

Degradable photopolymerized thiol-based solid polymer electrolytes towards greener Li-ion batteries



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ABSTRACT

Thermoset initiator-free membranes are prepared by the UV-induced photopolymerization of thiol and (meth)acrylic monomers having polyethylene oxide chains, being known that the use of such monomers can lead to the formation of readily degradable membranes. The photopolymerization of different formulations is studied and the influence of the addition of a monofunctional methacrylate is investigated. By incorporation of lithium bis(oxalate)borate salt, solid polymer electrolytes are prepared and used as electrolyte membranes in Li-ion batteries. The ionic conductivity of the samples is measured and correlated to their thermal characteristics. The best performing sample shows encouraging cycling behaviour when tested in a truly-solid state lab-scale lithium test cell, thus enlightening the promising prospects of the newly designed polymer electrolytes. Furthermore, a preliminary degradation study is performed demonstrating the possibility to hydrolytically degrade the proposed UV cured networks making them extremely appealing for the development of sustainable and easily recyclable, thus greener, energy power sources.

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1. Introduction

Nowadays, electrical energy storage systems and, in particular, Li-ion batteries are fundamental for powering portable electronics, but they are still under intense investigation to achieve the optimal performances required by green transportation, to supply stationary load-leveiling in intermittent power generation as well as for space and military applications [1,2].

Typically, lithium batteries are formed by laminating a composite graphitic anode (or lithium metal in case of lithium metal batteries), a lithium-ion conducting electrolyte (in commercial cells a liquid electrolyte soaked in a polyolefin separator) and a composite lithium transition metal oxide/phosphate cathode in a sandwiched structure and proper packaging [3,4]. The performances of the devices mainly depend upon the different materials employed, thus intensive work has been done towards the development of highly performing nanostructured electrode materials and highly ionic conductive, mechanically robust and safe electrolytes. Furthermore, although the unrelenting requests from markets, one of the fundamental goals to be pursued at present is

the accomplishment of the “12 principles of Green Chemistry” by designing and/or improving environmentally “conscious” materials, products and processes in order to, at least, try to reduce the environmental impact of systems and devices throughout all the phases of their life cycle, thus protecting and benefiting the economy, people and planet [5].

Considering the selection of the ionic conducting medium, solid polymer electrolytes eliminate the necessity of liquid solvents and, in turn, allow to simplify the cell design as well as to improve safety and durability; their main drawback still remains the relatively limited ionic conductivity at ambient/sub-ambient temperature [6–9].

In the field of lithium batteries, solid polymer electrolytes were studied since 1975 [10]. They are commonly prepared by dissolving a supporting lithium salt in poly(ethylene oxide)-based materials, but such a process requires long time and the use of solvents. Thus, an interesting alternative is dissolving the salt in liquid monomers and then polymerize them in situ. A fast and reliable method is represented by photoinduced polymerization, usually employing UV light. UV curing is a fast and energy saving process largely used for the production of membranes, it does not require the use of solvents and, when also the initiator is avoided, costs and environmental impact are definitely reduced [11–13]. This technique

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has been proposed for the preparation of solid or gelled polymer electrolytes mainly based on PEO-acrylates systems [14].

Furthermore, at present, little attention has been paid to the environmental impact of battery electrolytes [15–18], particularly in terms of their recycling/degradation features. An additional goal is then degradability. Thiol-ene systems are largely used for the preparation of UV cured coatings and adhesives [19,20]; they have been also proposed for biomedical applications [21–24] and, very recently, some examples of their potential characteristics as polymer electrolytes for lithium batteries have been published [25–27]. The UV curing of thiols together with ethylene oxide based acrylates, can lead to the synthesis of membranes able to dissolve lithium salt and support the ionic motion. When the right monomers are chosen, the network can hydrolytically degrade at controlled pH with faster rate with respect to other systems through the dissolution of single ester groups located near sulphide bonds, as explained by Rydholm et al. [21–23]. A solid polymer electrolyte might actually represent the best solution for battery applications if it could match together the high energy and long life of the lithium ion process, the reliability and easy processability typical of the UV-cured networks and an easy degradation process.

In this respect, here we propose initiator-free UV cured solid polymer electrolytes based on thiol-acrylate systems incorporated with supporting lithium bis(oxalate)borate (LiBOB) salt. LiBOB salt has been chosen because of the number of significant advantages it offers. It meets the basic requirements for a salt to be used in lithium-based cells: acceptable ionic conductivity at low temperature, sufficient electrochemical stability, SEI layer forming ability. Moreover, it does not contain hazardous fluorine groups, is highly thermally stable and low cost and, noteworthy, it generates environmentally friendly decomposition and hydrolysis products [6,28–30].

The proper matching of the newly proposed polymer electrolyte formulations and techniques results in extremely appealing solid polymer electrolytes showing excellent electrochemical behaviour at moderately high temperature together with promising degradation ability. Furthermore, for the first time galvanostatic cycling behaviour of degradable thiol-based solid polymer electrolytes is shown.

