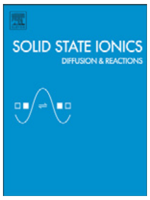
Solid State Ionics 236 (2013) 22–29

Contents lists available at SciVerse ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



New structural lithium battery electrolytes using thiol–ene chemistry

Markus Willgert [a], Maria H. Kjell [b], Göran Lindbergh [b], Mats Johansson [a,*]

[a] KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Fibre and Polymer Technology, Sweden
[b] KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemical Engineering and Technology, Applied Electrochemistry, Sweden

ARTICLE INFO

Article history:
Received 10 August 2012
Received in revised form 21 December 2012
Accepted 26 January 2013
Available online 6 March 2013

Keywords:
Solid polymer electrolyte (SPE)
Mechanical properties
Ionic conductivity
Structural batteries
Thiol–ene chemistry
Multi-functionality

ABSTRACT

A series of solid poly(ethylene oxide)-methacrylate lithium ion electrolytes containing thio-ether segments have successfully been produced and evaluated with respect to mechanical and electrical performance. The series have been varied in crosslink density and thio-ether content. The study presents thiol–ene compounds as yet another tool to design multifunctional electrolytes, and that they are compatible with and usable for polymer electrolyte systems. The electrolytes, produced in a solvent free process where the oligomers are active diluents of the lithium salt, express a broad range of both mechanical as well as ion conducting properties. Conductivity values presented ranges up to about 8×10^{-7} S/cm, and a wide spectrum of values of the storage modulus is presented in a range from 2 MPa to 2 GPa at 20 °C. The influence of the crosslink density of the poly(ethylene oxide)-methacrylates with and without thio-ether segments is discussed. In order to present correlations between crosslink density and how the lithium ion transport is affected by incorporating multifunctional thiol monomers, density measurements have been undertaken to calculate the average molar mass between the crosslinks.

1. Introduction

In the ongoing research and development of portable electrical devices, such as laptop computers and cell phones, there are increased requirements to find better medias for storing electrical energy that will be used in the device [1]. This is also the case in the automotive industry where extensive work is carried out in order to maximize the performance provided by the battery in electrical vehicles (EVs) and hybrid electrical vehicles (HEVs) [2]. The research conducted on energy storage is of large interest especially as the development of portable devices demands not only longer battery times, but also more energy units per energy storage volume. Because of its high energy density, the lithium-ion type battery is the battery type mainly considered in portable devices today [3]. A great deal of research being made is regarding safety aspects of the battery [4,5], where for instance a short circuit may be detrimental. On that note, lithium-ion batteries used today often contain liquid or semi-liquid electrolytes, where normally a lithium salt is dissolved in an organic solvent. Organic solvent liquid electrolytes are generally considered relatively unsafe and, if released, have a negative impact on people and environment [6]. They are also typically quite harsh on the electrodes [7]. Furthermore, the rapid progress in development of portable devices [3] calls for new smart solutions to store the energy, especially as batteries tends to hold a significant part of the total item weight and space. This is certainly an unfavorable property in a portable device.

Among previous and currently proceeding work with the aim to resolve the issues described above, one way to lower the weight parasitic nature of a battery is to not only let it perform one task (storage of energy), but also incorporate it in the construction of the device, making it a mechanical load bearing component, a so called structural battery [8]. Consequently, the battery is then replacing a load bearing part in the structure and reduces the overall weight of the product. One concept to achieve such an electrolyte is to design a solid polymer electrolyte (SPE) with the ability to carry mechanical load as well as transport ions. This approach to take on the issues has been described in previous work, not least by Snyder et.al. [9,10]. Furthermore, it has been shown that SPEs can be produced in either a solvent free process or techniques where solvents are used, and a lithium salt is dissolved directly in a monomer mixture with or without solvents prior to curing [11–15]. The monomers can be reactive diluents and be swiftly cured with UV irradiation, which is a technique well established to be rapid, relatively environmentally friendly, impose low thermal impact during cure and create well defined thermosetting polymers [16,17]. The polymers mainly in focus has been methacrylate or acrylate cross-linked polymer networks (gel polymer electrolytes) possessing ethylene oxide (EO) units.

