



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

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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 LiFePO₄ as cathode and Li metal as anode. The preliminary results are interesting, exhibiting good reversibility and cyclability.

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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 $\geq 10^{-2} \text{ S cm}^{-1}$ 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

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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(perfluoroethylsulfonyl)imide [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) sulfoniimide (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 N₂ 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 N₂ 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 cm² 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

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