



UV-cured Al₂O₃-laden cellulose reinforced polymer electrolyte membranes for Li-based batteries



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ABSTRACT

A methacrylate based plasticised polymer electrolyte membrane is prepared via a rapid and facile UV curing process, the major concerns of mechanical integrity are overcome by simply using appropriately modified cellulose handsheet laden with nano-sized acidic alumina particles as a reinforcement. The use of the cellulose handsheets greatly enhances the flexibility and mechanical properties of the membrane while the addition of alumina particles helps to maintain satisfactory conductivity values. The reinforced composite electrolyte membrane is also tested in a real lithium cell, exhibiting excellent performance which account for its use in futuristic lithium batteries having low cost, environmentally friendly and easily scalable properties.

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1. Introduction

The development of high performing polymer electrolytes is a cutting edge subject in the field of lithium batteries. Solid polymer electrolyte membranes are highly appreciated in terms of safety and mouldability but they generally suffer from low ionic conductivity at ambient and/or subambient temperature.[1–3] The incorporation of liquid plasticizers with the conversion of the solid matrix into a gelled polymer, is a possible option to fulfil the basic needs of an electrolyte but, in this case, sacrifices must be done in terms of mouldability, safety and mechanical stability. [4,5] Other proposed methods include cross-linking of the polymer matrix, thus an acceptable compromise can be achieved and above discussed problems can be limited. [5–9]

Photopolymerisation process has been demonstrated as a possible way to develop crosslinked membranes which can be explored as polymer electrolytes.[6,10,11] Ultraviolet (UV) curing process is well established for various industrial applications. This technique has many advantages, among them high cure speed allows a high production rate with reduced energy consumption, resulting in reduced production cost. Moreover, being volatile

organic emissions very low, it is an environmental-friendly technique.[12,13]

When the production of a gel polymer electrolyte is envisaged a proper organic solution containing the lithium salt can be directly added to the UV- reactive formulation leading in few minutes to the production of a membrane ready to be used. [14–17]

In order to enhance the mechanical stability and handability of the electrolyte membranes, both envisaging fast production processes (meaning high stresses) and applications in flexible batteries, paper can be used as reinforcement just by impregnating an appropriately prepared cellulose handsheet with a UV curable formulation.

Cellulose reinforced polymer electrolyte membranes have already been proposed in literature [16,18,19] and it has been shown that the use of such reinforcement can increase the flexibility and mechanical resistance of a UV cured plasticized polymer electrolyte membranes, but, when cellulose is used in the form of handsheet, it generally affects the ionic mobility inside the matrix. [16]

According to the literature on composite polymer electrolytes and aiming to restore satisfying conductivity values, a finely designed paper handsheet containing alumina (Al₂O₃) nano particles has been produced to be used as reinforcement in a UV cured plasticised polymer electrolyte membrane, being known that the addition of such fillers improves the conductivity of polymer hosts and their interfacial properties in contact with the lithium electrode. [20–27]

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The production process of nanoparticles-laden handsheets is well known in papermaking industry where commercial papers are generally produced by adding to the cellulose fibres a large variety of additives, with the aim of modifying the bulk properties, tuning surface properties or giving processing aids (e.g., calcium carbonate particles due to their special white colour are added to make bright and smooth opaque paper [28]). The whole process is water based and the waste generated related to this process is minimal. The promising prospect of the reinforced hybrid composite al Li-ion battery electrolyte is thoroughly investigated and the results are here presented.

2. Experimental

2.1. Materials

Cellulose fibres derived from Hardwood (HW, Eucalyptus) and Softwood (SW, Pine) plants were used to produce paper handsheets. Alumina (Al_2O_3 , Aldrich nano powder avg. size $<50\text{ nm}$) was used as an additive in one series of samples. For the polymer electrolyte membrane formulation, bisphenol A ethoxylate (15 EO/phenol) dimethacrylate (BEMA, $M_n = 1700$, Aldrich), poly(ethylene glycol) methyl ether methacrylate (PEGMA, average $M_n = 475$, Aldrich), 1:1 w/w ethylene carbonate – diethyl carbonate solution (EC-DEC, Fluka), lithium bistrifluoromethanesulfonimide salt (LiTFSI, $\text{CF}_3\text{SO}_2\text{N}(\text{LiSO}_2\text{CF}_3)$, Solvionic), 2-hydroxy-2-methyl-1-phenyl-1-propanon (Darocur 1173, D-1173, Ciba Specialty Chemicals) and benzophenone (BP, Aldrich) were used. Before their use, the reagents were kept open in the inert atmosphere of a dry glove box (MBraun Labstar, O_2 and H_2O content $<0.1\text{ ppm}$) filled with extra pure Ar 6.0 for several days and also treated with molecular sieves (Molecular sieves, beads 4 \AA , 8–12 mesh, Aldrich) to ensure the complete removal of traces of water/moisture from the liquid monomers.

