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ORIGINAL PAPER

Highly ionic conducting methacrylic-based gel-polymer electrolytes by UV-curing technique

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Abstract Today, special interest is focused on polymer systems showing high ionic conductivity at ambient and/or sub ambient temperatures, since they find unique practical applications, such as separators in high power, versatile, rechargeable Li-based batteries. Thermo-set membranes prepared by free radical photo polymerisation (UV-curing) could be an interesting alternative to existing polymer electrolytes. In the present paper, we report the application of this technique to the synthesis of gel-polymer membranes which can be used as electrolytes for lithium battery application. These membranes are prepared by mixing a dimethacrylic (BEMA) and/or a diacrylic monomer (PEGDA), a methacrylic reactive diluent (PEGMA) and a radical photo-initiator with the in situ addition of a EC/DEC solution. The above mixtures are UV irradiated to obtain transparent, flexible, easy to handle gel-polymer films. The gel-polymer electrolytes (GPEs) are then prepared by swelling these membranes in different liquid electrolytes. The results obtained indicate some superior and satisfactory performances in terms of ionic conductivity at ambient temperature for various GPEs prepared with different lithium salt solutions. The relevance of these features in view of practical application is here demonstrated by the response of lithium cells based on prepared GPEs.

Keywords UV-curing · Acrylate · Methacrylate · Gel-polymer electrolyte · Ionic conductivity · Lithium polymer cell

1 Introduction

The development of advanced materials for energy storage and conversion has been receiving wide attention to meet the rising demand for clean energy technologies. In particular, a large effort is being 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.

Beyond the others, rechargeable lithium polymer batteries, which are generally formed by a lithium metal anode, a polymer electrolyte separator 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 densities, good cyclability, reliability and safety [1–3].

Although a commercial reality, these power sources are still the object of intense R&D aiming to improve their performances for high-end applications [4, 5]. High performing innovative materials are fundamental for all the three main components of the cell, i.e. anode, cathode and electrolyte. The electrode materials need to have high capacity and durability, while the electrolyte should be a membrane capable of high ionic conductivity even at ambient temperature, with good mechanical and interfacial properties and stable performances. In all cases, the materials must be low cost, ecologically friendly and safe.

In line with this tendency, in the recent years our research group carried out a systematic investigation on those materials which appear particularly promising for the

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development of lithium-based batteries with improved characteristics and performances [6–10].

In the polymer electrolyte area our efforts were concentrated on novel methacrylic-based gel-polymer membranes, prepared by free radical photo polymerisation (UV-curing) which is a well established polymerisation technique, taking place at room temperature under UV light [11]. The potentials of this technique, commonly employed for the preparation of coatings and inks and for the production of optical and electronic devices, can be diverted to our field of interest to obtain very fast and low-cost production with an environmentally friendly approach, as the use of solvent is almost avoided [12]. In fact, highly cross-linked polymers are readily synthesized by the irradiation of appropriate formulations of mono and multifunctional monomers, namely acrylates and methacrylates, in the presence of a proper free radical photo initiator [7].

In our previously published papers, we have illustrated and discussed about the application of free radical polymerisation to prepare methacrylic-based gel-polymer electrolytes (GPEs) which can be used as electrolytes for lithium battery application [7, 8]. The process was very easy, reliable and rapid and the obtained membranes showed good behaviour in terms of both ionic conductivity and cyclability in lithium cells.

We have recently extended our investigations on these thermo-set membranes as gel-polymer electrolytes in different directions, i.e. substituting the dimethacrylic monomer (BEMA) with a diacrylic monomer (PEGDA) and comparing the characteristics of the resulting membranes. Moreover, research on the BEMA-based GPE has been deepened by both improving its ionic conductivity and studying the effect of different liquid electrolytes on this highly cross-linked 3D-network. The obtained results have been reported in the present paper. Finally, the promising perspectives of such kind of GPEs in the field of lithium-based batteries are illustrated by the experimental data reported on the electrochemical response of a lithium polymer cell laboratory prototype.

2 Experimental

2.1 Synthesis

The reactive formulation for the preparation of gel-polymer membranes was based on a dimethacrylic monomer, i.e. bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA, average M_n: 1700, Aldrich), and/or a diacrylic monomer, i.e. poly(ethylene glycol) diacrylate (PEGDA, avg. M_n: 700, Aldrich). Poly(ethylene glycol) methyl ether methacrylate (PEGMA, avg. M_n: 1100, Aldrich) was used as reactive diluent which can control the cross-linking during polymerisation. 2-hydroxy-2-methyl-1-phenyl-1-propanon (Darocur 1173, Ciba Specialty Chemicals) was the free radical photo-initiator. Ethylene carbonate and diethyl carbonate (EC-DEC, Ferro Corp., battery grade) solutions were used as plasticiser. Before their use, all chemicals were kept open in the inert atmosphere of an Ar-filled dry glove box for several days and also treated with molecular sieves (Molecular sieves, beads 4 Å, 8–12 mesh, Aldrich) to assure the complete removal of traces of water from the monomers, as they may create problems in long-term properties when these membranes are considered for application as electrolytes in rechargeable lithium batteries.

