



# Highly conductive, flexible polymer electrolyte membrane based on poly(ethylene glycol) diacrylate-co-thiosiloxane network



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## ABSTRACT

An amorphous co-network consisting of poly(ethylene glycol) diacrylate (PEGDA) and thiosiloxane was prepared by means of thiol-ene “click” reaction to impart high ion conduction via enhanced segmental mobility of the co-network. By varying PEGDA-thiosiloxane ratios, several polymer electrolyte membranes (PEM) have been fabricated to control the glass transition temperature ( $T_g$ ), while keeping the equal molar ratio of succinonitrile (SCN) plasticizer and bis(trifluoromethane sulfonyl)imide (LiTFSI) salt for solid-state lithium ion batteries. It was found that the addition of thiosiloxane into the PEM network not only results in improved thermal stability and greater extensibility, but also reduces  $T_g$  leading to higher ionic conductivity that reaches the level of superionic conductor at room temperature, which further increases to  $10^{-2} \text{ Scm}^{-1}$  at high battery operating temperatures (60–70 °C). To evaluate their electrochemical performance, half-cells comprising of  $\text{LiFePO}_4/\text{PEM}/\text{Li}$  foil were tested by means of cyclic voltammetry. An initial discharge capacity of  $148 \text{ mAhg}^{-1}$  was obtained at a current rate of 0.2 C with capacity retention of about 89%.

## 1. Introduction

Nowadays, lithium-ion batteries have been commonly used in our daily life to power portable electronics, wearable devices, and emerging technologies including high power, high energy all solid-state battery for electric vehicles. The current Li-ion battery technology is designed based on organic liquid electrolytes such as mixtures of cyclic ethylene carbonate (EC) with volatile diethylene carbonate (DEC) or dimethyl carbonate (DMC) solvents to afford high Li-ion conduction [1]. However, because of their poor thermal stability and volatility coupled with low flash points, these liquid electrolyte solutions can easily catch fire during battery operation [2–4]. To overcome the aforementioned flammability of liquid electrolytes, solid-state polymer electrolyte membranes (PEM) have been developed in order to alleviate fire hazard of lithium ion battery [5].

The first solid electrolyte was reported by Wright in 1975 based on a mixture of poly(ethylene oxide) (PEO) and alkaline salt that showed an ionic conductivity of  $10^{-7} \text{ Scm}^{-1}$  at room temperature [6]. One major drawback of the early generation of PEO based solid polymer electrolytes (SPE) has been their low ionic conductivities at room temperature, i.e.,  $10^{-9}$ – $10^{-7} \text{ Scm}^{-1}$ , which is several orders of magnitude lower than that of liquid electrolyte counterparts ( $10^{-3}$ – $10^{-2} \text{ Scm}^{-1}$ ) [7,8].

It was later in 1979, Armand et al. [9] developed lithium-ion batteries by mixing succinonitrile (SCN) plastic crystals and various lithium salts that have improved high ionic conductivity to the range of  $10^{-4}$ – $10^{-3} \text{ Scm}^{-1}$ , but such electrolytes had a paste-like appearance with poor mechanical integrity.

The solid-state PEM needs not only to be mechanically sturdy, but also room-temperature ionic conductivity, thermal and electrochemical stability must be improved. The simultaneous improvement of these properties is hard to come by because ionic conductivity and mechanical strength have diametrically opposing effects [10]. PEMs hitherto developed were primarily based on functional polymers and lithium salts such as polyphosphazene [11], oligoethers [12] and PEO-modified polysiloxanes [13]. The manner in which these PEMs were made was by first dissolving lithium salt into a polymer precursor (i.e., pre-polymer or macromonomer) and then photo-cured via UV irradiation to obtain a self-standing solid film.

PEO-modified polysiloxane is an interesting approach in the development of novel polymer matrix. Neat polysiloxanes are characterized by their good mechanical strength, chemical, thermal stability, and low glass transition temperatures, but poor conductivity [14,15]. However, siloxane modification with PEO can afford high ion conduction in conjunction with good physical properties of siloxane, making these

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polymer matrices highly desirable for use in all solid-state lithium ion batteries. However, neat polysiloxane derivatives are difficult to be dissolved in PEO matrix. One common approach is to modify these siloxanes by covalently linking with polar polyether groups to improve solubility in the PEO matrix. In 1988, Khann synthesized *comb*-like polysiloxane having oligo(oxyethylene) side branches and subsequently incorporated them in the PEM [16]. The ionic conductivity values of these PEMs were improved to the acceptable conductivity range of the order of  $10^{-4} \text{ Scm}^{-1}$ , albeit still low.

