrane and a LiFePO$_4$/C disk composite cathode (electrode area: 0.785 cm^2) as in the order. The latter (LiFePO$_4$/C) was prepared in the form of thin film by spreading on an aluminium (Al) current collector, by the so-called "doctor blade" technique, a N-methyl-2-pyrrolidone (NMP, Aldrich) slurry of the LiFePO$_4$ active material (90 wt.%, typically about 3.5 mg cm^{-2}) with carbon black as electronic conducting additive (6 wt.%, Shawinigan Black AB50, Chevron Corp., USA) and poly(vinylidene fluoride) as binder (4 wt.%, PVdF, Solvay Solef 6020). High surface area nanostructured LiFePO$_4$/C was synthesized by mild hydrothermal synthesis in the presence of an organic surfactant following the procedure reported in Meligrana et al. [19]. The electrodes/electrolyte assembly was housed in a Teflon-made Swagelok cell equipped with two SS-316 current collector electrodes. Both electrode fabrication and assemblage of the cell prototypes were performed in an environmentally controlled Ar-filled dry glove box (MBraun Labstar, [O$_2$] and [H$_2$O] $\leq$ 0.1 ppm). The electrochemical performances were investigated at 45 °C in terms of charge/discharge galvanostatic curves at different current regimes, rate capability and cycle life using an Arbin Instruments model BT2000 – Battery Testing System.

3. Results and discussion

3.1. Materials

EMIPFSI is a novel ionic liquid which is extremely hydrophobic, has improved thermal stability and shows no reactivity towards water or air. It is thermally stable to temperatures exceeding 350 °C, and it has electrochemical potential window of 4.2 V, density 1.579 g cm^{-3}, with an ionic conductivity value of >1 mS cm^{-1} at ambient temperature [15,16]. Its structure is depicted in Fig. 1.

The relatively high hydrophobicity of EMIPFSI is attributed to the fluorinated anion, which can prevent the absorption of water. This is due to the larger and more electronegative nature of the fluoroethyl group than its fluoromethyl counterpart. This anion is also non-reactive towards Al, which is the most commonly used current collector in lithium-based battery systems. The PFSI$^-$ anion also holds strong dipole interactions due to the presence of the fluorine atoms which would furthermore prevent the absorption of water.

Bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA) is a UV-curable difunctional oligomer. It can be readily polymerised

by free radical photo-polymerisation to obtain a highly cross-linked membrane with a complete conversion of the methacrylic double bonds [12]. The mechanism involved is a free radical one and the initiating reaction is due to the photosensitive species *I* able to generate radicals *R**, which in turn react with the monomer *M*, according to the following scheme:

Initiation : $\quad I \xrightarrow{h\nu} R* \xrightarrow{M} RM*$
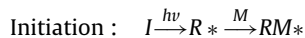
In this work, the photo-initiator was a benzoin ether derivative which generates radicals by a intramolecular scission; *M* is the dimethacrylate BEMA whose propagation reaction leads to a three-dimensional network as sketched below:
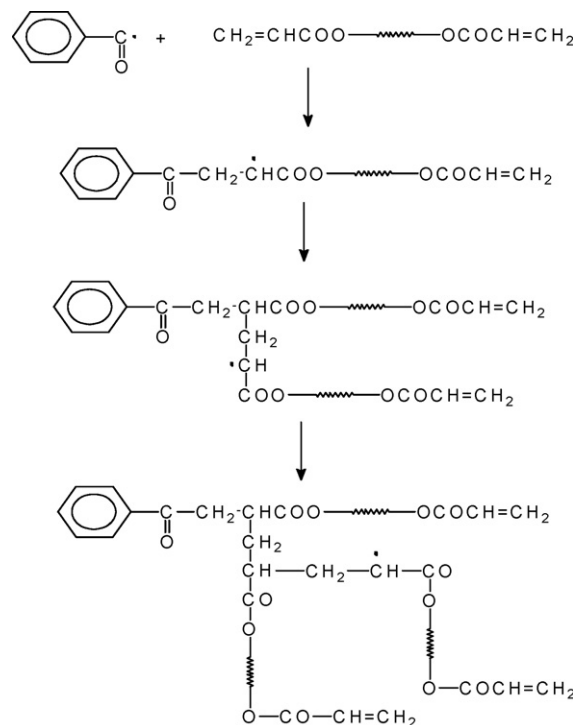
The 3D network obtained is flexible, as its T_g is low, and, at the same time, it is resistant up to 300 °C. Such a highly cross-linked thermo-set polymer network can efficiently hold the RTIL: it contains many ethoxy groups which can help the transport of Li$^+$ ions through the matrix [12].