A polymeric membrane (hereafter named BMPE) was obtained by UV-curing a reactive mixture of BEMA and PEGMA in 70:30 ratio, in the presence of 2 wt% of free radical photo-initiator. Another polymeric membrane (hereafter named PDPE) was obtained replacing BEMA by PEGDA. The PEGDA to PEGMA ratio was again 70:30, in the presence of 2 wt% of free radical photo-initiator. In both cases, once the preformed monomer mixtures were made, a 45 wt% of 1:1 w/w EC-DEC solution was added, thus maintaining the overall monomers to plasticiser ratio =55:45.

The mixtures prepared were later drawn into films by coating them onto glass plates with a calibrated, wire-wound applicator to obtain a thickness of about 200 μm. The coated plates were then exposed to UV-irradiation for approx. 3 min in three steps, each of 1 min. The photochemical 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}. These conditions assured maximum curing (disappearance of the methacrylic double bonds, checked by FT-IR). During the overall process, the samples were held under a pure N_2 atmosphere in small sealed boxes equipped with a quartz window. Later free films were peeled off from the glass plates.

The second preparation step involved the activation of the precursor polymer membranes by soaking them into a proper liquid electrolyte swelling solution for about 2 h. A 1.0 M $LiPF_6$ in EC/DEC (1:1 w/w) solution (Ferro Corp., battery grade) was used to swell both the BMPE and PDPE membranes. In a different experiment, two other swelling solutions were used, i.e. 1.0 M LiTF (lithium trifluoromethane-sulfonate, $LiCF_3SO_3$) in EC/DEC (1:1 w/w) and 1.0 M LiTFSI (lithium bistrifluoromethane-sulfonimidate, $CF_3SO_2NLiSO_2CF_3$) in EC/DEC (1:1 w/w) (Ferro Corp., battery grade), in order to evaluate the effect of these different kinds of liquid electrolytes on the ionic conductivity of the thermo-set membranes.

By the above-explained method we are able to produce transparent, flexible and easy to handle films of varying thickness (measured with a Vernier digital calibre) and

Li^+-ion content, with an active swelling percentage of more than 50 wt%. Overall this process usually takes less than 3 h for the production of ready-to-use gel-polymer membranes.

All the above reported procedures were performed in the inert atmosphere of an Ar-filled dry glove box (MBraun Labstar, O_2 and H_2O content <0.1 ppm).

2.2 Analyses and film characterisation techniques

The characterisation of the UV-cured film included the evaluation of the kinetics of the photo-polymerisation, the determination of the gel content, differential scanning calorimetry and thermo-gravimetric analyses.

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 of the band attributable to the methacrylate groups at 1630 cm^{-1}. The tests were carried out at ambient temperature on a SiC wafer, which is transparent to UV, 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 an ORIEL photometer.

The gel content of the cured products was determined by measuring the weight loss of the samples contained in a metal net after 24 h extraction at room temperature with chloroform (relative error = ±1%) [13–15].

The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) measurements, performed with a METTLER DSC-30 (Greifensee, Switzerland) instrument equipped with a low temperature probe.

The thermal stability was tested by thermo-gravimetric analysis using a TGA/SDTA-851 instrument from METTLER (Switzerland) under N_2 flux at a heating rate of 10 °C min^{-1}. Temperature range = 25–600 °C for the neat polymers, 25–200 °C when the membranes contained the EC/DEC solution.

2.3 Electrochemical characterisation techniques

The ionic conductivity of the gel-polymer membrane at various temperatures was determined by electrochemical impedance spectroscopy (EIS) analysis of cells formed by sandwiching discs of 0.785 cm^2 of the given GPE between two stainless-steel 316 blocking electrodes. The cells were housed in an oven to control the temperature. A PARSTAT 2273 instrument 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 Power Suite software (version 2.58, Princeton Applied Research).

The gel-polymer electrolytes were tested for interfacial stability with the lithium metal electrode by monitoring the time evolution of the impedance response of a symmetrical Li/GPE/Li cell at room temperature.

The electrochemical stability window was evaluated by running a sweep voltammetry in a 2-electrodes Teflon-made Swagelok cell. Acetylene black over Al current collector and Li metal as electrodes and the given membrane as electrolyte was the cell configuration adopted for anodic scan (potential scan range from O.C.V. to 6.0 V vs. Li), while Cu foil and Li metal as electrodes and the given membrane as electrolyte was the cell configuration adopted for cathodic scan (potential scan range from O.C.V. to 0.0 V vs. Li). In both cases, the potential scan rate used was 0.100 mV s^{-1}. The current onset of the cell was associated with the decomposition voltage of the electrolyte.