Wang et al. [17] synthesized siloxane polymer and then mixed it with lithium *bis*(trifluoromethyl sulfonyl)imide (LiTFSI) salt. However, the highest ionic conductivity value thus obtained was on the order of  $10^{-4} \text{ Scm}^{-1}$  at room temperature. Similarly, Zhang et al. [18] prepared a solid PEM via hydrosilylation of polymethylhydrosiloxane (PMHS) and subsequently mixed with LiTFSI salt. They achieved a similar order of magnitude in ionic conductivity (i.e.,  $10^{-4} \text{ Scm}^{-1}$ ) with their crosslinked siloxane-based solid PEM network having a low  $T_g$  of approximately  $-50^\circ \text{C}$ . Burjanadze et al. [19] investigated the electrochemical stability of crosslinked salt-in-polysiloxane membranes containing two lithium salts, i.e., boron based anions, viz., LiDFOB (lithium difluoro(oxalato)borate) and LiBOB (lithium *bis*(oxalato)borate). The ionic conductivity values were relatively low that only reached the order of  $10^{-5} \text{ Scm}^{-1}$  at room temperature, but with an enhanced electrochemical stability up to 4.7 V against Li/Li<sup>+</sup>.

One interesting approach in fabricating the siloxane-PEO compounds without performing tedious chemical synthesis is to conduct crosslinking reactions between polyethylene glycol derivatives such as poly(ethylene glycol) diacrylate (PEGDA) and thiol (SH) containing compound such as thiosiloxane via the thiol-ene ‘click’ reaction between thiol (SH) of siloxane and the C=C double bonds of functional acrylate groups of the polyether backbone [20]. This click reaction is reported to be fast, easy to execute, and more importantly provides high yield. In fact, such chemical route has been already demonstrated by the co-authors while they were at DOE [21,22], who reported the achievement of completely amorphous crosslinked co-networks consisting of PEGDA and thiosiloxane. These thiosiloxane/PEGDA co-networks have high selectivity and separation of carbon dioxide (CO<sub>2</sub>) from nitrogen (N<sub>2</sub>) or methane (CH<sub>4</sub>) with potential applications in control of greenhouse gas emission [23]. The presence of both polar and non-polar moieties in the thiosiloxane/PEGDA co-network has been attributed to be the key factor in the enhancement of gas permeability and selectivity.

In this article, the aforementioned thiol-ene ‘click’ crosslinking reaction was employed to afford an amorphous thiosiloxane/PEGDA co-network for use as a polymer matrix in the polymer electrolyte membrane for solid-state lithium ion battery. Firstly, the miscibility of a binary thiosiloxane/PEGDA mixture was determined in order to provide guidance to the formation of isotropic amorphous polymeric co-network. Secondly, various thiosiloxane/PEGDA ratios were further mixed with lithium salt (LiTFSI) and succinonitrile (SCN) plasticizer to produce a completely amorphous, solid-state polymer electrolyte membrane (PEM). Mechanical and ion conduction properties of the above thiosiloxane/PEGDA membranes were evaluated by means of tensile tests and AC impedance spectroscopy, respectively. Cyclic voltammetry measurements were also carried out in order to evaluate electrochemical performance and discuss potential utilization of siloxane-PEGDA PEMs as solid electrolytes for all solid-state lithium ion batteries.

## 2. Materials and methods

(Mercaptopropyl) methyl siloxane prepolymer (thiosiloxane), Mw = 5000 was purchased from Gelest. Poly(ethylene glycol) diacrylate (PEGDA), Mw = 700 g/mol was bought from Sigma-Aldrich. Photo-initiator Irgacure®651 (2,2-dimethoxy-2-phenylacetophenone, DMPA) was obtained from CIBA. Lithium *bis*(trifluoromethyl sulfonyl)

imide (LiTFSI) (purity 99.9%), succinonitrile (purity > 99%) (SCN) and 2-butanone (purity  $\geq 90\%$ ) were purchased from Sigma-Aldrich.

