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Conductivity and properties of polysiloxane-polyether cluster-LiTFSI networks as hybrid polymer electrolytes

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HIGHLIGHTS

- Hybrid polyether/polysiloxane polymer electrolytes were prepared by sol-gel process.
- The materials are amorphous and mechanically stable beyond 100 °C.
- The ionic conductivity reaches $8 \cdot 10^{-5}$ S cm^{-1} at 30 °C.
- The lithium transference number is comprised between 0.3 and 0.1.
- A LFP/Li-polymer cell delivers 100 mAh g^{-1} at 60 °C and 0.1 mA cm^{-2}

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ABSTRACT

This report describes the synthesis and the properties of a series of polymer electrolytes, composed of a hybrid inorganic-organic matrix doped with LiTFSI. The matrix is based on ring-like oligo-siloxane clusters, bearing pendant, partially cross-linked, polyether chains. The dependency of the thermo-mechanic and of the transport properties on several structural parameters, such as polyether chains' length, cross-linkers' concentration, and salt concentration is studied. Altogether, the materials show good thermo-mechanical and electrochemical stabilities, with conductivities reaching, at best, $8 \cdot 10^{-5}$ S cm^{-1} at 30 °C. In conclusion, the cell performances of one representative sample are shown. The scope of this report is to analyze the correlations between structure and properties in networked and hybrid polymer electrolytes. This could help the design of optimized polymer electrolytes for application in lithium metal batteries.

1. Introduction

The development of safer electrolytes is one of the leading topics in the field of secondary lithium batteries research [1]. Solid polymer electrolytes (SPEs), in particular, represent one of the hottest subjects, despite this class of compounds being introduced already almost forty years ago [2]. The continuous interest on polymer electrolytes is motivated, in first instance, by their intrinsic safety, compared to liquid electrolytes. In addition, SPEs offer better resistance to lithium dendrites growth, thus opening the way to the use of metal lithium as anode in lithium-metal polymer batteries [3–5].

Despite having favorable properties, such as low cost, low toxicity, and no flammability, the application of polymer electrolytes has been so far limited. This is due mainly to their low conductivity, which, in the case of classic PEO-salt complexes, is about 10^{-6} S cm^{-1} at room temperature. As comparison, the estimated necessary conductivity for practical purposes is almost 10^{-3} S cm^{-1} at operating temperature [6].

Enhancements in the conductivity and of the thermo-mechanical properties have been achieved by modifying the host

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matrix, especially with comb-like [7–10], and block-copolymer electrolytes [11]. Alternatively, a simple strategy consists in adding inorganic particles to the host matrix, i.e. by preparing composite polymer electrolytes [12–16]. In this case, it was soon observed that the addition of nano-sized particles has greater effects compared to micrometer-sized particles [17]. This ultimately led to the development of hybrid-inorganic-organic electrolytes, where the inorganic components are mixed with the organic matrix on a nanometric scale [18]. The family of hybrid polymer electrolytes comprises a huge variety of structures, such as three-dimensional networked hybrid electrolytes (3D–HION–APEs) [19–22], zeolitic hybrid polymer electrolytes (ZIOPEs) [23–26], or the hybrid electrolytes based on the ORMOCER®s structure [27–29].

More recently, hybrid electrolytes have been developed by ring-opening reaction of PEG-functionalized tetrasiloxane [30], by surface functionalization of silica or titania nano-particles [31], by sol-gel process [32–34], and by introduction of silsesquioxane-like (POSS) moieties [35–40]. In some of these works, conductivities higher than 10^{-4} S cm^{-1} at room temperature are reported, even without addition of any plasticizer [32,34].

In a previous report [41], we discussed the synthesis and the properties of ORMOCER®-like hybrid polymer electrolytes based on partially cross-linked polyether chains covalently bound to tridimensional polysiloxane clusters. The materials showed high conductivity, and good thermo-mechanical and electrochemical stabilities. Nonetheless, the lengthy of the epoxy-curing step represented a major obstacle for any practical application. Another issue regarded the use of lithium hydroxide, which was added during the sol-gel step to lower the siloxane condensation degree and prevent the gelation of the precursor. The use of lithium hydroxide slows down the condensation reaction, increasing the risk of having unstable alkoxysilanes or silanols in the product.

In this reports, we try to solve these problems, by modifying the starting components and the synthetic approach. In addition, we utilize the modularity of the synthesis to study the dependence of thermo-mechanical and electrical properties of these hybrid electrolytes on structural parameters such as polyether chains length, density of chemical cross-links and salt concentration.