The lithium polymer cell laboratory prototypes were assembled by contacting in sequence a lithium metal disk anode, a layer of the gel-polymer electrolyte and a $LiFePO_4$/C disk composite cathode (electrode area: 0.785 cm^2). The latter was prepared in the form of thin film by spreading on an Al current collector, by the so-called “doctor blade” technique, a N-methyl-2-pyrrolidone (NMP, Aldrich) slurry of the $LiFePO_4$ active material (82 wt%, typically about 3 mg cm^{-2}) with carbon black as electronic conducing additive (10 wt%, Shawinigan Black AB50, Chevron Corp., USA) and poly(vinylidene fluoride) as binder (8 wt%, PVdF, Solvay Solef 6020). High surface area nanostructured $LiFePO_4$/C was obtained by a quick and low cost mild hydrothermal synthesis in the presence of an organic surfactant as reported in a previous work [6]. The electrodes/electrolyte assembly was housed in a Teflon-made Swagelok cell equipped with two stainless-steel 316 current collector electrodes. Both electrode fabrication and cell assembly were performed in the environmentally controlled Ar-filled dry glove box. The lithium cell prototypes were tested for their electrochemical performance at room temperature in terms of charge/discharge galvanostatic cycling at different current regimes using an Arbin Instrument Testing System model BT-2000.

3 Results and discussion

3.1 Chemical and structural characterization of the polymer membranes

The gel-polymer membrane obtained by copolymerising the monomers BEMA and PEGMA with the in situ addition of the EC-DEC (1:1 w/w) solution on exposure to UV irradiation, namely BMPE, is a transparent, freestanding, extremely flexible and non-sticky membrane, as shown in Fig. 1. Its most relevant chemical and structural characteristics have been already discussed in Nair et al. [7] and they are summarised in Table 1.

The di-functional monomer BEMA, whose structure is shown in Fig. 2, can be readily polymerised by UV-curing, resulting in a highly cross-linked thermo-set membrane, which is rather flexible and, at the same time, resistant up to 300 °C [7, 11]. The mono-functional monomer PEGMA (see the structure in Fig. 3), which acts as a reactive diluent and it is incorporated into the network, is added in order to control the cross-linking density and to reduce the T_g of the membranes. Moreover, it increases the mobility of lithium ions inside the polymer matrix and it enhances the ionic conductivity by the presence of pendant ethoxy groups. EC-DEC solution was added to the monomers mixture to further reduce the T_g and to enhance the Li^+ transport as it is a major component of generally used liquid electrolytes for lithium battery systems.

Figure 4 shows the differential scanning calorimetry curves, obtained in the −140 to 100 °C range, for BMPE prepared both with and without the addition of the EC-DEC solution. The value of T_g for BMPE membrane, synthesised using BEMA and PEGMA monomers without the addition of EC-DEC solution (curve A in Fig. 4), is detected to be below −44 °C, indicating that at room temperature the polymer membrane is in a rubbery state. T_g is further reduced to the very low value of −61.1 °C due to the in situ addition of 45 wt% of EC-DEC (1:1 w/w) solution (see curve B in Fig. 4). Though the $T_g < -60$ °C, the membrane is still self withstanding, extremely flexible and easy to handle.

Fig. 1 Appearance of the BMPE gel-polymer membrane obtained by copolymerising the monomers BEMA and PEGMA via UV irradiation with the in situ addition of the 1:1 w/w EC-DEC solution

The polymer membrane PDPE was prepared by incorporating PEGDA into the system in place of BEMA. The diacrylate monomer PEGDA, whose structure is shown in Fig. 5, has the same structural characteristics of BEMA, like low T_g and flexible ethoxy group to enhance the Li^+ ions transport. In both the polymers, the concentration of PEGMA was same, that is 17 wt%, with 45 wt% of EC-DEC (1:1 w/w) solution.

As shown in Table 1, the chemical and structural characteristics of PDPE polymer membrane are almost similar to that of BMPE. The percentage of double bond (>C=C<) conversion during UV exposure was evaluated from kinetic studies using real-time FT-IR technique. Results obtained show that the reactivity of the monomers mixture in PDPE was very high and a quantitative yield of about 91% can be obtained in less than 80 s. The gel content, which represents the percentage of materials insoluble in chloroform, was found to be 94.8%, thus indicating the high cross-linking of this thermo-set material. This test was carried out for polymers prepared without the addition of EC-DEC solution. The results obtained are in good agreement with the conversion results obtained by the kinetics studies. Thus, PDPE shows only a little less conversion rate and gel-content percentage. These may be due to the higher reactivity and concentration of acrylate functional groups in the monomer mixtures. In fact, acrylate groups rapidly forms the cross-linking, thus restricting the mobility of unreacted groups in the polymer system at higher conversion rates if compared to the methacrylate groups.

