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## 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



polyme

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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 ( $4.5 \times 10^{-5}$  S cm<sup>-1</sup> at 30 °C) which is about three times of magnitude larger than that of the matrix polymer (SPP13) electrolyte ( $1.5 \times 10^{-5}$  S cm<sup>-1</sup> 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

0032-3861/\$ - see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.polymer.2013.08.049 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 ( $\sim 10^{-7}$  S cm<sup>-1</sup>) 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<sub>n</sub>)<sub>8</sub>, 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 ( $n \le 6$ ), because they contain many chain ends on a rigid POSS core [26]. Therefore, when PEs were mixed with lithium salts, they exhibited guite high ionic conductivities over 10<sup>-4</sup> S cm<sup>-1</sup> at room temperature and about 10<sup>-6</sup> S cm<sup>-1</sup> 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<sup>-5</sup> S cm<sup>-1</sup> 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<sup>®</sup> (3-(3,5,7,9,11,13,15-heptacyclohexylpentacyclo[9.5.1.1<sup>3,9</sup>,1<sup>5,15</sup>,1<sup>7,13</sup>]-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  $\mu$ L) 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%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm, tetramethylsilane (TMS) ref): 3.59 (t, 16H, CH<sub>2</sub>–OH), 2.73 (s, 8H, OH), 1.64 (m, 16H, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>), 0.61 (t, 16H, CH<sub>2</sub>–Si), 0.16 (s, 48H, Si(CH<sub>3</sub>)<sub>2</sub>).

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%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ/ppm, TMS ref): 4.13 (t, 16H, CH<sub>2</sub>-O), 1.93 (s, 48H, (CH<sub>3</sub>)<sub>2</sub>-C(Br)(C=O)), 1.72 (m, 16H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 0.66 (t, 16H, CH<sub>2</sub>-Si), 0.18 (s, 48H, (CH<sub>3</sub>)<sub>2</sub>-Si). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ/ppm, TMS ref): 171.7 (C=O), 68.3 (CH<sub>2</sub>-O), 56.0 (C-C=O), 30.9 ((CH<sub>3</sub>)<sub>2</sub>C(Br)(C=O)), 22.2 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 13.6 (CH<sub>2</sub>-Si), -0.2 ((CH<sub>3</sub>)<sub>2</sub>–Si). <sup>29</sup>Si NMR (71.5 MHz, CDCl<sub>3</sub>, TMS ref): 12.0 (OSi(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>), -109.8 (SiO<sub>4</sub>). GPC-RI analysis: M<sub>n</sub> = 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 N<sub>2</sub> flow, the flask was subjected to two more freeze–pump–thaw cycles and back-filled with N<sub>2</sub> to restore atmospheric pressure and maintain

an inert environment. Then the flask was placed into an oil bath thermostated at 65 °C. Finally, PMDETA (15  $\mu$ L, 0.069 mmol) was injected into the reaction flask to initiate polymerization. After 6 h of polymerization, the solution was exposed to the air. The mixture was diluted with dichloromethane and passed through an alumina column to remove copper catalysts. After removing most of the solvent, the solution was precipitated into an excess of hexane. The dissolution—precipitation procedure was repeated for three times, yielding a white mass (2.4 g). The monomer conversion was determined by <sup>1</sup>H NMR to be 42% and 26% for PEGMA and MA-POSS, respectively. Other SPPs were prepared using the same procedure except the monomer feed ratio (PEGMA:MA-POSS) (Table 1). The composition of monomers in SPPs was calculated from the <sup>1</sup>H NMR spectra as follows:

$$MA - POSS content(mol\%) = 3I_c/(3I_c + 35I_e)$$
(1)

#### PEGMA content(mol%) = 100 - MA - POSS content(mol%)(2)

where  $I_c$  and  $I_e$  are the integrated intensities of the c and e proton peaks in Fig. 1(a), respectively. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm, TMS ref) of SPP13: 4.1 (CH<sub>2</sub>-O-C(O)), 3.5-3.9 (CH<sub>2</sub>-CH<sub>2</sub>-O), 3.41 (CH<sub>3</sub>-O), 1.73 (cyclohexyl, CH<sub>2</sub>), 1.24 (cyclohexyl, CH<sub>2</sub>), 0.76 (cyclohexyl, CH), 0.7-2 (methacrylate backbone, CH<sub>2</sub>-C(CH<sub>3</sub>)(C= O)). GPC-RI analysis:  $M_n = 42,700$ , PDI = 1.21.

#### 2.2.3. Synthesis of allyl-poly(ethylene glycol) (Allyl-PEG)

The following procedure was used for the preparation of Allyl-PEG9.5 with average 9.5 ethylene oxide (EO) units. PEGME (20 g, 54 mmol) in distilled THF (100 mL) was added dropwise to a suspension of sodium hydride (1.5 g, 60 mmol) in distilled THF (50 mL) at room temperature. The mixed THF solution was stirred for 3 h in an oil bath at 60 °C. After which the solution was cooled down to room temperature. Allyl bromide (8.1 g, 65 mmol) in distilled THF (50 mL) was then added dropwise to the solution. After stirred for 12 h, the reaction solution was filtered to remove sodium bromide and sodium hydride. THF and allyl bromide were removed under reduced pressure. The yellowish product was dissolved in toluene and washed with water three times, followed by three extractions with chloroform and subsequently dried with magnesium sulfate. Finally, all volatile materials were removed by rotary evaporation and subsequently by high vacuum, yielding pale yellow liquid (92%). The product was stored over 4 Å molecular sieves in a glove box. Allyl-PEG3 with three EO units was synthesized from the same procedure using TEGME rather than PEGME. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm, TMS ref) of Allyl-PEG9.5: 5.89 (m, 1H, CH<sub>2</sub>=CH-), 5.24 (d, 2H, CH<sub>2</sub>=CH-), 4.04 (d, 2H, CH<sub>2</sub>=CH-CH<sub>2</sub>O-), 3.53-3.66 (m, 38H, -CH<sub>2</sub>CH<sub>2</sub>O-), 3.38 (s, 3H, -OCH<sub>3</sub>).

