

# UV-cured methacrylic membranes as novel gel–polymer electrolyte for Li-ion batteries

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## Abstract

In this paper, we report the synthesis and characterisation of novel methacrylic based polymer electrolyte membranes for lithium batteries. The method adopted for preparing the solid polymer electrolyte was the UV-curing process, which is well known for being easy, low cost, fast and reliable. It consists of a free radical photo polymerisation of poly-functional monomers: Bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA) was chosen, as it can readily form flexible 3D networks and has long poly-ethoxy chains which can enhance the movement of Li<sup>+</sup>-ions inside the polymer matrix. The preliminary results reported here refer to systems where LiPF<sub>6</sub> solutions swelled the preformed polymer membranes.

The tests on the conductivity, stability and cyclability of the membranes put in evidence the importance of the polymerisation in presence of mono-methacrylates acting as reactive diluents. Good values of ionic conductivity have been found, especially at ambient temperature. Much better results can be expected by choosing an appropriate mono-methacrylate to modify the polymeric membrane properties and by modifying the methodology of Li<sup>+</sup>-ions incorporation inside the polymer matrix.

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## 1. Introduction

The main efforts in the development of Li-ion battery systems are mostly addressed to the field of portable electronic devices. Consumer electronics needs an always increasing battery energy and power density, and a number of different case shapes allowing to fully utilise the limited volume at disposal. Moreover, the Li-ion system has succeeded in entering the huge market of electric vehicles (EVs) and hybrid-electric vehicles (HEVs) where high production volumes, low cost, ecological friendliness and high safety standards, beyond high specific performance, are a must [1–3]. In particular, the investigation of new materials for the electrolyte is one of the basic lines of research in the present scenario.

Polymer electrolytes represent the ultimate in terms of desirable properties of Li-ion batteries because they can offer an

all-solid-state construction, a wide variety of shapes and sizes, light-weight, low cost of fabrication and a higher energy density. No corrosive or explosive liquid can leak out and internal short-circuit are less likely, hence greater safety is guaranteed. All these attractive features make polymer Li-ion batteries the power sources of choice for the next generation of lightweight consumer devices [4,5].

Two classes of materials have been primarily used as polymer electrolyte: solvent-free membranes, formed by blending a thermoplastic polymer with the lithium salt and gel membranes formed by thermoplastic polymers trapping the liquid solution of the electrolyte. Typically, the solvent-free membrane is based on poly(ethylene oxide) and still suffer from poor conductivity at ambient temperature [6]. The gel membrane is made of poly(vinylidene fluoride), its preparation requires a long mixing and drying time to form a free-standing film and, once obtained, can dissolve in the same swelling solvent especially if the temperature increases. Thermoset membranes prepared by UV curing could be an interesting alternative to the present products.

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By the above-explained method we are able to produce flexible, transparent films of varying thickness (measured with a Vernier digital calibre) and Li<sup>+</sup>-ion content, with an active swelling percentage of more than 50 wt%. Overall this process usually takes less than 3 h for production of gel-polymer membranes.

## 2.2. Analyses and film characterisation techniques

The thermal stability of polymers was tested by thermogravimetric analysis using a TGA/SDTA-851 instrument from METTLER (Switzerland) under N<sub>2</sub> flux at a heating rate of 10 °C min<sup>-1</sup>. The temperature range varied from 25 up to 600 °C for the neat polymers, and from 25 to 200 °C when the membranes contained 1:1 (w/w) EC/DEC solution.

The glass transition temperature ( $T_g$ ) of the samples was determined by Dynamic-mechanical thermal analysis (DMTA) on a MK III Rheometrics Scientific Instrument at 1.0 Hz frequency in the tensile configuration and heating rate of 5.0 °C min<sup>-1</sup>. The size of the specimen was about 20 mm × 4 mm × 0.2 mm. The storage modulus,  $E'$ , and the loss factor,  $\tan \delta$ , were measured from -60 up to 80 °C. The  $T_g$  value was assumed as the maximum of the loss factor curve.

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<sup>-1</sup>. The tests were carried out at ambient temperature on a SiC wafer, which is transparent to UV, by irradiating the mixtures of monomers for 2 min. The UV lamp used was Lightning curve LC-8 with an intensity of 15–16 mW cm<sup>-2</sup>. 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 CHCl<sub>3</sub> (relative error = ±1%) [9–11].