Alkali metal cations are known to be able to coordinate to and form complexes with the EO units and enable ion transport throughout the polymer [18,19]. The mobility of the ion is largely dependent on the mobility of the complexing EO segments in the polymer chain in the amorphous regions [18,20,21], where ionic transport is taking place through cation coordination to these segments. When this complexation occurs, simulation studies have shown that the mobility of the cation drops severely [22]. This is the main reason why

---

* Corresponding author at: Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden. Tel.: +46 8 790 92 87; fax: +46 8 790 82 83.
E-mail address: matskg@kth.se (M. Johansson).

0167-2738/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ssi.2013.01.019

the mobility and the segmental motion of the complexing EO segments are largely influencing parameters on the conductivity. However, in a polymer electrolyte the transport of both the lithium cation as well as its counter anion will contribute to the overall ionic conductivity [23]. Polymer electrolytes in which this is avoided through covalent attachment of the anion to the polymer structure, allowing only the lithium cation to be transported, are so called single ion conductors. Studies have shown that this results in a dramatically decreased ionic conductivity due to unsatisfactory dissociation of the lithium cation in such materials [24]. Therefore, a lithium cation with a proper counter anion has to be chosen to secure sufficient mobility.

As mentioned above, increased ion transport number correlates to how mobile the terminal EO units throughout the electrolyte are i.e. whether EO segmental motion of the polymer backbone is possible [21,25]. Larger mobility of EO polymer chains as well as increased free volume in the network result in a softer, more ductile material with enhanced ionic conductivity. On the other hand, a more cross-linked electrolyte offers improved mechanical properties and dimensional stability [26], but decreased ionic conductivity. Therefore, the ability of the thermoset SPE to transport ions and carry mechanical load are two counteracting properties of which an optimum needs to be established. Additionally, the usage of too large, linear EO compounds promotes the formation of crystalline regions in the SPE which is detrimental to the ionic conductivity. This phenomenon can be reduced with for instance increased crosslinking density or by addition of fillers [27–29].

An advantageous trade-off when designing a battery with a solvent free SPE includes the built-in property of obtaining an effective electrode separator (and electric insulator). It reduces the overall usage of organic solvents, a significant advantage given the issues described above.

In order to meet the demands and conditions prevailing in the work of designing SPEs, it is important to investigate novel routes through which they can be made. A polymerizing system that has revived and obtained a significant interest in the field of polymer science during the last decades is the so called “thiol–ene” system. It is a well-known, versatile polymerization technique, where the thiol compound can be used in stoichiometric equivalence to the “ene” groups, or as an additive at lower amounts [30–34]. Thiol–ene systems comprise of a combination of alkene and thiol monomers that can react free radically to form thio-ether links between the monomers, even without the utilization of a photo initiator [35]. A main difference to most other free radical polymerizations is that the reaction proceeds via a stepwise reaction mechanism (that proceeds by a free-radical chain mechanism [36]). In the case of thermosets this is associated with a gel point at higher monomer conversions, resulting in a more homogenous polymer network. The aim of the present study is firstly to reveal if thiol–ene chemistry can be performed in the presence of a lithium salt and secondly how the incorporation of thio-ether links affects the performance of material as a SPE.

Furthermore, introduction of thio-ethers might have an interesting influence on both mechanical properties as well as the ion conducting ability of the SPE. If compatible to the system, introduction of sulfur to the polymer network may result in a looser overall coordination strength to the lithium ion, since the interaction between sulfur and a lithium ion is weaker than the interaction between oxygen and lithium [27], thus improving the ionic conductivity at a lower cost of mechanical performance since the complexation mentioned above would be weaker.