3.2. Polymer electrolyte membranes characterisation

The formulations described in Section 2.1, obtained by incorporating the oligomer BEMA, the EMIPFSI – RTIL and the LiTFSI salt with a proper photo-initiator, upon exposure to UV irradiation, formed almost transparent, self-standing, extremely flexible and non-sticky membranes: Fig. 2 shows the appearance of the ILBM-60 polymer electrolyte membrane (representative for all the samples prepared).

The characterisation of the UV-cured polymer electrolyte membranes included the evaluation of the conversion of the photo-polymerisation process by means of FT-IR, the determination of the glass transition temperature (T_g) by differential scanning calorimetry and the determination of the thermal stability by means of thermo-gravimetric analyses.
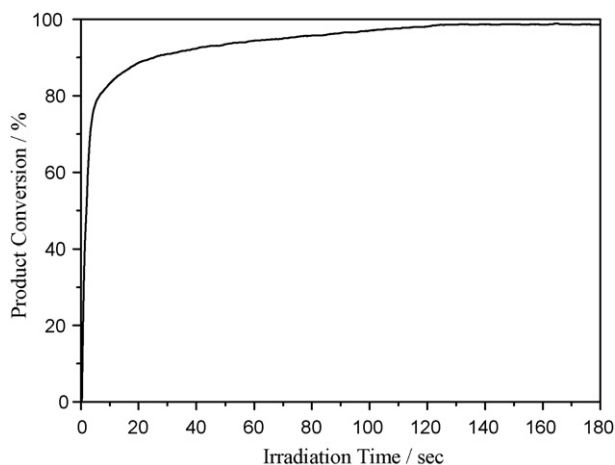
The rate of conversion of the reactive mixtures into polymer membranes (kinetics of the photo-polymerisation reaction) was followed by real-time FT-IR spectroscopy, monitoring the disappearance of the methacrylic double bonds under UV-radiation. These tests were carried out on the reactive mixtures prepared
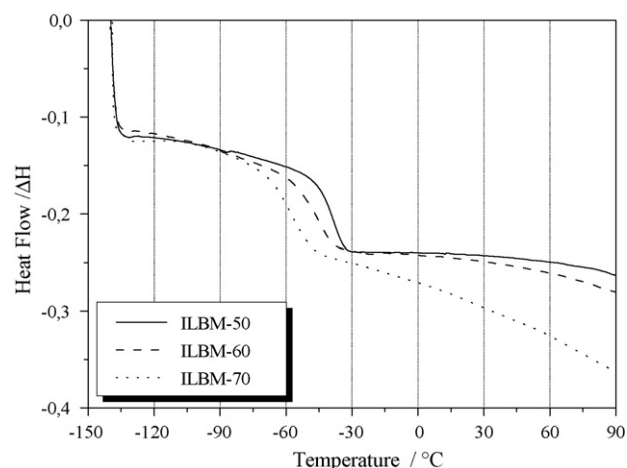
Fig. 2. Self-supporting polymer electrolyte membrane obtained by one-shot photo-polymerisation of the monomer BEMA with 60 wt.% of EMIPFSI and 10 wt.% of LiTFSI via UV irradiation (ILBM-60).
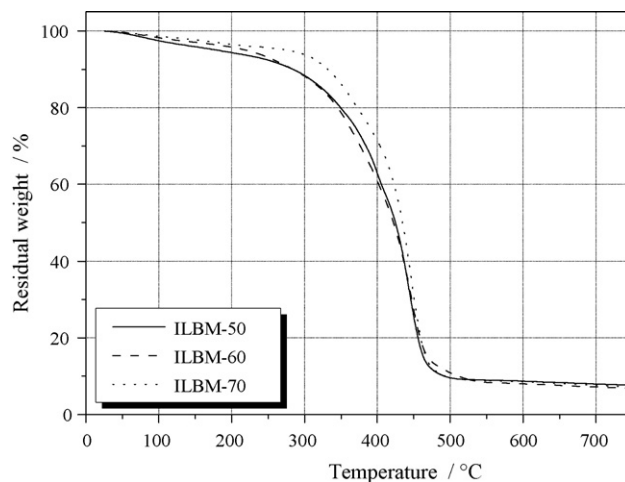