The thermal stability of the polymeric film was assessed by thermo-gravimetric analysis under flowing nitrogen. In the temperature range between 25 and 600 °C the thermal stability of the PDPE membrane is high, up to 300 °C. Even though the EC-DEC addition reduced the thermal stability up to approx. 120 °C, when the solvents began to evaporate, it is well in the limit of applications as electrolyte for lithium battery. This result indicates that the gel-polymer membrane can be safely used in lithium polymer batteries up to 100 °C.

3.2 Electrochemical characterization

In view of its possible application as electrolyte in lithium polymer batteries, BMPE was swelled in 1.0 M $LiPF_6$ in EC-DEC (1:1 w/w) solution. The membrane was soaked in this electrolyte solution for about 2 h. The percentage of active swelling was higher than 60%. This lithium salt doped BMPE was tested in terms of its general electrochemical properties.

The membrane PDPE was also prepared as electrolyte in the same way as that of BMPE and tested for its electrochemical properties. As already reported, the difference of PDPE from BMPE is that the former one had PEGDA

Table 1 Brief summary of the most relevant features of the synthesized gel-polymer membranes

Sample	Conversion (%)	Gel content (%)	Swelling (%)	TGA analysis (°C)	T_g (°C)
BMPE	98	98.9	61	~300/~120	−61.2
PDPE	91	94.8	59	~300/~120	−59.7

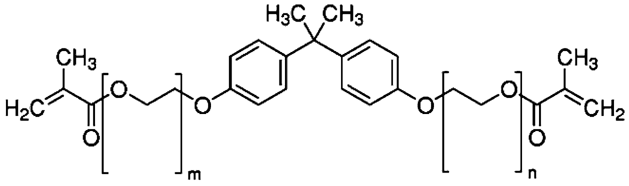

Fig. 2 Structure of bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA); m and n are the numbers of ethoxy repeating units in the individual species

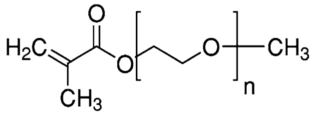

Fig. 3 Structure of poly(ethylene glycol) methyl ether methacrylate (PEGMA); n represents the numbers of ethoxy repeating units in the individual species

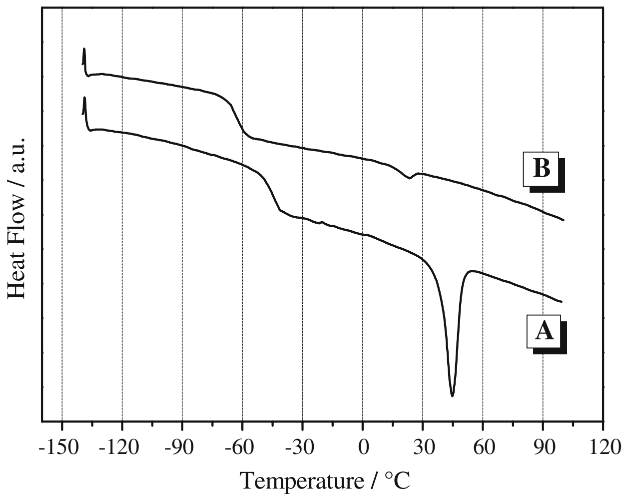

Fig. 4 DSC curves of BMPE membrane prepared both without (A) and with (B) the addition of 1:1 w/w EC:DEC solution

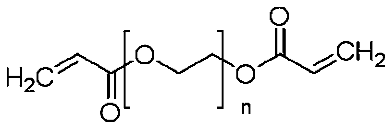

Fig. 5 Structure of poly(ethylene glycol) diacrylate (PEGDA); n represents the numbers of ethoxy repeating units in the individual species

instead of BEMA as multifunctional monomer. PEGDA was used in the system to study the effect of the addition of more pure ethoxy functional group. Actually, as BEMA has a bulky bisphenol A group in the centre of the chain, it may restrict the flexibility.

The ionic conductivity was evaluated by impedance spectroscopy and the Arrhenius plots are shown in Fig. 6. The ionic conduction in gel-polymer electrolytes follows the VTF (Vogel-Tamman-Fulcher) relation [16–18] which describes the transport properties in a viscous matrix. At sufficiently high temperatures, as in our case, the VTF behaviour approaches Arrhenius behaviour. The BMPE membrane showed an ionic conductivity of 2.1×10^{-3} S cm^{-1} at room temperature, which is almost comparable with that of common liquid electrolytes used for lithium battery applications. The ionic conductivity increased with increase in temperature, resulting in the high value of 8.7×10^{-3} S cm^{-1} at 80 °C. The ionic conductivity values reported here are higher with respect to what has been shown in Nair et al. [7] because of the purification procedure by molecular sieves we have adopted for the reactive monomers in order to completely remove moisture or other impurities, and also because of the higher degree of purity of the battery grade solutions used for the tests here reported. 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 PDPE was 6.7×10^{-4} S cm^{-1} at room temperature, increasing with temperature to 3.2×10^{-3} S cm^{-1} at 80 °C.