2. Experimental

2.1. Materials

The monomers/oligomers used are depicted in Fig. 1. Tetraethylene glycol dimethacrylate (SR209) (**a**), and methoxy polyethylene glycol (350) monomethacrylate (SR550) (**b**), were kindly supplied by Sartomer Company, Europe. Trimethylol-propane-tri(3-mercaptopropionate) (**c**) was kindly supplied by Bruno Bock Chemische Fabrik GmbH & Co (Germany). 2,2-dimethoxy-2-phenylaceto-phenone Irgacure 651 (DMPA) was thankfully received from Ciba Specialty Chemicals (Switzerland). Lithium trifluoromethanesulfonate (lithium triflate) (97%) was purchased from Chemtronica AB (Sweden). All reagents were used as received with no further purification, except for the lithium triflate salt which was dried under vacuum at 80 °C for two days before entering the glove box.

2.2. Techniques & procedures

2.2.1. Sample preparation and photopolymerization

The following general procedure was used for the curing of the polymer electrolytes. Details of all sample compositions are found in Table 1. Monomers **a** and **b** were mixed in vials in a glove box under dry conditions, (<1 ppm H_2O), in argon atmosphere and the dried lithium salt was dissolved in the mixture (8 wt,% of the weight of **a**, **b** and **c**). The vials were then sealed and put on a shaking table overnight, allowing the lithium salt to dissolve completely. The thiol monomer **c**, as well as the photoinitiator (2 wt,%, relative to the weight of **a** + **b**) was then added and the mixture was stirred until the initiator was dissolved. At this stage, 0.3 ml of each sample solution was transferred into a teflon mold (15×20×1 mm) using a syringe. Finally, the solution was cured for 4 min under UV irradiation at 15 cm distance from the UV light source. The temperature of the sample did not exceed 42 °C during cure. The SPEs obtained were transparent and smooth. The light source used for curing was a Blak Ray B-100AP (100 W, 365 nm) Hg UV lamp, which after 4 min of irradiation had cured the sample with a total dose of 1.25 J cm^{-2}, as determined using an Uvicure Plus High Energy UV Intergrating Radiometer (EIT, USA), measuring UVA at 320–390 nm. After curing, the cured solids were taken out of the molds and cut into pieces of appropriate size, using a scalpel, for further characterization.

2.2.2. Electrical Impedance Spectroscopy (EIS)

The electrochemical performance of the SPEs was quantified using a four-electrode test cell, consisting of four gold wires (two working electrodes with 20 mm distance and two reference electrodes, 5 mm distance) and two Plexiglas plates with screws to hold the sample, that measures 15×20×1 mm, in place (the thickness was measured with a digital slide caliper). The impedance was potentiostatically measured in the frequency range 1 Hz to 300 kHz, at 10 points per decade. The instrument utilized was a Gamry Series G 750 Potentiostat/Galvanostat/ZRA interface, in an argon-filled glove box (<1 ppm H_2O) at 25 °C.

2.2.3. Dynamical mechanical analysis (DMA)

Dynamical mechanical analysis (DMA) tests were performed on a TA instruments DMA, model Q800 in tensile mode. Sample pieces were cut from the initial sample pieces from the curing so they possessed a geometry of 7×5×1 mm. The specimens were tightened in the clamps of the sample holder, and the temperature was then decreased to and held at the starting temperature (−60 °C) for 5 min before the measurements were started. The temperature was then increased by 5 °C/min up to a top value of a sufficient magnitude where the glass transition temperature, T_g, was passed by as data was recorded. The oscillation frequency was held at 1 Hz at constant amplitude of 10.0 μm. DMA measurements gave values for storage modulus (E' both at 20 °C and in the rubber plateau region), loss modulus (E''), loss factor (tan δ) and T_g for the electrolytes presented in Table 2.

2.2.4. Fourier-transform infrared (FT-IR) and FT-Raman spectroscopy

The samples were characterized before and after curing (to obtain a reference value). FT-IR analysis was performed using a Perkin-Elmer Spectrum 2000 FT-IR instrument (Norwalk, CT) equipped with a single reflection (ATR: attenuated total reflection) accessory unit having