## 2.3. Electrochemical characterisation techniques

The conductivity of the gel membranes at different temperatures was determined by electrochemical impedance spectroscopy (EIS, frequency range from 100 KHz to 1 Hz) using a PARSTAT 2273 instrument. For testing, discs of 0.785 cm<sup>2</sup> were cut from the polymer film and sandwiched between two Stainless-Steel electrodes.

The electrochemical stability window of the membranes was evaluated by running a sweep voltammetry in 2-electrodes Teflon cells. Super-P carbon over aluminium 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 versus Li). Potential scan rate used was 0.100 mV s<sup>-1</sup>.

The galvanostatic cycling tests were carried out at room temperature, setting the cut off voltages to 2.80–4.00 V versus Li<sup>+</sup>/Li. The LiFePO<sub>4</sub> electrodes were prepared in the form of thin films over aluminium current collectors, as reported in Meligrana et al. [12], and assembled in electrochemical cells having the gel polymer membrane as separator and Li metal as anode. The assembly of the cell prototypes and their testing procedures were carried out in an environmentally controlled dry glove-box.

Both the electrochemical stability and galvanostatic cycling tests were performed with an Arbin Instrument Testing System model BT-2000.

## 3. Results and discussion

### 3.1. Chemical and structural characterisation of the polymer membranes

It is well known that BEMA, whose chemical structure is presented in Fig. 1, is a UV-curable monomer which can be readily polymerized by free radical photo-polymerisation obtaining a highly cross-linked membrane with a complete conversion of the methacrylic double bonds. The 3D network is rather flexible as its  $T_g$  is low, at the same time is resistant up to 300 °C [13]. Moreover, due to the chemical structure of the BEMA monomer, the thermo-set polymer obtained contains many ethoxy groups which can help the flow of Li<sup>+</sup>-ions through its matrix. In fact, different papers, mainly describing thermoplastic membranes based on poly(ethylene oxide), reported the ability of ethoxy groups in conducting Li<sup>+</sup> ions through the polymer [1,14–16].

The introduction of the mono-functional monomers (PEG-MA)s is expected to reduce the  $T_g$  of the network (moreover, it could increase the mobility of lithium ions in the polymer matrix and enhance the conductivity by the presence of ethoxy groups, as it will be discussed in the following section).

Fig. 2 represents the percentage of conversion of BEMA and its mixtures with mono-methacrylates into polymers under UV irradiation as a function of the irradiation time. These tests were carried out on reactive mixtures prepared without the addition of EC:DEC solution. The reactivity of all the monomers is very high in the initial stages of the UV-curing and reaches its maximum very rapidly (the maximum conversion achieved after 120 s was around 99%). The result for sample BM-0 (solid curve in Fig. 2) showed that the rate of polymerisation is very fast and the reaction reaches its maximum in almost 60 s. By addition of mono-functional PEG-MA)s, having different molecular weights (samples BM-1 and BM-2), the rate of photo-polymerisation reaction was slower due to the different functionality of the systems (see dash and dot curves in Fig. 2).

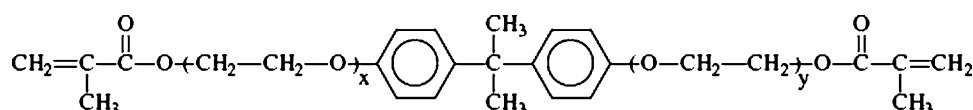


Fig. 1. Structure of Bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA).

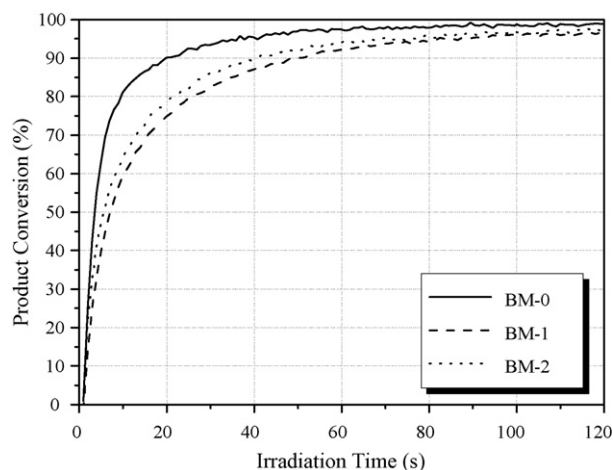


Fig. 2. Methacrylic double bond conversion of the reactive monomer mixtures, without addition of EC:DEC solution, checked by real-time FT-IR spectroscopy as a function of the irradiation time.