This result suggests that the ionic conduction of lithium ions into the polymer network was not improved by the addition of PEGDA. This may be due to the lesser chain length of PEO groups in PEGDA and, also, to an increase in the cross-linking density due to the increase in number of acryl functional groups. Actually, as the molecular weight of PEGDA is 700, the same percentage in weight of PEGDA in place of BEMA increases the number of acryl group, resulting in a lesser flexible film. Thus, though the addition of PEGDA increased the mechanical properties, it inversely reduced the ionic conductivity.

Once the BMPE characteristics were studied with the $LiPF_6$-based electrolyte, it is again compared with other commercially available generally used high performing salts, i.e. LiTF and LiTFSI, in terms of ionic conductivity. Figure 7 shows the ionic conductivity of BMPE in the three different electrolyte solutions. The swelling was carried out for same amount of time (i.e. about 2 h) for all the electrolytes and the active swelling percentage was

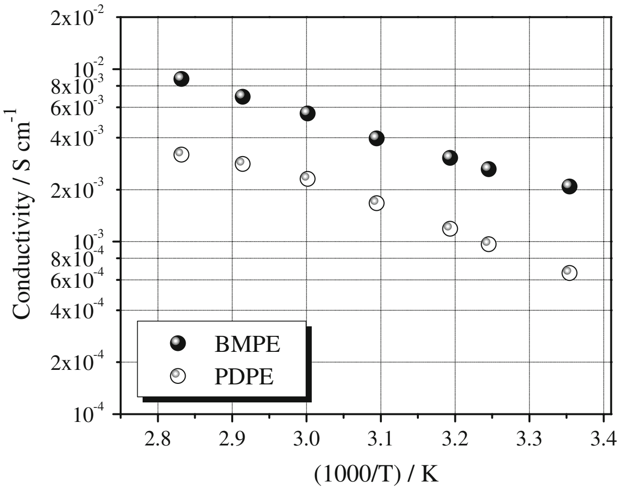

Fig. 6 Ionic conductivity vs. temperature plots of BMPE and PDPE gel-polymer membranes, swelled in 1.0 M LiPF$_6$-EC-DEC solution. Data obtained by impedance spectroscopy

very similar, close to 60 wt%. From the figure it is observed that the LiTFSI-BMPE shows the highest ionic conductivity, i.e. 2.9×10^{-3} S cm^{-1} at ambient temperature and 1.8×10^{-2} S cm^{-1} at 80 °C. These are very high values, and such a result is in good agreement with data published by different research groups stating that LiTFSI could be a better liquid electrolyte both in case of safety, electrochemical stability window and ionic conductivity.

In addition to high ionic conductivity, BMPE membrane shows a series of interesting properties that make it particularly valuable in view of practical battery application. One is the wide electrochemical stability window. This is shown in Fig. 8 which illustrates the full current-voltage response of the gel-polymer membrane obtained in the voltage range between 0.0 and 6.0 V vs. Li at room temperature by combining both cathodic and anodic scan. The current drop related to the deposition of lithium on the copper substrate is clearly visible at the end of the cathodic scan (approx. 0 V vs. Li). Moreover, two important features can be recognised from the trend of this curve. First, the onset of the current during anodic scan, which is representative of the decomposition of the electrolyte, indicates an anodic break-down voltage of approx. 4.8 V vs. Li, showing that the GPE has a high anodic stability. Such a high decomposition voltage is certainly welcome for practical application. Secondly, 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 the prepared GPE and the synthesising method adopted, because the system as a whole is sensitive to oxygen, water and other impurities.

When PEGDA is used instead of BEMA an important difference can be detected (see the inset of Fig. 8, which shows the current-voltage curve at ambient temperature of the PDPE gel-polymer electrolyte). Even if the current rises at a lower voltage, its trend consistently deviates from that observed for BMPE, showing a sort of "passivation" phenomenon which apparently extends the anodic stability up to higher voltage, i.e. more than 5 V vs. Li. The reason for this particular behaviour is still unclear to us; however, such a high decomposition voltage is certainly welcome and, so, worth investigation further.

The properties of the lithium metal electrode/BMPE gel-polymer electrolyte interface were determined by monitoring its impedance response at progressively longer contact periods under open circuit voltage conditions. The impedance spectra of the Li/GPEs/Li symmetrical cell at