Fig. 4. DSC curves of ILBM-50 (solid line), ILBM-60 (dash line) and ILBM-70 (dot line) polymer electrolyte membranes prepared with the addition of different amounts of EMIPFSI RTIL.

with the addition of various amounts of EMIPFSI. In all the cases, the reactivity was very high in the initial stages of the UV-curing and it reached its maximum very rapidly. The result for the ILBM-60 membrane is depicted in Fig. 3 and it showed that the rate of polymerisation was very fast, with a quantitative conversion of the methacrylic double bonds reached in about 120 s. This result is representative for all the polymer electrolyte membranes prepared: in fact, the experimental analysis performed on all the reactive mixtures showed that the addition of different amounts of RTIL did not influence the rate of photo-polymerisation to a great extent.

Fig. 4 shows the differential scanning calorimetry curves, obtained in the −140 to 120 °C range, for the membranes prepared with different amounts of EMIPFSI. The value of T_g for the ILBM-50 membrane (denotes 50 wt.% of EMIPFSI) was detected to be around −38.6 °C, indicating that at room temperature the polymer membrane is in a rubbery state. T_g was further reduced to very low values as the RTILs content was increased. As a result, ILBM-60 (i.e., 60 wt.% of EMIPFSI) showed a T_g of −45.1 °C, and a very low value of −59.3 °C was observed for ILBM-70 (i.e., 70 wt.% of EMIPFSI). Though the T_g was far below ambient temperature, the membranes were self-withstanding, at the same time extremely flexible and easy to handle. The lowering of the T_g by increasing the EMIPFSI content guarantees a higher flexibility in the poly-

mer chains which will ultimately give more free path for Li$^+$ ions migration.

The thermal stability of the samples was evaluated by thermo-gravimetric analysis under nitrogen flux and the results are shown in Fig. 5. In our earlier communication (i.e., Nair et al. [12]), we have shown that the thermal stability of methacrylic-based membranes was reasonably high, and the weight loss was less than 10 wt.% up to 250 °C. The addition of RTILs did not influence the polymer thermal stability to a great extent. On the contrary, it was also observed that an increase in EMIPFSI content improved the thermal stability of the membranes (see ILBM-70, dot line, with respect to ILBM-50 and ILBM-60, solid and dash lines in Fig. 5, respectively). These results indicate that the obtained polymer electrolyte membranes are potential candidate to be safely used in lithium polymer batteries at high temperatures, i.e. up to 200 °C.

3.3. Electrochemical measurements

To demonstrate the possible application as electrolyte for lithium polymer batteries, ILBM series of polymer electrolyte membranes based on lithium salt doped RTILs were tested in terms of their general electrochemical properties. AC impedance spectroscopy was used to access the ionic conductivity, the time

Fig. 3. Methacrylic double bonds conversion of the ILBM-60 reactive mixture (representative for all the samples prepared), checked by real-time FT-IR spectroscopy as a function of the irradiation time.

Fig. 5. Thermo-gravimetric analysis in the temperature range between 25 and 750 °C under N$_2$ flux of the three different polymer electrolyte membranes prepared: ILBM-50 (solid line), ILBM-60 (dash line) and ILBM-70 (dot line).
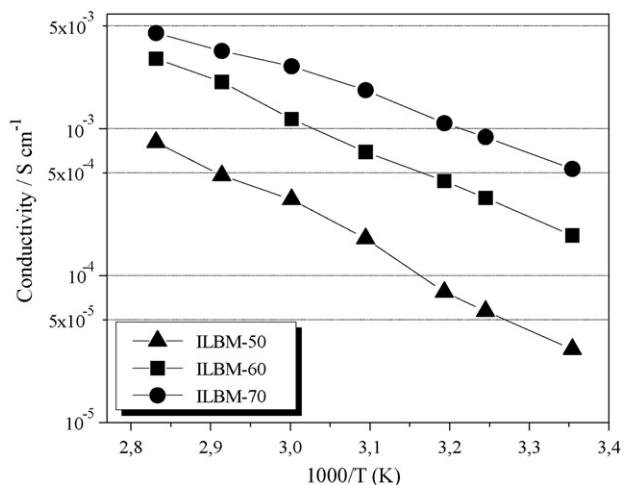
Fig. 6. Ionic conductivity as a function of temperature of the prepared polymer electrolyte membranes (ILBM-50, ILBM-60 and ILBM-70). Data obtained by impedance spectroscopy.

dependent resistance of the polymer electrolyte membranes and the interfacial stability vs. lithium metal. Anodic breakdown voltage and galvanostatic charge/discharge cycles were also carried out to complete the electrochemical testing.