However the reaction reached the maximum conversion in about 80 s and the final conversion remained almost quantitative in all cases.

The membranes were free-standing films, transparent and highly insoluble in chloroform, meaning that they are highly cross-linked. Their gel-content (i.e. the insoluble fraction after extraction in chloroform) was always very high, as reported in Table 1, in good agreement with the conversion results obtained by the kinetics studies (see Fig. 2). From the DMTA spectra, the  $T_g$  is detected as the maximum of  $\tan \delta$  peak and varies from about  $-42^\circ\text{C}$  for BM-0 to approx.  $-50^\circ\text{C}$  for the copolymers BM-1 and BM-2 (see Table 1). As expected, the introduction of the mono-methacrylates helps in making the films slightly more flexible.

The thermal stability of the polymeric films was assessed by TGA and the thermograms are reported in Fig. 3. In the temperature range  $25\text{--}600^\circ\text{C}$  they evidence the high thermal stability of the membranes (up to  $300^\circ\text{C}$ ). From the same figure it can be confirmed that the polymers are safe to use at high temperatures.

The membranes prepared by UV-curing the same formulation described before, but after addition of EC:DEC solution, despite the liquid component, were still free-standing, non-tacky, although extremely flexible and almost transparent, as shown in Fig. 4. The photo-polymerisation took place and gave quantitative conversion of the methacrylic double bonds.

These plasticised polymers showed temperature stability up to  $130^\circ\text{C}$ , when the solvents began to evaporate, as illustrated in Fig. 5 which reports TGA profiles in the temperature range

Table 1  
Summary of the properties of the membranes prepared without addition of EC:DEC solution

Sample	Maximum conversion (%)	Gel-content (%)	$T_g$ ( $^\circ\text{C}$ )
BM-0	99	99.7	-42
BM-1	97	97.2	-47
BM-2	98	98.9	-49

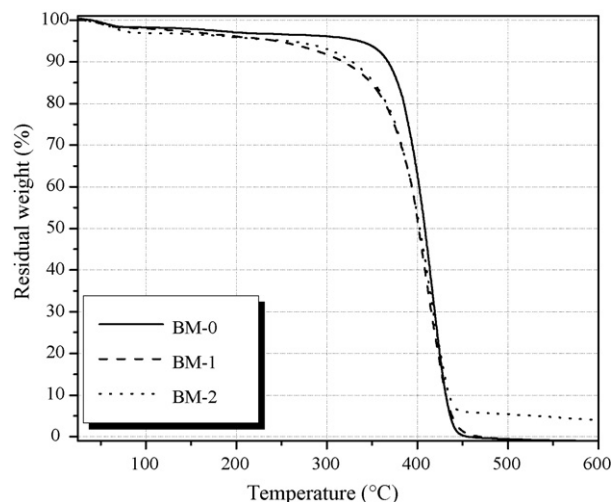


Fig. 3. TGA analysis under  $\text{N}_2$  flux (temperature range  $25\text{--}600^\circ\text{C}$ ) of polymer membranes prepared without addition of EC:DEC solution.