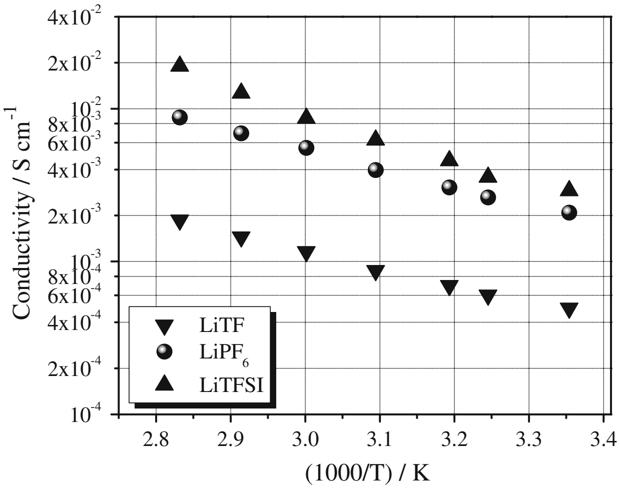

Fig. 7 Ionic conductivity vs. temperature plots of BMPE gel-polymer membrane, swelled in three different liquid electrolyte solutions, i.e. 1.0 M LiPF$_6$-EC-DEC, 1.0 M LiTFSI-EC-DEC and 1.0 M LiTF-EC-DEC. Data obtained by impedance spectroscopy

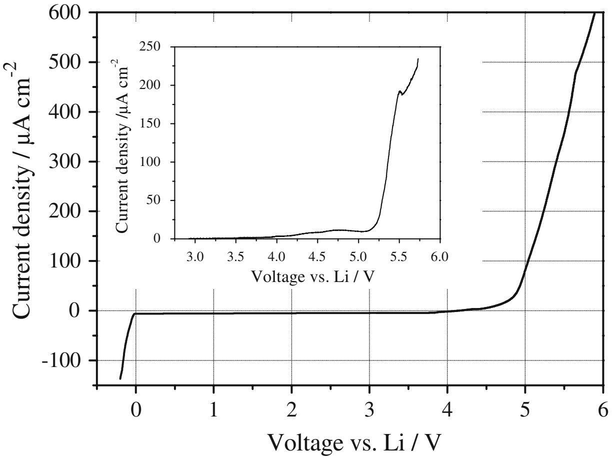

Fig. 8 Full electrochemical stability window at room temperature for BMPE gel-polymer electrolyte, swelled in 1.0 M LiPF$_6$-EC-DEC. In the inset: anodic stability window at room temperature for PDPE gel-polymer electrolyte swelled in 1.0 M LiPF$_6$-EC-DEC. Potential scan rate: 0.100 mV s^{-1}

various times under open circuit voltage (O.C.V.) conditions at ambient temperature are shown in Fig. 9. It is well known that the resistance of the cell is composed of the bulk resistance (R_b) of the electrolyte and the interfacial resistance (R_i) which reflects the interfacial situation between the electrodes and the electrolyte [19–21]. At high frequency, the intercept with the real part (Z_{re}) corresponds to the bulk resistance, and this allows calculation of the ionic conductivity of the GPE. This value showed a certain increase (approx. 30%) with time; still the liquid electrolyte embedded into the polymer network maintains, as a whole, its electrochemical properties because of the non-volatile nature of the organic solvents and it shows good compatibility with lithium metal [21].

The value of R_i increased quickly during the first three days which indicates the formation of the passivation layer on the surface of the lithium electrode as a result of the reactivity with the polymer electrolyte. It subsequently decayed and, finally, it almost stabilised at a value of 600 Ω cm^2, only slightly increasing with time, suggesting an overall good compatibility of this GPE with lithium metal.

3.3 Electrochemical response of the BMPE gel-polymer electrolyte in a lithium polymer cell

In view of the possible practical application of the BMPE gel-polymer electrolyte, to get a more thorough insight in its performances, it was assembled in a complete lithium polymer cell laboratory prototype, and its electrochemical behaviour was investigated by means of galvanostatic charge/discharge cycling. The response of the prototype, assembled by combining a lithium metal anode with a LiFePO$_4$/C cathode and using the BMPE membrane as the separator, is reported in Figs. 10 and 11.

In particular, Fig. 10 shows some typical voltage vs. time profiles, which are obtained at room temperature at various current rates with respect to LiFePO$_4$. The galvanostatic charge-discharge profiles reflect the good properties of the LiFePO$_4$/C cathode, namely appreciable specific capacity (a thinner polymer layer would surely help to raise the performances of the cell) and steepness of the plateau with minimum over-potential. In fact, the curves show very flat voltage plateaus at 3.47–3.55 V vs. Li on charge and at 3.38–3.30 V vs. Li on discharge. The flatness of the plateau is related to the biphasic Li$^+$ extraction/insertion mechanism typical of LiFePO$_4$ cathode.

The cell delivers a specific capacity of approx. 125 mAh g^{-1} on charge (115 mAh g^{-1} on discharge) when using a low current density of C/10; that is approximately 0.73 lithium atoms per formula unit can be extracted from the LiFePO$_4$ structure at a closed-circuit voltage of 3.47 V vs. Li, and slightly lower amount can be reversibly inserted back into the FePO$_4$ structure on discharge. As the current density increases, the voltage plateau and the specific discharge capacity decrease only slightly. Actually, at a high discharge rate of 1C, the cell is able to deliver a discharge capacity of approx. 98 mAh g^{-1} with a plateau at 3.35 V vs. Li; that is approx. 0.58 lithium atoms per formula unit can be reversibly inserted back into the structure on discharge. The voltage drop in passing from charge to discharge was observed to be small, which means lower resistance of the cell. Thus, the gel layer on both sides of GPE separator could promote strong interfacial adhesion between electrodes and separator, and the intimate contact may contribute to lower the interfacial resistance of the cell.