Fig. 6 illustrates the Arrhenius plots, i.e. ionic conductivity as a function of the temperature for the different samples prepared. The graphs exhibited the typical Vogel–Tamman–Fulcher (VTF) curvature associated with amorphous materials. The VTF (Vogel–Tamman–Fulcher) relation describes the transport properties in a viscous matrix [20–22]. At sufficiently high temperatures, as in the present investigation studies, the VTF behaviour approaches the Arrhenius behaviour [12]. The ILBM-50 membrane showed a quite low value of ionic conductivity of about 3.1×10^{-5} S cm^{-1} at room temperature, which is due to the low RTILs content in the sample. Ionic conductivity value increased with temperature, and demonstrated values of 1.7×10^{-4} S cm^{-1} at 50 °C and 8.0×10^{-4} S cm^{-1} at 80 °C. It is important to note that all impedance spectra obtained in the selected temperature range were linear, with no sign of high-frequency semicircles which could indicate lack of gel homogeneity due to crystalline phase separation. The ionic conductivity of the polymer electrolyte membranes increased by increasing the ionic liquid content, resulting in appealing values of 1.9×10^{-4} S cm^{-1} at room temperature, 7.0×10^{-4} S cm^{-1} at 50 °C and 3.0×10^{-3} S cm^{-1} at 80 °C for the sample ILBM-60. As expected, the ILBM-70 membrane showed the highest values of ionic conductivity, i.e. 5.3×10^{-4} S cm^{-1} at room temperature, 1.8×10^{-3} S cm^{-1} at 50 °C and 4.5×10^{-3} S cm^{-1} at 80 °C. Thus, there was a marked enhancement in the ionic conductivity values by increasing the amount of RTILs from 50 to 60 wt.%, while moving from ILBM-60 to ILBM-70 the improvement was not so drastic. The comparative investigation of membranes conductivities and salt/ILs solutions conductivities (under study at the moment) could be certainly important to get a deeper insight on the topic.

In addition to high ionic conductivity, these prepared ILBM polymer electrolyte membranes compasses of RTILs demonstrated a high anodic breakdown voltage, which is an appealing property in view of practical battery application. This is shown in Fig. 7 which illustrates the current–voltage response of the ILBM-60 membrane (representative for all the samples discussed, which demonstrate comparable anodic stability values). Data were obtained in the voltage range between O.C.V. and 5.5 V vs. Li at room temperature by linear sweep voltammetry. It is worth observing that the plateau is very flat and straight; this very low residual current level prior to

breakdown voltage, with no peaks in the lower voltage range, confirms the high purity of both the prepared membranes and relative materials and the synthesis method adopted for their preparation, because the system as a whole is sensitive to oxygen, water and other impurities. The onset of the current during scanning would indicate an anodic breakdown voltage of about 4.5 V vs. Li. This value, similar for all the three polymer membranes prepared, showed that all samples have a good anodic stability. However, it is interesting to note that the real marked and rapid current increase, tied to the electrolyte decomposition, takes place at higher potential for all samples (i.e., >5.2 V vs. Li). An electrolyte with such an extended anodic stability would represent a very important result in view of a possible practical application in high voltage battery. Thus, investigations on the nature of the process causing the shoulder before 5.2 V vs. Li, to ascertain that there is no connection to the electrolyte decomposition, are under development.

As for the stability vs. storage time, the results obtained in terms of the time evolution of the impedance responses (not showed here), evaluated in a Stainless Steel/ILBM-60/Stainless Steel symmetrical cell at O.C.V. at 45 °C, demonstrate that the membrane was able to retain its high ionic conductivity for more than 1 month. In fact, no losses of RTILs and/or phase separation occurred (no shifts of the real axis intercepts and deviation from linearity were observed).

The interfacial stability towards the lithium metal electrode at ambient temperature is not at the level of the remarkable properties just recalled. The impedance response of the Li/ILBM-60/Li symmetrical cell at progressively longer contact periods of time under open circuit voltage (O.C.V.) conditions at ambient temperature is shown in Fig. 8. The impedance response evolved as an elongated semicircle containing the charge transfer process and the passivation layer formation. The real component of the impedance at the lowest frequency is representative of the Li/electrolyte interfacial resistance, being the combination of electrolyte, charge transfer and passivation layer resistances [12,23,24]. The observed variations of the interfacial resistance in time are due to the passivation layer modification with time. As a general behaviour, after a first enhancement of the impedance, due to the increase of the layer depth, the layer characteristics stabilise giving a lower and constant value of the interfacial resistance.