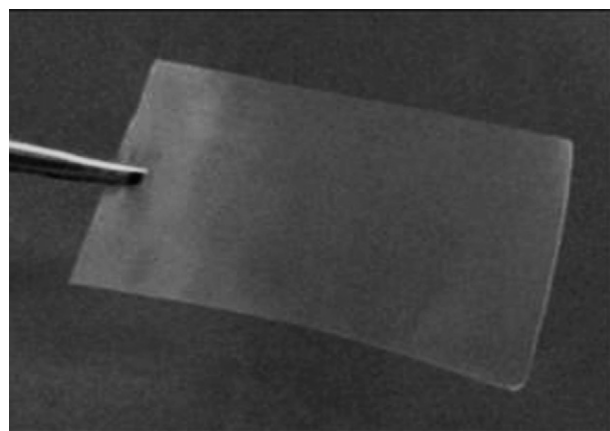


Fig. 4. Appearance of the gel-polymer membrane.

between  $25$  and  $200^\circ\text{C}$  (the curves are almost overlapped in this temperature range). As evidenced by this test, the three prepared gel-polymer membranes can be safely used in lithium polymer batteries up to  $100^\circ\text{C}$ .

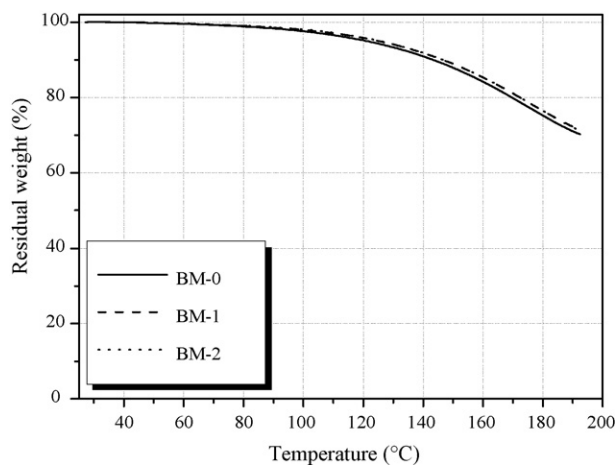


Fig. 5. TGA analysis under  $\text{N}_2$  flux (temperature range  $25\text{--}200^\circ\text{C}$ ) of polymer membranes prepared by in situ incorporation of 45 wt% 1:1 (w/w) EC:DEC solution.

### 3.2. Electrochemical measurements

In our first attempts to synthesize gel polymer electrolytes for Li-ion battery systems we adopted the swelling method to incorporate the electrolyte solution into a polymer matrix. A neat BEMA polymer which was made by photo polymerisation was swelled in 1.0 M LiPF<sub>6</sub> in 1:1 (w/w) EC/DEC mixture. The effect of swelling against time was studied (from 1 to 24 h), showing a marginal increase in weight of polymer membrane with time. The equilibrium was reached in approx. 8 h and the maximum active swelling obtained was low (about 33 wt%) and the impedance measurements showed high resistance values. The conductivity of the membranes at varying temperature was also studied, showing a linear increment of conductivity with temperature. The problems we identified were leakage, low swelling and improper dissolution of the liquid electrolyte.

These problems were solved by plasticising the polymer with 45 wt% of 1:1 EC:DEC solution using in situ polymerisation, and then swelling it in liquid electrolyte (sample BM-0). By this way we were able to reduce the  $T_g$  of the polymers further and to increase the swelling ability of the membranes. Swelling time was drastically reduced and maximum active swelling of approx. 53 wt% was achieved in about 2 h. The leakage of liquid electrolyte with time was also reduced by this method. Ionic conductivity values as high as  $2.1 \times 10^{-4} \text{ S cm}^{-1}$  at 25 °C and  $1.6 \times 10^{-3} \text{ S cm}^{-1}$  at 80 °C were obtained, as reported in Fig. 6. Unfortunately, this was not enough to drive our polymer systems to the desired properties.

Then, in order to reduce the  $T_g$  of the network (refer to the previous section), to obtain more Li<sup>+</sup>-ion mobile membranes and to increase the solvent holding power of the polymer matrix we copolymerised BEMA with PEGMAs (samples BM-1 and BM-2). The improvement of ionic conductivity was very interesting; thus, the copolymerisation can be considered as a turning point in our work. In fact, the membranes showed an enhanced conductivity, in particular at room temperature (i.e.,  $1.4 \times 10^{-3} \text{ S cm}^{-1}$  for BM-1 and  $1.1 \times 10^{-3} \text{ S cm}^{-1}$  for BM-2,

