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Cellulose/acrylate membranes for flexible lithium batteries electrolytes: Balancing improved interfacial integrity and ionic conductivity

A. Chiappone [a,b,*], Jijeesh R. Nair [a], C. Gerbaldi [a,b], E. Zeno [c], R. Bongiovanni [a]

[a] DISAT Politecnico di Torino, C.so Duca degli Abruzzi, 24 Torino 10129, Italy
[b] Istituto Italiano di Tecnologia, CSHR@Polito, C.so Trento, 21, Torino 10129, Italy
[c] Centre Technique du Papier (CTP), Domaine Universitaire, B.P. 251, 38044 Grenoble, France

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ABSTRACT

Methacrylic-based thermo-set gel–polymer electrolytes obtained by the easy and reliable photo-polymerisation process and mechanically reinforced by a cellulose handsheet (paper) for flexible lithium batteries application are here presented. Adhesion between cellulose and polymer is improved by "in situ" grafting supported by benzophenone; the ionic conductivity of the electrolyte is enhanced by the use of specifically designed handsheets containing alumina. Thermal and mechanical properties of the new membranes are characterised and the effect of the different composition of the reinforcement on the ionic conductivity of the membranes is discussed.

1. Introduction

Energy storage systems are a key factor in today's society because of the urgent requests of the portable electronics market [1] and because of the necessity of storing energy from the non-continuous green energy sources such as solar and wind [2]. A cheap and sustainable energy supply system is requested and lithium ion batteries, due to their high-energy efficiency, appear as ideal candidates for this purpose [3]. Such devices are already well established commercial products, but enhancement in safety, cost and energy density are still desired. In this respect, a big portion of R&D is nowadays devoted to the improvement of the characteristics and performances of the various battery components (anode, cathode and electrolyte) [4]. As far as the electrolyte is concerned, the main goal is to replace the highly volatile and flammable liquid electrolyte with a safer solid one [5]. The passage to a solid configuration gives concrete promise of increasing cell safety and reliability while offering, at the same time, modularity in design, flexibility and ease of handling [4,6]. The main drawback of fully solid configuration is the low ionic conductivity when compared to the commonly used liquid electrolytes: the polymer network restricts the lithium ion mobility resulting in poor performance. A good compromise is the development of gel polymer electrolytes, thus matching together the high safety and processability of polymers and the conductivity properties of liquids [7,8].

Photopolymerisation process is a possible way to develop crosslinked self-standing membranes which can be successfully used as gel or solid polymer electrolytes [9–12]. The UV curing process is well established in many industrial fields such as inks and coatings, optical and electronics being fast, low cost, energy saving and versatile [13,14]. In fact a fully cured polymer is obtained in seconds at ambient conditions irradiating a proper mixture of reactive molecules and photoinitiator. In view of preparing

* Corresponding author at: Istituto Italiano di Tecnologia, CSHR@Polito, C.so Trento, 21, Torino 10129, Italy. Tel.: +39 011 090 3422; fax: +39 011 090 3401.
E-mail address: annalisa.chiappone@iit.it (A. Chiappone).

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membranes conceived for Li battery application, along with reactive monomers (containing ethoxylate –EO– groups) and photoinitiator, lithium salts and a proper solvent can be added [15].

In previous works, aiming at obtaining flexible and handy materials, the mechanical properties of UV cured electrolytes were improved by developing novel composite polymer membranes in which an acrylic-based formulation was grafted, in order to assure the good adhesion, to a cellulosic reinforcement in the form of paper hand-sheets [16,17]. As a matter of fact, in the fabrication of such a system, the cellulose handsheet is an ideal flexible substrate showing high mechanical properties and sustainable characteristics [18,19]. Furthermore, the exploitation of papermaking techniques combined with the UV curing process for the development of paper-based electrolytes and ideally, in the near future, of paper-based batteries can be considered of great interest.

As a drawback, we found out that, when adding the cellulosic substrate, the ionic conductivity of the gel polymer electrolyte was reduced [16,17]. In this work novel paper-based gel polymer electrolytes (GPE) reinforced by cellulose are developed improving their in ionic conductivity by preparing specifically designed cellulose handsheets. As it is well known from the literature that the addition of inorganic fillers (e.g., alumina) to the polymer matrices highly improves this fundamental characteristic of an electrolyte [20–23], handsheets containing alumina nanoparticles are prepared and used as reinforcement, a process assuring a chemical bonding between the handsheet and the polymer gel is proposed. The thermal and mechanical properties of the new membranes are characterised and the effect of the different composition of the cellulose reinforcement on the electrochemical performance of the membranes is discussed.

2. Materials and methods

2.1. Materials

Cellulose fibres deriving from Hardwood (Eucalyptus) and Softwood (Pine) plants were used to produce paper sheets. Alumina (Al_2O_3, Aldrich nanopowder avg. size <50 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, $CF_3SO_2NLiSO_2CF_3$, 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 ppm) filled with extra pure Ar 6.0 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 handsheets

Untreated cellulose fibres (Softwood and Hardwood 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) [24]. This mechanical modification was done by 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.

To obtain the handsheets, a suspension of fibres with a concentration of 1.5 g L^{-1} was prepared a litre of this was introduced into a sheet-former and, when needed, a 5% suspension of alumina was added in order to have 10 wt.% of Al_2O_3 content with respect to cellulose. The suspension was stirred by bubbling for 3 min. The filtrate laying on copper wires was then dried at 90 °C for 7 min under high vacuum to give handsheets (namely, SW40) of about 1.5 g in weight corresponding to a grammage of about 51 g m^{-2} and thickness of 110 ± 2 μm.

2.3. Composite reinforced gel polymer electrolyte membrane preparation

Composite reinforced GPEs were prepared by the fast "One Shot" method consisting of few and easy steps. An active formulation containing BEMA:PEGMA:1 M LiTFSI in EC:DEC and the photoinitiators was prepared in dry box and successively casted using a coating bar of 100 μm on the cellulosic substrates (area 4 cm^2) laying on a polyethylene (PE) substrate (note that the formulation spread on the substrate was always in excess). Each membrane was then UV cured for 3 min by using a medium vapour pressure Hg lamp (Helios Italquartz, Italy), with a radiation intensity of 30 mW cm^{-2}, the whole process was carried out in the dry room.

2.4. Characterisation methods

Morphological characterisation 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 minimise 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 membranes 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 pans, prepared in dry glove box. In a typical measurement, the electrolyte samples were cooled from ambient temperature down to −80 °C and then heated (10 °C min^{-1}) up to 120 °C. For each sample, the same heating module was applied and the final heat