In our case, it can be observed that there was an increase in the interfacial resistance within the first days of storage, indicating an
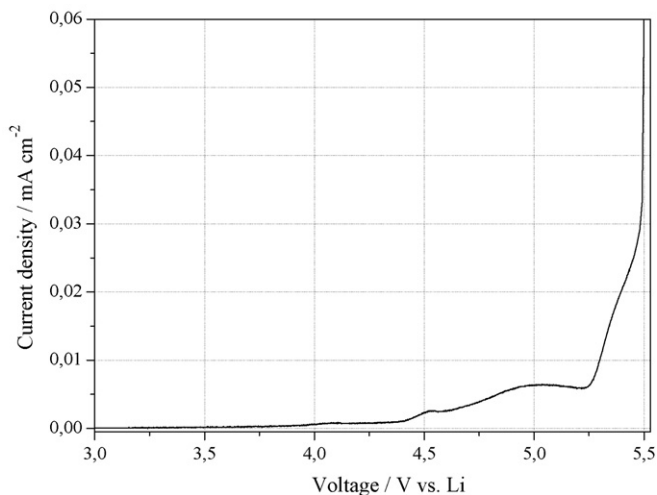
Fig. 7. Current–voltage curves at 25 °C of the ILBM-60 polymer electrolyte membrane. Cell configuration adopted: acetylene black carbon over Al current collector as working electrode, Li metal as counter electrode and the given membrane as separator. Anodic potential scan range from O.C.V to 5.5 V vs. Li at 0.100 mV s^{-1}.
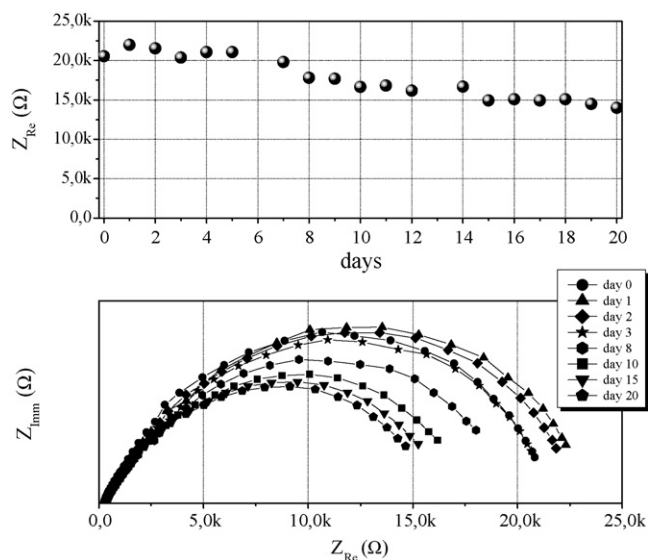
Fig. 8. Time evolution of the impedance spectra (upper layer, A) and Nyquist plots (lower layer, B) of a Li/ILBM-60/Li symmetrical cell, stored under O.C.V. conditions at ambient temperature. Electrode area: 0.785 cm². Frequency range: 1 Hz to 100 kHz.

increase in the thickness of the passivation layer. The initial (day 0) low frequency real part impedance value reported in the upper plot was surely high, but it reduced with time and stabilised very soon to a value below 15,000 Ω within 10 days. On the contrary, the variation with time of the electrolyte resistance (i.e., the high-frequency real part impedance value) was almost negligible at room temperature, pointing towards that the RTIL embedded into the polymer network does not lose its properties because of the non-volatile nature of the RTIL, and it shows good compatibility with lithium metal.

Moreover, as it can be found in the literature [23,24], the inter-facial resistance values are very much affected by the temperature and, in most of the cases, satisfying values can only be obtained at higher temperatures. We verified that this was true even for our membranes: in fact, when the temperature was raised to 45 °C the real part of the low frequency impedance lowered by twofold, while the total interfacial resistance showed a fivefold lowering, even decreasing with time and stabilising very soon. This is the reason why we have carried out our lithium polymer cell electrochemical tests at 45 °C.