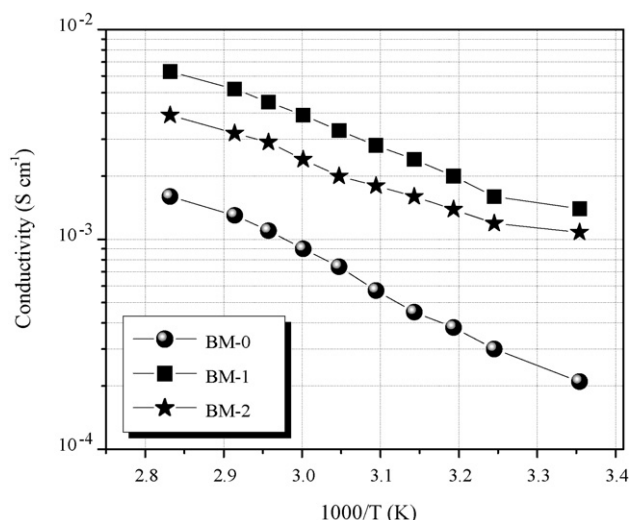


Fig. 6. Conductivity vs. temperature plots of the three tested polymers (BM-0, BM-1 and BM-2). Data obtained by impedance spectroscopy.

values almost comparable with those of common Li-ion liquid electrolytes). The conductivity increased with increase in temperature, resulting in high values of  $6.3 \times 10^{-3} \text{ S cm}^{-1}$  for BM-1 and  $3.9 \times 10^{-3} \text{ S cm}^{-1}$  for BM-2 at 80 °C. The comparison of Arrhenius plots for the three prepared membranes is reported in Fig. 6. All the plots exhibit the typical Vogel–Tamman–Fulcher (VTF) curvature associated with amorphous materials. The reasons for the enhancement in ionic conductivity are the reduction in  $T_g$  and the presence of a higher number of ethoxy groups in the copolymer network. In fact, the number of flexible ethoxy groups per gram of monomer is higher in PEGMA than in BEMA. Moreover, PEGMA is linked to the main network by one end and the ethoxy chain is dangling freely so that it can assist the lithium ions in moving.

In view of their possible application as electrolytes in Li-ion polymer batteries, the gel polymer membranes have been further tested in terms of other general electrochemical properties, such as electrochemical stability window, stability while storage and interfacial stability.

The first results regarding the electrochemical stability at potential values anodic with respect to lithium were carried out at room temperature. The current–voltage curves, reported in Fig. 7, were obtained for a working Super-P electrode swept in a cell using the gel electrolyte membranes and a Li metal counter electrode. The onset of the current, which is representative of the decomposition of the electrolyte, indicates an anodic breakdown voltage of approx. 4.0, 4.2 and 4.8 V versus Li for BM-0, BM-1 and BM-2, respectively. A high decomposition voltage like the one showed by BM-2 membrane is certainly welcome in a practical viewpoint [15,17].

The anodic scan showed very low residual current observed prior to breakdown voltage, confirming the purity of the synthesised membranes and the way of synthesising method we adopted, because the system as in whole is sensitive to oxygen, water and other impurities.

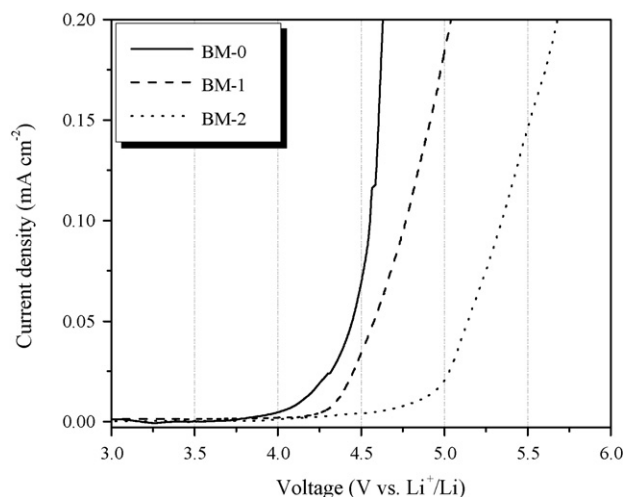


Fig. 7. Comparison of current–voltage curves at 25 °C of the three membranes BM-0, BM-1 and BM-2. Cell configuration adopted: Super-P carbon over aluminium current collector as working electrode, Li metal as counter electrode and the given membrane as electrolyte. Anodic potential scan range from O.C.V to 6.0 V vs. Li at 0.100 mV s<sup>-1</sup>.

