



Preparation of solid-state composite electrolytes based on organic/inorganic hybrid star-shaped polymer and PEG-functionalized POSS for all-solid-state lithium battery applications



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ABSTRACT

A series of composite electrolytes (CEs) consisting of organic/inorganic hybrid star-shaped polymer (SPP13), plasticizer (PEG-functionalized POSS derivatives), and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) were prepared to investigate the effects of the composite compositions and PEG chain length of PEs on the properties of CEs. SPP13 was prepared via ATRP from poly(ethylene glycol) methyl ether methacrylate (PEGMA) and methacryl-cyclohexyl-POSS (MA-POSS) using an octafunctional initiator, and the PEG-functionalized POSS derivatives were synthesized by the hydrosilylation reaction of octakis(dimethylsilyloxy)silsesquioxane (OHPS) and allyl-PEG. The CEs were found to be dimensionally-stable enough to separate the electrodes in batteries, but they still possessed high mobility of ion-conducting P(PEGMA) segments, as estimated by the low glass transition temperatures (T_g). The CEs having solid-state show quite high ionic conductivity ($4.5 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C) which is about three times of magnitude larger than that of the matrix polymer (SPP13) electrolyte ($1.5 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C). The CEs were electrochemically stable up to +4.2 V without the decomposition of electrolytes. An all-solid-state lithium battery prepared from the CEs exhibited larger discharge capacity than that prepared from the SPP13 electrolyte at 60°C .

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1. Introduction

Lithium ion batteries have attracted significant interest as an appealing power source for a variety of applications, such as portable electronic devices and electric or hybrid electric vehicles due to their high energy density and operational voltage [1,2]. Conventional lithium ion batteries contain liquid electrolytes composed of low molecular weight organic solvents and lithium salts due to their high ionic conductivities [3]. However, there are several drawbacks related to safety issues such as leakage, volatility, spontaneous combustion of the electrolytes, limited temperature range of operation, and lack of mechanical stability [3,4]. Solid polymer electrolytes (SPEs) have been studied extensively over the last two decades to overcome the disadvantages of the liquid electrolytes, due to advantages such as non-volatility, low flammability, chemical and electrochemical stability, and widely tunable shape conformations [5–7]. Although high molecular

weight poly(ethylene oxide) (PEO) has been studied as a representative SPE material, the material cannot be applied to a practical SPE, because it has a highly crystalline structure that results in low ionic conductivity ($\sim 10^{-7} \text{ S cm}^{-1}$) at room temperature [8–10]. In order to decrease the crystallinity, efforts have been directed toward the development of low molecular weight PEO-based electrolytes, while they normally could not be used as SPEs because they do not have the sufficient dimensional stability due to their waxy nature [11,12]. It is desirable for SPEs to exhibit dimensional stability for separating the electrodes, as well as high ionic conductivity.

To achieve a balance between the ionic conductivity and dimensional stability of SPEs, several strategies have been investigated over the past two decades, such as composite polymer electrolytes [13,14], block copolymer electrolytes [15,16], interpenetrating network polymer electrolytes [17,18], and pore-filling polymer electrolytes [19]. In our recent study, organic/inorganic hybrid star-shaped polymers (SPP) with polyhedral oligomeric silsesquioxane (POSS) and poly(ethylene glycol) (PEG) side groups were synthesized and applied to SPE matrices [20]. It has been reported that POSS can improve the mechanical strength of

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polymers due to the filler effect [21–23], without decreasing the chain mobility much by providing additional free volume to the polymer matrix [24]. In addition, star-shaped polymers are known to have larger chain mobility than linear polymers due to their unique structures with multiple chain ends and larger free volume [25]. These features of POSS and star-shaped architecture could provide both high lithium ionic conductivity and dimensional stability to the SPP-based SPEs. The incorporation of POSS side groups into star-shaped polymers with PEG side groups can change the wax-state of the polymers into dimensionally-stable free-standing films without significant decreases in PEG chain mobility [20]. However, the ionic conductivity of solid-state SPP-based electrolytes was still lower than that of the wax-state star-shaped polymer electrolyte with only PEG side groups. The ionic conductivity of SPP-based electrolytes needs to be further increased.

PEG-functionalized POSS derivatives (PEs:POSS-(PEG)_n), where *n* is the number of ethylene oxide (EO) units in PEG moieties) have been studied as electrolytes for lithium batteries by Wunder et al. [26–29]. PEs were found to be completely amorphous when the PEG groups were short (*n* ≤ 6), because they contain many chain ends on a rigid POSS core [26]. Therefore, when PEs were mixed with lithium salts, they exhibited quite high ionic conductivities over 10^{−4} S cm^{−1} at room temperature and about 10^{−6} S cm^{−1} even at −20 °C [27]. In addition, the non-volatile PEs have advantages for the electrolyte applications over the volatile PEG oligomers. Since PEs are viscous liquids at room temperature, they cannot be applied as solid-state electrolytes. The PEs should be mixed with rigid polymer matrices for the practical applications as the solid-state electrolyte films [27,29]. For example, solid-state composite electrolytes were prepared from high molecular weight PEO and PEs [29]. However, those composite electrolytes exhibited maximum ionic conductivities even lower than 10^{−5} S cm^{−1} at room temperature. Moreover, the effect of PEG chain length of PEs on the properties of the composite electrolytes has not been studied in the previous work.