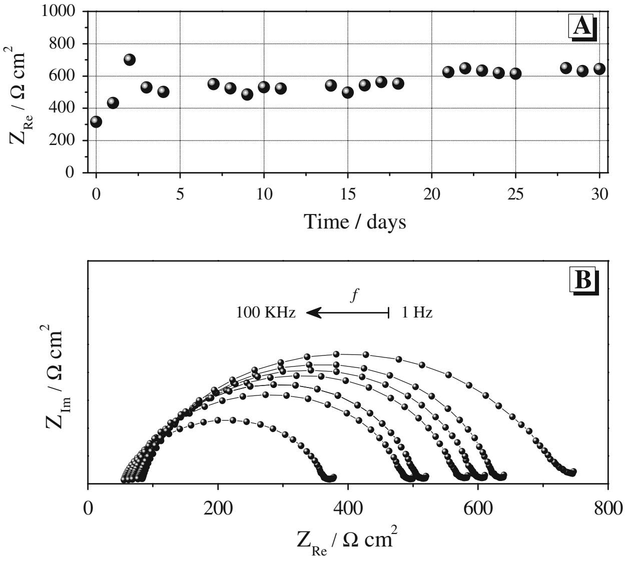

Fig. 9 Time evolution of the impedance spectra (upper layer, A) and Nyquist plots (lower layer, B) of a Li/BMPE/Li symmetrical cell, stored under O.C.V. conditions at ambient temperature. Electrode area: 0.5 cm^2. Frequency range: 1 Hz–100 KHz

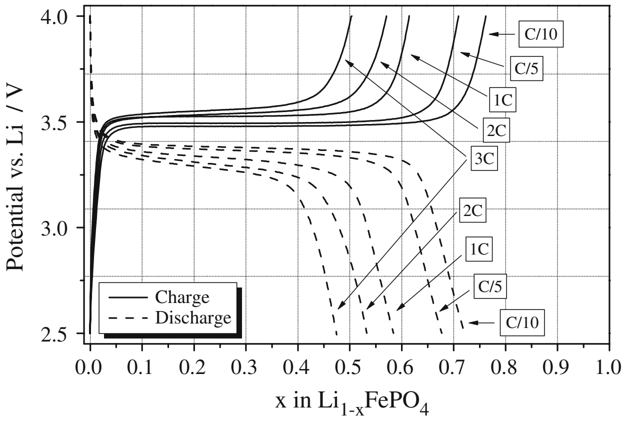

Fig. 10 Room temperature galvanostatic charge-discharge profiles of the lithium polymer cell, assembled by sandwiching the BMPE gel-polymer electrolyte between LiFePO$_4$/C cathode and Li metal anode, at different current rates (from C/10 to 3C)

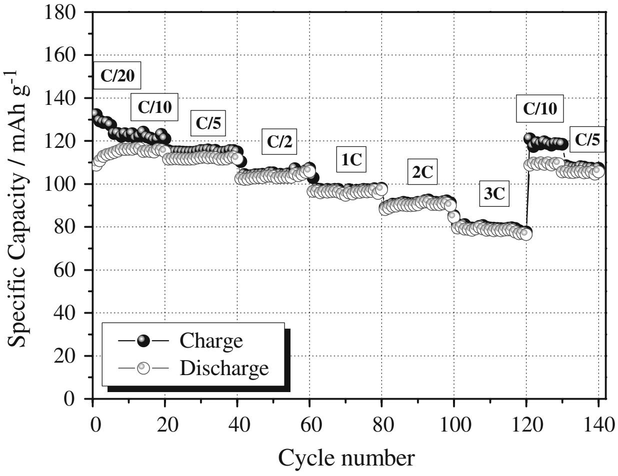

Fig. 11 Room temperature galvanostatic charge-discharge cycling test of the lithium polymer cell, assembled by sandwiching the BMPE gel-polymer electrolyte between $LiFePO_4$/C cathode and Li metal anode, at different C-rates (from C/20 to 3C)

Figure 11 shows the cycling performance of the cell as a function of cycle number, at room temperature and at different C-rates ranging from C/20 to 3C. This figure shows good capacity retention with the repeated cycling. This is a convincing indication of a good interfacial contact between electrodes and separator. The coulombic efficiency is quite low (about 86%) during the initial cycles; then, after ten cycles it is 95% and it is maintained to be higher than 99% after the 40th cycle, at C-rates higher than C/5. An increase of coulombic efficiency can be associated with an improved interfacial property during charge-discharge cycles of the cell. This presumption must be confirmed by ac impedance analysis of the cell with the repeated cycling [22, 23]. The rate capability of the lithium metal polymer cell was also good, with a slight decrease in both average discharge voltage and discharge capacity. Good performance at high current rate may be ascribed to the efficient ionic conduction in the polymer-coated separator and the favourable interfacial charge transport between electrodes and electrolyte in the cell. The extraction and insertion of lithium ions into the structure of $LiFePO_4$ is not only reversible on repeated cycling; the capacity actually increases slightly with the initial cycling. Moreover, reducing the C-rate completely restores the specific capacity (see, in Fig. 11, the restoring of the specific capacity values from 3C to C/10 after the 120th cycle).