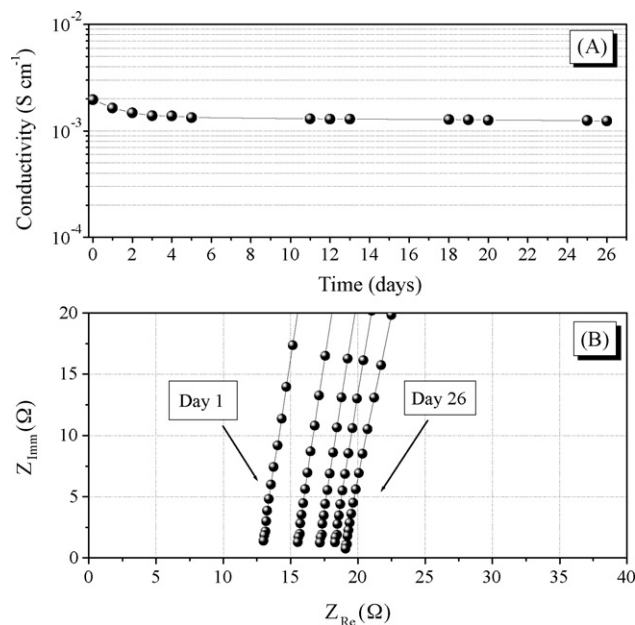


Fig. 8. (A and B) Conductivity time evolution at room temperature of the BM-2 gel polymer electrolyte (A) and impedance response of the conductivity cell used for the measurements (B).

We also evaluated the stability window of gel polymers with  $\text{LiClO}_4$  as lithium salt instead of  $\text{LiPF}_6$ , and the tests were carried out at  $90^\circ\text{C}$ . This high temperature was used for testing because it is an extreme condition that can be applied to our membranes, and it is expected that cell reactions are more vigorous. The results obtained showed similar behaviour with respect to all the three polymers, but little difference in values; actually, as expected, the anodic breakdown voltages for  $\text{LiClO}_4$  at  $90^\circ\text{C}$  occur at lower voltage values of 3.8–4.0 V for BM-0, 4.1 V for BM-1 and 4.5 V for BM-2.

The stability versus storage time of gel polymer membrane BM-2 was evaluated by running impedance measurements of a symmetrical Stainless Steel/gel-polymer membrane BM-2/Stainless Steel cell kept under open-circuit conditions at  $25^\circ\text{C}$ . The results are shown in both Fig. 8(A), which reports the time evolution of the room temperature conductivity, and Fig. 8(B), which shows the trends of the impedance responses, at increasing storage time. The results demonstrate that the membrane is able to retain its high ionic conductivity. In fact, some losses of liquid electrolyte and/or phase separation occurred, as evidenced by shifts of the real axis intercepts and slight deviation from linearity [18].

All these favourable properties for BM-2 membrane (i.e. high ionic conductivity, high anodic breakdown voltage, stability while storage) are somewhat contrasted by the interfacial stability towards the lithium metal electrode, even at room temperature. This is shown in Fig. 9 which illustrates the time evolution of the impedance of a symmetrical Li/gel-polymer membrane/Li cell kept under open-circuit conditions at  $25^\circ\text{C}$  [19]. The impedance response evolves as a semicircle whose amplitude is representative of the Li/electrolyte interfacial resistance [20,21]. It was observed that there is an increase in interfacial resistance with time, indicating an increase in the