Poly(vinylidene fluoride) (PVDF) having Mw of 534,000 (Sigma-Aldrich) was dissolved in anhydrous (99.5%) 1-methyl-2-pyrrolidinone (NMP) (Sigma-Aldrich) solvent. Electrode material, viz., lithium iron phosphate (LiFePO<sub>4</sub>) obtained from MTI Corp., was blended with acetylene black (AB) (also from MTI) to improve electron conductivity of the cathode. In the cathode fabrication, the solution mixture consisting of PVDF (10 wt%), acetylene black (10 wt%), and active electrode material (LiFePO<sub>4</sub>) (80 wt%) in NMP was used as electrode binder in the slurry form.

### 2.1. Binary thiosiloxane-PEGDA system

Various thiosiloxane/PEGDA binary mixtures were prepared in accordance with the predetermined weight ratios thiosiloxane:PEGDA 10:90, 15:85 and 25:75. These binary components were fully dissolved upon mixing in the liquid state. By adding the indicated amount of DMPA photoinitiator, the thiol (SH) group of thiosiloxane was activated and subsequently reacted with acrylate groups of PEGDA via the so-called thiol-ene ‘click’ reaction. Note that the photo-initiator (DMPA) amount was kept at 3 wt% with respect to the total prepolymer amount. This thiol-ene reaction produced a crosslinked network between non-polar siloxane and polar PEGDA. Upon photo-crosslinking, the binary blend membrane remained homogeneous and transparent, suggestive of the formation of an isotropic co-network.

### 2.2. Pseudo-ternary system – thiosiloxane-PEGDA/SCN/LiTFSI

Binary mixtures of thiosiloxane/PEGDA and SCN/LiTFSI were prepared separately inside a glovebox under Argon atmosphere. Thiosiloxane/PEGDA blends in the indicated weight ratios were found to be completely miscible. However, the SCN/LiTFSI mixture had to be heated above the crystal melting temperature of SCN (i.e., 60 °C) for several minutes in order to completely dissolve and form a clear melt mixture. Subsequently, these individual binary mixtures were further mixed with thiosiloxane/PEGDA in their melt state. The initial quaternary (thiosiloxane:PEGDA/SCN/LiTFSI) liquid mixture exhibited a cloudy appearance, but it turned transparent upon adding 2-propanone as a common solvent. After exposure to UV irradiation for 5 min, copolymerization occurred between thiosiloxane and PEGDA via the ‘click’ reaction and formed a thiosiloxane-PEGDA copolymer. Upon removal of solvent, a clear, solid polymer electrolyte membrane (PEM) consisting of thiosiloxane-PEGDA copolymer, SCN and LiTFSI (viz., pseudo-ternary constituents) was obtained.

### 2.3. Polymer electrolyte membrane

The polymer electrolyte membranes (PEM) compositions are given in weight ratios, e.g., 20/40/40 (thiosiloxane:PEGDA)/SCN/LiTFSI. In the PEM formulation, the copolymer ratio of thiosiloxane:PEGDA was varied as 2:18(10/90)/40/40, 3:17(15/75)/40/40 and 5:15(25/75)/40/40, while fixing their total amount at 20 wt%. Also the weight percent for SCN/LiTFSI was kept as constant (at 40 wt% each) such that the only variable is the copolymer ratio. The amount of photo-initiator (DMPA) was kept at 3 wt% with respect to the total prepolymer amount. It should be pointed out that the above PEM mixture belongs to the isotropic region of their ternary phase diagram (figure not shown).

This transparent mixture was spread within a spacer (10 mm × 10 mm frame and 0.3 mm thick). Subsequently, it was photo-crosslinked under uniform UV irradiation at 350 nm with an intensity 5 mW cm<sup>-2</sup> for 2 min. After curing, solid films thus obtained were subsequently dried for 60 min at 80 °C and then kept inside a glovebox overnight under argon atmosphere. These fabricated PEM film samples were characterized by using various characterization techniques such as Fourier transformed infrared (FTIR), Raman, wide angle X-ray

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