In the current work, we have prepared solid-state composite electrolytes (CEs) composed of different contents of SPP as a SPE matrix providing both dimensional stability and ionic conductivity and PEs with 3 and average 9.5 ethylene oxide units in the PEG moieties as a plasticizer to enhance the ionic conductivity. Flexible free-standing electrolyte films could be fabricated from the composites when the PE contents in CEs were smaller than 20 wt%. The ionic conductivities of solid-state CEs were found to be noticeably higher than that of the solid-state SPP electrolyte and close to that of the wax-state star-shaped polymer electrolyte with only PEG side groups, which resulted in the larger capacity of all-solid-state batteries with CEs than that with the SPP electrolyte. The high ionic conductivity of CEs could be ascribed to the enhanced lithium ionic mobility by the plasticizing effect of PEs in the CEs. The detailed synthesis and properties including the dimensional stabilities, thermal behaviors, ionic conductivities, and electrochemical performances of the CEs containing lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) are described in this paper.

2. Experimental

2.1. Materials

Octakis(dimethylsilyloxy)silsesquioxane (OHPS, 97%), allyl alcohol (99%), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Pt(dvs), 2 wt% Pt solution in xylene), 2-bromo-2-methylpropionyl bromide (98%), copper(I) bromide (CuBr, 98%), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), tri(ethylene glycol) monomethyl ether (TEGME, 95%), poly(ethylene glycol) monomethyl ether (PEGME, average *M*_n = 450), sodium

hydride (95%), allyl bromide (97%), all from Aldrich, were used as received. Methacryl Cyclohexyl POSS® (3-(3,5,7,9,11,13,15-heptacyclohexylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane-1-yl) propyl methacrylate, MA-POSS) was obtained from Hybrid Plastics Inc. and used as received. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, average *M*_n = 475, Aldrich) was passed through a column filled with alumina to remove the inhibitor before use. Toluene was distilled over calcium hydride. Tetrahydrofuran (THF) was distilled from Na/benzophenone. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.95%, trace metal basis, Aldrich) was dried under high vacuum at 130 °C for 2 days and stored in an argon (Ar)-filled glove box. All other reagents and solvents were used as received from standard vendors.

2.2. Synthesis of materials

2.2.1. Synthesis of octakis(2-bromo-2-methylpropionoxypropyldimethylsiloxy)octasilsesquioxane (OBPS)

OHPS (0.50 g, 0.49 mmol) was placed in a 50 mL round-bottom flask equipped with a magnetic stirring bar. Distilled toluene (6.0 mL) was added to dissolve the OHPS, followed by the addition of allyl alcohol (0.34 mL, 4.9 mmol). Pt(dvs) (60 μL) was injected via a syringe and the mixture was stirred at room temperature for 1 h. The brownish bottom layer containing the product was recovered. After residual allyl alcohol and toluene were removed under vacuum, octakis(3-hydroxypropyldimethylsiloxy)octasilsesquioxane was obtained (100%). ¹H NMR (300 MHz, CDCl₃, δ/ppm, tetramethylsilane (TMS) ref): 3.59 (t, 16H, CH₂-OH), 2.73 (s, 8H, OH), 1.64 (m, 16H, CH₂-CH₂-CH₂), 0.61 (t, 16H, CH₂-Si), 0.16 (s, 48H, Si(CH₃)₂).

The octakis(3-hydroxypropyldimethylsiloxy)octasilsesquioxane (0.74 g, 0.49 mmol) was dissolved in anhydrous dichloromethane (23 mL) in a 100 mL round-bottom flask equipped with a magnetic stirring bar, followed by the addition of triethylamine (1.2 mL, 8.0 mmol). The solution was immersed in an ice bath, and 2-bromo-2-methylpropionyl bromide (1.0 mL, 8.0 mmol) was added dropwise by a syringe. After stirred for 12 h at room temperature, the mixture was filtered, and the solution was transferred to a separatory funnel and washed twice with deionized water. The solution was then dried over anhydrous magnesium sulfate and concentrated under vacuum. The obtained product was further purified by silica gel column chromatography with ethyl acetate/*n*-hexane (1/3 v/v) as an eluent. A yellowish wax was obtained with yield of 79%. ¹H NMR (300 MHz, CDCl₃, δ/ppm, TMS ref): 4.13 (t, 16H, CH₂-O), 1.93 (s, 48H, (CH₃)₂-C(Br)(C=O)), 1.72 (m, 16H, CH₂-CH₂-CH₂), 0.66 (t, 16H, CH₂-Si), 0.18 (s, 48H, (CH₃)₂-Si). ¹³C NMR (75 MHz, CDCl₃, δ/ppm, TMS ref): 171.7 (C=O), 68.3 (CH₂-O), 56.0 (C-C=O), 30.9 ((CH₃)₂C(Br)(C=O)), 22.2 (CH₂-CH₂-CH₂), 13.6 (CH₂-Si), −0.2 ((CH₃)₂-Si). ²⁹Si NMR (71.5 MHz, CDCl₃, TMS ref): 12.0 (OSi(CH₃)₂CH₂), −109.8 (SiO₄). GPC-RI analysis: *M*_n = 2,100, PDI = 1.01.

2.2.2. Synthesis of organic/inorganic hybrid star-shaped polymers (SPP: star-shaped P(PEGMA-*r*-MA-POSS))

The abbreviation of star-shaped polymers containing PEGMA and MA-POSS monomeric units is SPP. The following procedure was used for the preparation of SPP13 containing 13 mol% MA-POSS and 87 mol% PEGMA monomeric units. OBPS (46 mg, 0.017 mmol), PEGMA (5.3 g, 11 mmol), MA-POSS (2.9 g, 2.6 mmol), and distilled toluene (20 mL) were placed into a 100 mL Schlenk flask equipped with a magnetic stirring bar and the mixture was deoxygenated by three freeze–pump–thaw cycles. After CuBr (10 mg, 0.069 mmol) was introduced to the flask under the protection of N₂ flow, the flask was subjected to two more freeze–pump–thaw cycles and back-filled with N₂ to restore atmospheric pressure and maintain

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