3.4. Electrochemical response of a polymer electrolyte membrane in a Li polymer cell

Experimental investigations, carried out on a large number of membranes of different compositions, pointed out that the amount of RTILs present in the polymer electrolyte membrane can markedly affect its electrochemical behaviour. In fact, as the membrane becomes more affluent in RTIL content, ionic conductivity increases. However, excessively high concentration of RTIL pro-gressively reduces the self-standing properties of the membrane and, consequently, its mechanical integrity, thus impairing the long term electrochemical performance. Accordingly, though ILBM-70 showed the best ionic conductivity values among the membranes tested, due to the very high amount of RTIL encompassed, it was dif-ficult to handle and its mechanical integrity after prolonged cycling was unsatisfactory. This is the reason why we report herewith the results of the electrochemical tests carried out on a sample mem-brane called ILBM-63, in which the exact composition of the system is BEMA:EMPFSI:LiTFSI = 27:63:10. The characteristics of the ILBM-63 membrane (i.e., thermal properties, ionic conductivity values
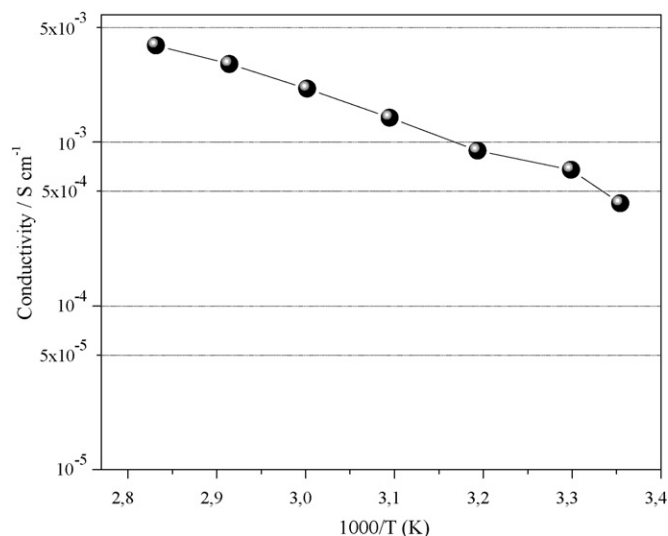

Fig. 9. Ionic conductivity as a function of temperature of ILBM-63 polymer elec-trolyte membrane. Data obtained by impedance spectroscopy.

and anodic breakdown voltage) are shown in Table 2, together with the results obtained for ILBM-60. ILBM-63, whose character-istics are very similar to ILBM-60 as clearly evident in Table 2, has been here chosen because its ratio of oligomer to RTIL is the opti-mum compromise between enhanced electrochemical behaviour and mechanical properties. In fact, as evident in the Arrhenius plot of Fig. 9, the sample ILBM-63 shows high ionic conductivity val-ues, which are very close to the values obtained for ILBM-70 and notably higher than ILBM-60 (see Fig. 6 for comparison). Moreover, its mechanical integrity was at the level of ILBM-60 membrane, and far better than ILBM-70.

To demonstrate the possible practical application of the ILBM-63 polymer membrane as an electrolyte, a lithium polymer cell was assembled and its galvanostatic charge/discharge cycling behaviour at 45 °C was investigated. The response of the cell, assembled by combining a lithium metal anode with a LiFePO$_4$/C cathode and using the ILBM-63 membrane as the separator, is reported in Figs. 10 and 11.

Fig. 10 shows the galvanostatic charge and discharge profiles at C/10 current regime with respect to the LiFePO$_4$ cathode (theo-retical specific capacity ≅170 mAh g^{-1}) after 10 cycles. The charge and discharge step average potential values (i.e., approx. 3.5 and
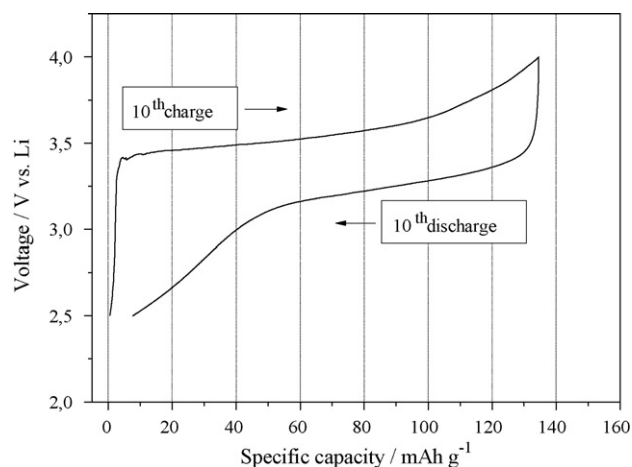
Fig. 10. Galvanostatic charge–discharge profiles of the lithium polymer cell, assembled by sandwiching the ILBM-63 polymer electrolyte membrane between LiFePO$_4$/C cathode and Li metal anode, at 45 °C and C/10 current rate (17 mA g^{-1}).

