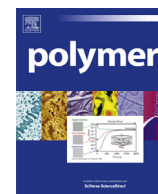




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# Preparation of organic/inorganic hybrid semi-interpenetrating network polymer electrolytes based on poly(ethylene oxide-co-ethylene carbonate) for all-solid-state lithium batteries at elevated temperatures

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## ABSTRACT

Organic/inorganic hybrid semi-interpenetrating network (semi-IPN) polymer electrolytes (HIPEs) based on poly(ethylene oxide-co-ethylene carbonate) (PEOEC) have been developed for all-solid-state lithium battery applications. In comparison to those of poly(ethylene oxide) (PEO), salient features of the PEOEC are the amorphous nature and high dielectric constant, which provide enhanced ionic conductivity. The organic/inorganic hybrid network matrix in the HIPEs is composed of different contents of photo-cross-linked octa-functional POSS acrylate (OA-POSS) and ethoxylated trimethylolpropane triacrylate (ETPTA). The effect of OA-POSS on solid-state electrolyte properties of the HIPEs is investigated in terms of the dimensional stability, thermal behavior, and ionic conductivity. Due to the presence of the rigid and bulky POSS moiety, the HIPEs exhibit improvement in ionic conductivity along with enhanced dimensional stability. The high capacity and good cycle performance of lithium batteries with the HIPEs demonstrate feasibility of applying the HIPEs to solid-state electrolytes for all-solid-state lithium batteries that can operate at elevated temperatures.

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## 1. Introduction

As lithium rechargeable batteries begin to be applied as a power source for electric or hybrid electric vehicles, battery safety is becoming increasingly important [1,2]. The safety issues of lithium batteries are closely related to the use of liquid electrolytes, which have several drawbacks such as leakage, volatility, spontaneous combustion, limited temperature range of operation, and lack of mechanical stability [3]. To surmount these shortcomings of liquid electrolytes, solid polymer electrolytes (SPEs) have received considerable attentions due to their advantages, including non-volatility, low flammability, chemical and electrochemical stability, and widely tunable shape conformations [1,4]. Most SPEs show an appreciable ionic conductivity ( $>10^{-4}$  S cm<sup>-1</sup>) only at elevated temperatures (above 60 °C) due to the restricted lithium ionic mobility at room temperature [4–6]. Although the low ionic

conductivity of SPEs is a drawback for battery applications in the consumer electronic market, it is acceptable to use the SPEs for batteries in electric vehicles, power storage, and load leveling, all of which can be operated at elevated temperatures [7–9]. To date, high molecular weight poly(ethylene oxide) (PEO) coupled with lithium salt has been frequently and thoroughly studied for SPE applications [4–6,10]. However, a PEO electrolyte cannot be applied as a practical SPE, because it has comparatively low ionic conductivity owing to the existence of crystalline domains that interfere with lithium ion conduction [4,10,11]. In addition, since the PEO electrolyte has relatively small dielectric constant value [5], it cannot allow an effective dissociation of the lithium salt, resulting in the formation of a large amount of contact ion pairs and/or ion aggregates in the electrolyte system [12,13]. This could also cause a detrimental effect on the ionic conductivity.

Previously, we reported on the synthesis of poly(ethylene oxide-co-ethylene carbonate) (PEOEC) via ring opening polymerization of ethylene carbonate [14]. We found that the PEOEC has an amorphous state due to the polar carbonate units linked by ether moieties. This unique structural feature of PEOEC can provide enhanced ionic conductivity when employed as a polymer matrix for SPEs.

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Jeon et al. studied a pore-filling polymer electrolyte based on a porous membrane filled with the PEOEC [15,16]. However, the application of the pore-filling polymer electrolyte could be limited due to the complicated preparation process. Elmér et al. also described the application of PEOEC for SPEs by utilizing cross-linked polymeric structures, although the ionic conductivity was below  $10^{-5}$  S cm $^{-1}$  at room temperature [13]. Therefore, a simple, effective approach to prepare PEOEC-based SPEs with high ionic conductivity needs to be suggested. In addition, the ionic conductivity behavior of the PEOEC electrolyte should be further investigated, because the effects of carbonate unit and molecular weight of PEOEC on the ionic conductivity have not been elucidated in detail.

Polyhedral oligomeric silsesquioxane (POSS) has been studied extensively as an effective nanofiller because of its well-defined nanoscale organic/inorganic hybrid structure [17,18]. POSS has been known to improve mechanical strength of polymers due to the molecular level dispersion of rigid POSS in the polymers [17–20], while its large volume can also maintain or decrease the glass transition temperature ( $T_g$ ) by changing the polymer chain topology and providing additional free volume to the polymer chains [21]. In our recent studies, we found that dimensionally-stable free-standing films could be obtained by incorporating POSS side groups into wax-state polymers with PEO side groups [20,22–24].  $T_g$ s of the copolymers with both PEO and POSS side groups were found to be close to those of the homopolymers with only PEO side group. This indicates that the incorporation of POSS into polymers can improve the dimensional stability of polymers without significant decreases in polymer chain mobility. It is desirable for SPEs to exhibit sufficient dimensional stability to separate the electrode as well as high ionic conductivity. Therefore, the effect of POSS on polymers suggests the possibility to fabricate organic/inorganic hybrid SPEs with enhanced dimensional stability and ionic conductivity.