With respect to the previously reported ORMOCER®-based electrolytes [28,29,41], the newly synthesized materials are obtained by sol-gel reaction of dialkoxysilanes, rather than of trialkoxysilanes. Dialkoxysilanes are preferred since their condensation products are viscous liquids, even without adding condensations limiters such as LiOH. It is important to have a liquid condensation product as this can be used to coat the battery electrodes without the need of additional solvents. After curing, the materials are expected to show elastomeric properties and low T_g [42], which is necessary to have a reasonable conductivity. In addition, it is easier to obtain a complete condensation with the dialkoxysilanes, so no end-capping reaction is needed to remove the residual silanol groups. Another difference consists in the use of the vinyl moieties whereas, previously, epoxy groups were used.

Three polyether-functionalized dialkoxysilanes are used as molecular precursors. As cross-linking component, or network former [42], triethylene glycol, α-vinyl, ω-ethyl(methyl)diethoxysilane ether (Vi-TEG-EMDES, Scheme S1 in Supplementary Information) is used. Through the polymerization of the terminal vinyl moieties, this component provides the mechanical stability to the structure. As non-cross-linking components (or network modifiers) [42], the short-chain triethylene glycol, α-methyl, ω-propyl (methyl)diethoxysilane ether (Me-TEG-PMDES) and the bulkier polyethylene glycol, α-methyl, ω-propyl (methyl)diethoxysilane ether (Me-PEG-PMDES) are utilized. The presence of flexibly, free-end, polyether chains is necessary to boost the chains mobility and the ionic conductivity. Two different chains' length components were utilized to study the effect of the polyether fragments molecular weight on the materials' physical properties.

As doping salt, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is used. Thanks to the flexibility and effective charge delocalization of the TFSI$^-$ anion, this salt provides good conductivity and low ion-aggregation phenomena [43,44].

After the curing step, the resulting hybrid matrix is composed by ring oligosiloxane clusters with pendant, partially cross-linked, polyether chains. This structure reminds the comb-like polysiloxane-based polymer electrolytes prepared by hydrosilylation reaction [9,10,45]. Contrarily to these, here the oligosiloxane clusters have closed-ring structure and lower molecular weight. In addition, the synthetic approach is different, as the starting point involves a sol-gel reaction of molecular precursors. In any case, these materials could be classified as a bridge between ORMOCER® and comb-like polymer electrolytes.

The report is divided in three parts: firstly, the synthesis and the properties of four hybrid polymer electrolytes with short pendant polyether chains are described. Special attention is paid to the effect of the cross-links concentration on the thermo-mechanical properties and conductivity. In the second part, a set of hybrid electrolytes with longer pendant polyether chains and variable salt concentration is studied. Finally, the electrochemical stability and the cell performance of a representative sample of this last series are presented.

2. Experimental section

2.1. Materials

Tri(ethylene glycol)divinyl ether (Sigma Aldrich, 98%), tri(ethylene glycol)monomethyl ether (Sigma Aldrich, 95%), and poly(ethylene glycol) (350) monomethyl ether (ABCR) were dried under vacuum at 50 °C for 24 h. Bis(trifluoromethanesulphonyl) imide (Sigma-Aldrich, 99.95%) was dried under vacuum at 70 °C for 24 h. Methyldiethoxysilane 97% and the Karstedt catalyst were purchased from ABCR and used without further purification. All other reagents and solvents were purchased from Sigma-Aldrich and used without further purification.

2.2. Synthesis of the precursors

The synthetic procedures are described in the Supplementary Information.

2.3. Electrolytes preparation

The liquid precursors are mixed with different amounts of LiTFSI and with 0.5 wt% of dibenzoyl peroxide (DBPO, Sigma Aldrich, 98%). The solid electrolytes are obtained by radical polymerization of the vinyl groups of Vi-TEG-EMDES. The mixture is poured into 18 mm wide aluminum pans and the samples are heated at 70 °C on a heating plate, under Argon atmosphere. The process lasts from 2 h to 15 h, depending on the cross-linker concentration. After cooling, the free standing pellets are peeled off and characterized. The electrolyte compositions are reported in Table 1.

2.4. Instruments and methods

Thermogravimetric analyses were carried out with a TGA 2950 (TA Instruments). The TG profiles were recorded under N_2 flow (20 mL min^{-1}), in a temperature range from 20 to 950 °C. A temperature ramp rate of 10 °C min^{-1} was used. Differential Scanning Calorimetry measurements (DSC) were carried out with a DSC Q 20