2.2. Fibre treatment and handsheet preparation

Untreated cellulose fibres (SW and HW fibres mixed in the 40:60 ratio) stored in the laboratory in the form of thick sheets were re-pulped and blended using a high speed blender. The resulting suspension of fibres was then submitted to the refining treatment to reach a refining degree of 35° SR (Schopper-Riegler). [29] This mechanical modification was done by means of a Valley beater (equipment for pulp refining), according to ISO 5264-1 standard, in order to beat the pulp in a uniform and reproducible way.

For handsheets production, the fibre suspensions were diluted to a concentration of 1.5 g L^{-1} ; a litre of this suspension was introduced into a sheet-former that steers the solution automatically. The filtrate laying on copper wires was then dried at 90° C for 7 minutes under high vacuum to give handsheets (namely, SW40) of about 1.5 g in weight corresponding to a grammage value of 51 g m^{-2} and thickness of $100 \pm 2\text{ }\mu\text{m}$.

A 5 wt % suspension of Al_2O_3 in deionised water was prepared; it is worth noting that the suspension was easily formed and stable for long time. This solution was added in appropriate quantities to achieve handsheets with 5, 10 or 15 wt % of Al_2O_3 nanoparticles content with respect to the cellulose content.

2.3. Composite reinforced gel polymer electrolyte membrane preparation

A reactive polymer formulation (precursor) containing 10 wt % BEMA, 10 wt % PEGMA, 60 wt % EC-DEC and 20 wt % LiTFSI along with the addition of the photo-initiators (i.e., D1173 3 wt %, BP 1 wt %) was prepared in the dry box. Cellulose handsheets were soaked in

the solution for 30 mins and the excess of reactive mixture was removed using a filter paper. This system was then kept on a polyethylene (PE) substrate. Each membrane was then UV cured for 3 minutes by using a medium vapour pressure Hg lamp (Helios Italquartz, Italy), with a radiation intensity of 30 mWcm^{-2} . All the above reported processes were carried out in an environmentally controlled dry room (10 m^2 , R.H. $<2\% \pm 1$ at 20° C) produced by SOIMAR (Caluso, Italy).

2.4. Characterisation methods

The quantity of polymer electrolyte present in the reinforced composite polymer membrane (RPEM) with respect to the paper weight, called Active Electrolyte Content (AEC %), was calculated by the formula:

$$\left[\frac{W_{\text{RPEM}} - W_{\text{pap}}}{W_{\text{RPEM}}}\right] \times 100$$

where W_{RPEM} is the weight of the final reinforced composite polymer electrolyte membrane and W_{pap} is the weight of the reinforcing cellulose substrate.

Morphological characterization was performed on a FEI Quanta Inspect 200LV scanning electron microscope (SEM, max magnification of 1.5×10^5) equipped with an energy-dispersive X-ray analyser EDAX Genesis system with SUTW detector. Prior to analysis, all the samples were coated with a thin Cr layer (thickness around 10 nm) to minimize the effect of the electron beam irradiation which may lead to charging and “burning” of the polymer network. For cross-sectional analysis, in order to avoid any change in the morphology, test samples were broken under cryogenic conditions after dipping in liquid nitrogen.

The glass transition temperature (T_g) of the materials was evaluated by differential scanning calorimetry (DSC) with a METTLER DSC-30 (Greifensee, Switzerland) instrument, equipped with a low temperature probe. Samples were put in aluminium crucibles. In a typical measurement, the electrolyte samples were cooled from ambient temperature down to -80° C and then heated ($10^\circ\text{ C min}^{-1}$) up to 120° C . For each sample, the same heating module was applied and the final heat flow value was 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 thermal stability was tested by thermo-gravimetric analysis using a TGA/SDTA-851 instrument from METTLER (Switzerland) over a temperature range of $25\text{--}800^\circ\text{ C}$ under N_2 flux (60 ml min^{-1}) at a heating rate of $10^\circ\text{ C min}^{-1}$.

Classical gravimetric analyses were also performed using the ceramic crucible at 500° C on the cellulose samples as ash test to quantify the actual alumina content in the handsheets.

Mechanical measurements on the samples before swelling were carried out through tensile experiments according to ASTM Standard D638, using a Instron 3366 dynamometer equipped with a load cell of 500 N . At least five specimens for each sample were tested; the standard deviation in Young modulus (E) was 5%.

Ionic conductivity tests were carried out on a heating stepped ramp from 20 to 80° C . Samples were sandwiched between two stainless steel (SS-316) blocking electrodes, placed into testing cells and housed in an oven (Mettmert GmbH, model UFE-400) with a temperature control of $\pm 1^\circ\text{ C}$. The bulk 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). Each cell was equilibrated at the experimental temperature for about 1 h before measurement. All measurements were carried out on at least three different fresh samples in order to verify the reproducibility of the obtained results. The ionic conductivity was calculated based on the

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