4 Conclusions

UV-curing confirmed to be a suitable method for synthesizing membranes to be used as gel-polymer electrolyte for Li-based batteries. Compared to other techniques, it appears highly advantageous due to its easiness and rapidity in processing. The copolymerisation process and in situ incorporation of EC-DEC are fundamental to obtain gel-polymer electrolytes with high anodic breakdown voltage and high ionic conductivity even at ambient temperature.

Spreading of the research on GPEs prepared by UV curing technique pointed out some new and interesting suggestions. The preparation of a new polymer containing the monomer PEGDA instead of BEMA, to study the effect of the addition of more pure ethoxy functional groups, caused an increase in the cross-linking density due to the increase in number of acryl groups. As a consequence, the mechanical properties increased but the ionic conductivity was reduced. The electrochemical stability window is extended of about 0.3 V towards higher potential values; this is a significant achievement when one thinks to high potential cathode materials which are particularly interesting to increase the accumulator power density.

Investigations on different Li salt solutions gave interesting results regarding in particular LiTFSI-EC-DEC solution. The use of this liquid electrolyte to swell a BMPE membrane increased the ionic conductivity of the resulting gel-polymer electrolyte, and it could perhaps allow to better mechanical properties and higher potential stability.

The thorough analysis of the electrochemical behaviour of BMPE gel-polymer electrolyte put in evidence a number of good results not only regarding performance, which is in any case appreciable, but in particular the Li-electrolyte interfacial stability, the cycling durability and coulumbic efficiency. If one adds the intrinsic safety, eco-compatibility, low production cost and easy industrialisation features, these results lead us to conclude that these kind of GPEs show promising perspectives in the field of Li-based batteries for automotive applications.

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References

1. Scrosati B (1995) Nature 373:557
2. Scrosati B (2005) Chem Rec 5(5):286
3. Beaton SP, Bishop GA, Ziang Y, Ashbaugh LL, Lawson DR, Stedman DH (1995) Science 268:991
4. Tarascon J-M, Armand M (2001) Nature 414:359
5. Aricò AS, Bruce P, Scrosati B, Tarascon J-M, Van Schalkwijk W (2005) Nature Mat 4:366
6. Meligrana G, Gerbaldi C, Tuel A, Bodoardo S, Penazzi N (2006) J Power Sources 160:516
7. Nair J, Gerbaldi C, Meligrana G, Bongiovanni R, Bodoardo S, Penazzi N, Reale P, Gentili V (2008) J Power Sources 178:751
8. Gerbaldi C, Nair J, Bonatto Minella C, Meligrana G, Mulas G, Bodoardo S, Bongiovanni R, Penazzi N (2008) J Appl Electrochem 38:985

9. Mulas G, Enzo S, Bonatto Minella C, Arca E, Gerbaldi C, Penazzi N, Bodoardo S, Hassoun J, Panero S (2008) J Solid State Electrochem (in press). doi:10.1007/s100008-008-0529-z
10. Bodoardo S, Gerbaldi C, Meligrana G, Tuel A, Enzo S, Penazzi N (2008) Ionics (in press). doi:10.1007/s11581-008-0259-3
11. Decker C (1996) Prog Polym Sci 21:593
12. Song M, Cho J, Cho BW, Rhee H (2002) J Power Sources 110:209
13. Malucelli G, Priola A, Sangermano M, Amerio E, Zini E, Fabbri E (2005) Polymer 46:2872
14. Priola A, Gozzelino G, Ferrero F, Malucelli G (1993) Polymer 34:3653
15. Malucelli G, Gozzellino G, Bongiovanni R, Priola A (1996) Polymer 37:2565
16. Vogel H (1922) Z Phys 22:645
17. Tamman VG, Hesse HG (1926) Anorg Allg Chem 19:245
18. Fulcher GS (1925) J Am Ceram Soc 8:339
19. Croce F, Scrosati B (1993) J Power Sources 44:9
20. Nagasubramanian G, Attia AI, Halpert G (1994) J Appl Electrochem 24:298
21. Kim HS, Cho BW, Kim JT, Yun KS, Chun HS (1996) J Power Sources 62:21
22. Choe HS, Giaccai J, Alamgir M, Abraham KM (1995) Electrochim Acta 40:2289
23. Kim D-W, Oh B-K, Choi Y-M (1999) Solid State Ionics 123:243