In this study, we demonstrate an approach to prepare organic/inorganic hybrid semi-interpenetrating network (semi-IPN) polymer electrolytes (HIPEs) based on PEOEC, which can impart high ionic conductivity and sufficient dimensional stability for SPE applications. Prior to investigating HIPEs, the ionic conductivity behavior of PEOEC electrolyte is studied and compared with that of PEO electrolyte. The HIPEs are prepared by a photo-cross-linking reaction of octa-functional POSS acrylate (OA-POSS) and ethoxylated trimethylolpropane triacrylate (ETPTA) in the presence of PEOEC. The discussion mainly focuses on the effect of OA-POSS on solid-state electrolyte properties of HIPEs, including dimensional stability, thermal behavior, and ionic conductivity. Based on the understanding of the characteristics of HIPEs, feasibility of applying HIPEs to solid-state electrolytes for lithium batteries is explored by electrochemical stability and cell performance analyses.

## 2. Experimental

### 2.1. Materials

Potassium hydroxide (KOH, Aldrich) was dried under high vacuum at 110 °C for 3 days and stored in an argon (Ar)-filled glove box. Ethylene carbonate (EC, 98%), poly(ethylene oxide) (PEO, GPC-MALLS analysis:  $M_w = 5300$  g mol $^{-1}$ ), ethoxylated trimethylolpropane triacrylate (ETPTA,  $M_n = 428$  g mol $^{-1}$ ), and 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP), all from Aldrich, were used as received. Octa-functional POSS acrylate (OA-POSS, Product Number: MA0736, Acrylo POSS $^{\text{®}}$ ) was purchased from Hybrid Plastics, Inc. and used as received. Lithium perchlorate (LiClO $_4$ , >99%, Aldrich) and lithium trifluoromethanesulfonate (LiSO $_3$ CF $_3$ , 99.995%, Aldrich) were dried under high vacuum at 130 °C for 2

days and stored in an Ar-filled glove box. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under a nitrogen atmosphere. All other reagents and solvents were used as received from standard vendors.

### 2.2. Synthesis of poly(ethylene oxide-co-ethylene carbonate) (PEOEC)

Poly(ethylene oxide-co-ethylene carbonate) (PEOEC) was synthesized via ring opening polymerization of ethylene carbonate (EC). The following procedure was used for the preparation of a PEOEC (H-PEOEC, GPC-MALLS analysis:  $M_w = 6100$  g mol $^{-1}$ ). EC (40 g, 0.45 mol) and potassium hydroxide (KOH, 0.13 g, 0.0023 mol) were added to a 100 mL round-bottomed flask equipped with a magnetic stirring bar in an Ar-filled glove box. Polymerization was conducted at 180 °C under nitrogen gas flow. After 2 h 30 min of polymerization, the flask was placed in liquid nitrogen and diluted with chloroform to quench the reaction. Then, the chloroform was removed using a rotary evaporator. After the polymer/monomer mixtures were dissolved in a small amount of ethanol, the solution was precipitated into an excess of diethyl ether to remove unreacted monomers. The dissolution-precipitation procedure was repeated several times. The purified polymer was dried under vacuum at room temperature for 3 days, yielding a yellowish wax (4.1 g). A lower molecular weight PEOEC (L-PEOEC, GPC-MALLS analysis:  $M_w = 3500$  g mol $^{-1}$ ) was also prepared using the same procedure except the EC/KOH feed ratio (1000/1) and reaction time (2 h).  $^1$ H NMR (300 MHz, CDCl $_3$ ,  $\delta$  (ppm), tetramethylsilane (TMS) ref): 4.28 (CH $_2$ -CH $_2$ -O-C(O)-O), 3.72 (CH $_2$ -CH $_2$ -O-C(O)-O), 3.65 (CH $_2$ -CH $_2$ -O).

### 2.3. Preparation of PEOEC and PEO electrolytes

The polymers (PEOEC or PEO) (0.2 g) and LiClO $_4$  in various blend compositions were dissolved homogeneously in distilled THF (0.8 mL). The concentration of lithium salt in polymer electrolytes is defined as the ratio of [LiClO $_4$ ]/([EO (ethylene oxide unit)] + [EC (ethylene carbonate unit)]). The solvent was evaporated using a rotary evaporator and the electrolytes were further dried at 80 °C under high vacuum for a week. The PEOEC and PEO electrolytes are designated as (H- or L-)PEOEC# and PEO#, where # is the lithium salt concentration in the electrolytes.

### 2.4. Preparation of organic/inorganic hybrid semi-IPN polymer electrolytes (HIPEs)

Organic/inorganic hybrid semi-IPN polymer electrolytes (H-HIPEs) containing H-PEOEC 0.15 and ETPTA/OA-POSS moieties were prepared by a solution casting and UV curing process. Polymers (H-PEOEC), cross-linkers (ETPTA and OA-POSS), photo-initiator (HMPP), and lithium salt were dissolved in distilled THF. The weight ratio of polymer : cross-linkers was fixed at 80 : 20, wherein the weight ratios of ETPTA:OA-POSS were 20:0, 15:5, and 10:10 for H-HIPE0, H-HIPE5, and H-HIPE10, respectively. The injected mass of HMPP was 0.1 wt% of that of the cross-linkers. Organic/inorganic hybrid semi-IPN polymer electrolytes (L-HIPEs) containing L-PEOEC 0.15 instead of H-PEOEC 0.15 were also prepared. The lithium salt concentration ([LiClO $_4$ ]/([EO] + [EC])) for the PEOEC in the HIPEs was 0.15, at which the highest ionic conductivities of PEOEC electrolytes were observed. The solution was casted on a glass substrate and the solvent was evaporated at room temperature for 12 h. Then, the casted mixture was exposed to UV light (B-100 series ultraviolet lamp, 50 Hz, UVP Inc., USA) for 10 min. The resultant film was dried at 80 °C under high vacuum for a week. The thickness of the HIPEs was in the range of 200–220  $\mu$ m.

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