Table 2
Comparison between the main characteristics of the ILBM-63 and ILBM-60 polymer electrolyte membranes. ILBM-63 membrane composition is BEMA:EMIPFSI:LiTFSI = 27:63:10, the percentage of radical photo-initiator added was 3 wt.%.

	Thermal stability ($^\circ$C)	T_g ($^\circ$C)	Ionic conductivity (S cm^{-1})	Anodic breakdown voltage (V)
ILBM-63	>250	−48.8	1.3×10^{-3} at 50 $^\circ$C	$\cong$4.5
ILBM-60	>250	−45.1	7.0×10^{-4} at 50 $^\circ$C	$\cong$4.5

3.2 V vs. Li, respectively) and the lack of flatness of the plateaus clearly indicate that an important contribution to irreversibility is present. Comparing the results reported in Meligrana et al. [19], obtained for a similar LiFePO$_4$/C system with a liquid electrolyte, one can attribute the high charge to discharge potential difference and the shape of the plateaus to an ohmic chute. This drop probably takes place at the electrodes–membrane interfaces and it is a critical point for all solid electrolytes. Another possible explanation is related to the Li$^+$ transport through the membrane which could be difficult (the Li-ion transport number on these membranes is under evaluation).

Nonetheless, Fig. 11 shows that the cycling behaviour of the system is of some significance. During the first cycle, the cell delivers a specific capacity of approx. 155 mAh g^{-1} on charge (130 mAh g^{-1} on discharge) when using a low current density of C/10; that is approximately 0.92 lithium atoms per formula unit can be extracted from the LiFePO$_4$ structure at an average circuit voltage of 3.52 V vs. Li, and a slightly lower amount can be reversibly inserted back into the FePO$_4$ structure upon discharge. As the number of cycles increases, the voltage plateau and the specific discharge capacity decrease only slightly. Actually, during the 10th cycle at C/10 current regime, the cell is able to deliver a discharge capacity of approx. 127 mAh g^{-1} at an average circuit voltage of about 3.32 V vs. Li; that is approx. 0.75 lithium atoms per formula unit can be reversibly inserted back into the structure upon discharge. By increasing the current density to C/5 rate, the cell delivers an average discharge capacity of about 118 mAh g^{-1}; that is approx. 0.70 lithium atoms per formula unit can be reversibly inserted back into the structure upon discharge. Thus, these data suggest the specific capacity is not much influenced by the increase in the C-rate.

The coulombic efficiency (i.e. the ratio between the specific discharge capacity and the specific charging capacity) is low (about 85%) during the first cycles; then, after five cycles it is 95% and it is maintained to be higher than 99% after the 10th cycle, at C/5 current rate. The low initial cycling efficiency can be related to dif-ferent phenomena. A well-known behaviour typical of the LiFePO$_4$ cathode implies an initial induction period, whose description is reported in [19,27]. The increase in coulombic efficiency can also be associated with an improved interfacial behaviour during the charge–discharge cycles of the cell lowering the problems of Li-ion transport. These hypotheses will be confirmed or discarded by an extensive and thorough impedance analysis of the cell during repeated cycling [25,26]. The rate capability of the lithium metal polymer cell was also good, with a slight decrease in both average discharge voltage and discharge capacity.

4. Conclusions

The preparation of new UV-cured polymer electrolyte membranes encompassing RTILs seems very promising. By a UV-induced process, we were able to produce electrolytes with good ionic conductivity even at ambient temperature along with very high thermal stability up to 250 $^\circ$C. The anodic breakdown voltage is high, above 4.4 V vs. Li. This is a significant achievement if one considers high potential cathode materials which are particularly interesting to increase the accumulator power density. The results regarding the electrochemical behaviour are, as preliminary data, satisfying.
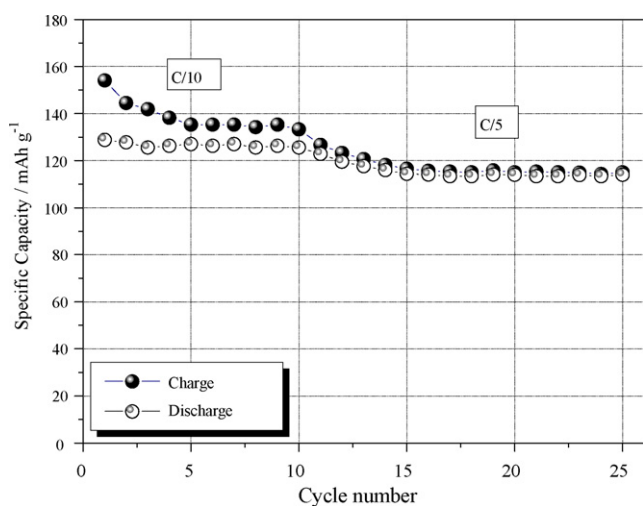
If one adds the intrinsic safety, eco-compatibility, low production time and easy industrialisation features of the materials proposed and their preparation processes, these results lead us to consider that these polymer electrolyte membranes show promising perspectives in the field of lithium-based batteries for portable and automotive applications and it is worth a hard research work to enhance their properties.