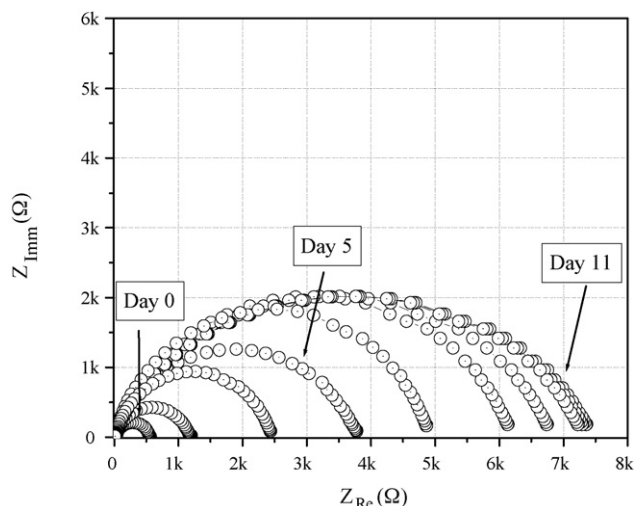


Fig. 9. Time evolution of the impedance spectra of the Li/BM-2 gel-polymer electrolyte/Li cell, stored under open-circuit conditions at  $25^\circ\text{C}$ .

thickness of the passivation layer, which stabilizes after a period of time of 11 days. The increase in bulk resistance was almost negligible at room temperature.

The tests performed at higher temperatures (i.e.  $90^\circ\text{C}$ ) showed a large increase in interfacial resistance and even an increase in bulk resistance of the cell with time, which indicates the leakage of the electrolyte from the membrane.

The gel polymer membrane BM-2 (the best performing one) was then tested for galvanostatic charge/discharge cyclability tests as electrolyte in a lithium cell with  $\text{LiFePO}_4$  [12] as cathode and Li metal as anode. The preliminary results appear promising, showing good reversibility and cyclability at room temperature. Fig. 10 shows a charge/discharge cycle of the  $\text{LiFePO}_4$ /BM-2 gel-polymer electrolyte/Li polymer cell at low current rate of  $C/20$ . The cycle evolves around 3.45 V versus  $\text{Li}^+/\text{Li}$  as indeed expected on the basis of the  $\text{LiFePO}_4$  electrode potential, with an almost stable voltage over the entire cycle and a capacity delivery of about  $130 \text{ mAh g}^{-1}$ .

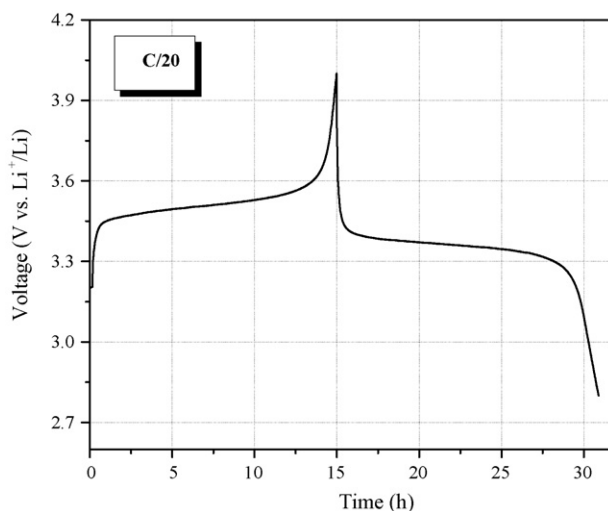


Fig. 10. Galvanostatic charge/discharge cycle of the polymer  $\text{LiFePO}_4$ /BM-2/Li lithium cell at room temperature and at  $C/20$  rate.

#### 4. Conclusions

The preliminary results reported in the present paper indicate that UV-curing is a suitable method for synthesizing polymer membranes to be used as electrolyte for Li-ion batteries. Compared to other techniques, it appears highly advantageous due to its easiness and rapidity in processing.

By this method we are able to produce flexible, transparent films of varying thickness in less than 5 min, and the whole process for production of gel-polymer membranes takes less than 3 h, although it is far from being optimised. The process is very versatile and easily permits to change the polymer composition.

The high values of conductivity for the samples BM-1 and BM-2 put in evidence that the copolymerisation process is fundamental to obtain gel-polymer electrolytes of high ionic conductivity and storage stability even at ambient temperature.

Among all the membranes we studied, BM-2 allowed to build an all-solid-state polymer lithium cell that shows a performance similar to the corresponding liquid electrolyte system, during the first cycles, with just a higher activation over-potential and slightly lower specific capacity.

Our next target is the introduction of other co-monomers able to improve the performance of the membrane, especially mechanical properties and interfacial stability versus lithium of the final polymer film.

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