2. Experimental

2.1. Materials

For the polymer electrolyte membrane, poly(ethylene glycol) diacrylate (PEGDA, $M_n = 700$, Aldrich), poly(ethylene glycol) methyl ether methacrylate (PEGMA, average $M_n = 475$, Aldrich), pentaerythritol tetrakis(3-mercaptopropionate) (T4, $M_w = 488.66$,

Aldrich) and lithium bis(oxalate)borate ($\text{LiB}(\text{C}_2\text{O}_4)_2$, LiBOB, Aldrich) were used. The corresponding chemical structures are shown in Fig. 1. Before use, the reagents were kept open in the inert atmosphere of a dry glove box (MBraun Labstar, O_2 and H_2O content <1 ppm) filled with extra pure argon for several days and also treated with molecular sieves (Molecular sieves, beads 4 Å, 8–12 mesh, Aldrich) to ensure the complete removal of traces of water/moisture from the liquid monomers.

2.2. Preparation of membranes and polymer electrolytes

Three different polymers were firstly prepared by photopolymerization of the 3 monomers T4, PEGDA, PEGMA in different ratios, keeping the equimolarity between thiol and (meth)acrylic moieties. As listed in Table 1, the amount of PEGMA was progressively increased while correspondingly decreasing the amount of PEGDA, for higher quantities of monofunctional monomer it was not possible to obtain self-standing membranes. The formulations (reactive mixtures) were casted on a polyethylene substrate, sealed in a quartz tube and irradiated (cured) by UV light for 4 min using a medium vapour pressure Hg lamp (Helios Italquartz, Italy), having a radiation intensity of 30 mW cm^{-2} .

The same polymers were used as electrolytes adding 10, 15, 20 wt.% of LiBOB supporting salt (namely, PMX-LiY , where X corresponds to the molar amount of PEGMA and Y to the weight percentage of LiBOB incorporated, e.g. PM0-Li10). All the preparation procedures were carried out inside the dry glove box.

2.3. Characterization methods

Infrared spectroscopy was performed using a FT-IR, BRUKER TENSOR 27 instrument. 25 μm -thick liquid reactive mixture films were coated on SiC wafers and covered with a PE film in order to preserve an inert atmosphere. A first spectrum was collected on the liquid sample, which was subsequently UV irradiated in 4 steps of 1 min each; FT-IR spectra were collected after each of the steps.

The thermal behaviour of the samples was tested by means of thermogravimetric analysis (TGA) using a Netzsch TG 209 F1 TGA instrument. Tests were performed under nitrogen atmosphere, from ambient temperature up to $600 \text{ }^\circ\text{C}$ (rate: $10 \text{ }^\circ\text{C min}^{-1}$).

The glass transition temperature (T_g) of the materials was evaluated by differential scanning calorimetry (DSC) with a Netzsch DSC 204 F1 Phoenix instrument, equipped with a low temperature probe. Samples were put in aluminium pans, prepared inside the dry glove box. In a typical measurement, the electrolyte samples were cooled from ambient temperature down to $-80 \text{ }^\circ\text{C}$ and then heated up to $80 \text{ }^\circ\text{C}$ (rate: $10 \text{ }^\circ\text{C min}^{-1}$). For each sample, the same heating cycle was applied and the final heat flow value recorded during the second heating cycle. The T_g was defined as the midpoint of the heat capacity change observed in the DSC trace during the transition from glassy to rubbery state.

The insoluble fraction (gel content) of the cured products was determined according to the standard test method ASTM D2765–84. The samples were held in a metal net, accurately weighed and, subsequently, extracted for 24 h at ambient temperature with CHCl_3 to dissolve the non-cross-linked polymer. When the samples containing LiBOB were measured, the salt, which is not linked to the matrix, was completely dissolved in chloroform and thus its weight was not considered in the calculation. The gel content was estimated according to

$$\eta\% = \frac{\eta_2 - \eta_1}{\eta_1} * 100$$

(relative error = $\pm 1\%$), where η_1 and η_2 are the weights of the

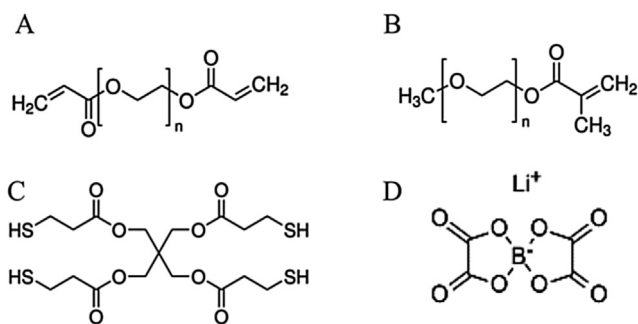


Fig. 1. Chemical structures of: monomers A) poly(ethylene glycol) diacrylate (PEGDA), B) poly(ethylene glycol) methyl ether methacrylate (PEGMA), C) pentaerythritol tetrakis(3-mercaptopropionate) (T4), and D) lithium bis(oxalate)borate (LiBOB).

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