Acknowledgement

Fig. 11. Galvanostatic charge–discharge cycling test of the lithium polymer cell, assembled by sandwiching the ILBM-63 polymer electrolyte membrane between LiFePO$_4$/C cathode and Li metal anode, at 45 $^\circ$C and different C-rates (from C/10 = 17 mA g^{-1} to C/5 = 34 mA g^{-1}).

References

[1] J.-M. Tarascon, M. Armand, Nature 414 (2001) 359.
[2] B. Scrosati, Chem. Rec. 5 (2005) 286.
[3] A.S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, W. Van Schalkwijk, Nat. Mater. 4 (2005) 366.
[4] T. Welton, Chem. Rev. 99 (1999) 2071.
[5] D. Adam, Nature 407 (2000) 938.
[6] Y.S. Fung, S.M. Chau, J. Appl. Electrochem. 23 (1993) 346.
[7] D.R. MacFarlane, J. Huang, M. Forsyth, Nature 402 (1999) 792.
[8] P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168.
[9] J.-H. Shin, A. Henderson, S. Passerini, Electrochem. Commun. 5 (2003) 1016.
[10] C. Decker, Prog. Polym. Sci. 21 (1996) 593.
[11] M. Song, J. Cho, B.W. Cho, H. Rhee, J. Power Sources 110 (2002) 209.
[12] J. Nair, C. Gerbaldi, G. Meligrana, R. Bongiovanni, S. Bodoardo, N. Penazzi, P. Reale, V. Gentili, J. Power Sources 178 (2008) 751.
[13] C. Gerbaldi, J. Nair, C. Bonatto Minella, G. Meligrana, G. Mulas, S. Bodoardo, R. Bongiovanni, N. Penazzi, J. Appl. Electrochem. 38 (2008) 985.
[14] C. Gerbaldi, J. Nair, G. Meligrana, R. Bongiovanni, S. Bodoardo, N. Penazzi, J. Appl. Electrochem. 39 (2009) 2199.
[15] S. Ahmad, M. Deepa, S. Singh, Langmuir 23 (2007) 11431.
[16] S. Ahmad, M. Deepa, Electrochem. Commun. 9 (2007) 1635.
[17] International Union of Pure and Applied Chemistry, IUPAC Gold Book, Compendium of Chemical Terminology, IUPAC Publications, 2006.
[18] G.B. Appetecchi, F. Croce, A. De Paolis, B. Scrosati, J. Electroanal. Chem. 463 (1999) 248.

[19] G. Meligrana, C. Gerbaldi, A. Tuel, S. Bodoardo, N. Penazzi, J. Power Sources 160 (2006) 516.
[20] H. Vogel, Z. Phys. 22 (1922) 645.
[21] V.G. Tamman, H.G. Hesse, Z. Anorg. Allg. Chem. 19 (1926) 245.
[22] G.S. Fulcher, J. Am. Ceram. Soc. 8 (1925) 339.
[23] F. Croce, A. D'Epifanio, J. Hassoun, P. Reale, B. Scrosati, J. Power Sources 119–121 (2003) 399.
[24] L. Persi, B. Scrosati, E. Plichta, M.A. Hendrickson, J. Electrochem. Soc. 149 (2002) A212.
[25] H.S. Choe, J. Giaccai, M. Alamgir, K.M. Abraham, Electrochim. Acta 40 (1995) 2289.
[26] D.-W. Kim, B.-K. Oh, Y.-M. Choi, Solid State Ionics 123 (1999) 243.
[27] S. Bodoardo, C. Gerbaldi, G. Meligrana, A. Tuel, S. Enzo, N. Penazzi, Ionics 15 (2009) 19.