### 2.2.4. Synthesis of PEG-functionalized POSS (PE:POSS-

#### $(PEG_{n=3,<9.5>})_8)$

The abbreviation of PEG-functionalized POSS is PE. The following procedure was used for the preparation of PE3 containing eight tri(ethylene glycol) moieties as vertex groups of POSS. 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 addition of Allyl-PEG3 (0.80 g, 3.9 mmol). Pt(dvs)  $(60 \mu L)$  was injected via a syringe and the mixture was stirred at 25 °C for 24 h. After the solution was diluted with chloroform, activated charcoal was added and stirred for 1 h, subsequently filtered to remove the charcoal. Solvent was evaporated under vacuum, yielding viscous liquid (95%). PE9.5 containing eight poly(ethylene glycol) moieties with average 9.5 ethylene oxide units at each corner of POSS was synthesized from the same procedure using Allyl-PEG9.5 rather than Allyl-PEG3 (Table 1). The composition between allyl-PEG and OHPS moieties in PEs was calculated from the <sup>1</sup>H NMR spectra as follows:

$$OHPS content(mol\%) = 3I_a/(3I_a + 48I_d)$$
(3)

 $Allyl - PEG \ content(mol\%) = \ 100 - OHPS \ content(mol\%)$ 

(4)

where  $I_a$  and  $I_d$  are the integrated intensities of the a and d proton peaks in Fig. 1(b), respectively. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm, TMS ref) of PE3: 3.53–3.66 (m, 96H,  $-CH_2CH_2O-$ ), 3.41 (m, 16H, -SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-), 3.38 (s, 24H,  $-OCH_3$ ), 1.61 (d, 16H,  $-SiCH_2CH_2$ -CH<sub>2</sub>O-), 0.59 (t, 16H,  $-SiCH_2CH_2O-$ ), 0.18 (s, 48H, (CH<sub>3</sub>)<sub>2</sub>–Si). GPC-RI analysis:  $M_n = 2300$ , PDI = 1.03.

#### 2.3. Preparation of composite electrolytes (CE)

The composite electrolytes containing organic/inorganic hybrid star-shaped polymer (SPP13), PEG-functionalized POSS (PE3 or PE9.5), and lithium salt (LiTFSI) in various blend compositions were prepared by a solution casting method. SPP13/PE3 or PE9.5 blends (in weight ratios of SPP13:PE3 or PE9.5 = 100:0-80:20) (0.08 g) and an appropriate amount of LiTFSI (in molar ratios of [Li] (lithium salt)/[EO] (ethylene oxide unit in the blends) = 0.03, 0.06, 0.09, 0.12) were dissolved completely in distilled THF (0.4 mL), and the homogeneous solution was casted onto a Teflon plate ( $2 \text{ cm} \times 2 \text{ cm}$ ). The resultant film was dried for 12 h at 25 °C, subsequently at 80 °C under high vacuum for a week to completely remove the residual solvent and water. The thickness of the films was in the range of  $220-250 \,\mu$ m. For the PE3 and PE9.5 electrolytes, PE3 or PE9.5 was doped with LiTFSI (at a ratio of [Li]/[EO] = 0.06) in distilled THF. The solvent was removed using a rotary evaporator at

Table	1
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Results of the synthesis of organic/inorganic hybrid star-shaped polymers (SPPs) and PEG-functionalized POSS derivatives (PEs).

Sample	Composition (PEGMA:MA-POSS) <sup>a</sup> or (Allyl-PEG:OHPS) <sup>b</sup>		Ethylene oxide (EO)	$M_{\rm n}{}^{\rm d}$ (×10 <sup>-3</sup> , RI)	$M_{\rm n}^{\rm e}$ (×10 <sup>-3</sup> , MALLS)	PDI <sup>d</sup> ,e	State <sup>f</sup>
	(mol%)	(wt%)	unit content <sup>e</sup> (wt%)				
SPP0	100:0 <sup>a</sup>	100: 0 <sup>a</sup>	84	53.5	267.1	1.25 (1.24)	Wax
SPP6	94:6 <sup>a</sup>	87:13 <sup>a</sup>	73	35.4	410.5	1.27 (1.16)	Sticky film
SPP13	87:13 <sup>a</sup>	74:26 <sup>a</sup>	63	42.7	179.5	1.21 (1.07)	Flexible film
SPP24	76:24 <sup>a</sup>	57:43 <sup>a</sup>	48	37.2	116.8	1.21 (1.15)	Brittle film
PE3	89:11 <sup>b</sup>	62:38 <sup>b</sup>	53	2.3	2.8	1.03 (1.05)	Viscous liquid
PE9.5	89:11 <sup>b</sup>	79:21 <sup>b</sup>	75	4.4	4.8	1.08 (1.06)	Viscous liquid

<sup>a</sup> Composition of PEGMA:MA-POSS, determined by <sup>1</sup>H NMR.

<sup>b</sup> Composition of Allyl-PEG:OHPS, determined by <sup>1</sup>H NMR.

<sup>c</sup> Calculated using the compositions and chemical structures of SPPs and PEs.

<sup>d</sup> Determined by gel permeation chromatography (GPC) using refractive index (RI) detector, calibrated with linear polystyrene standards (THF).

e Determined by GPC using multi-angle laser light scattering (MALLS) detector (THF).

<sup>f</sup> After casted on Teflon plate from THF solution and dried at room temperature.



Fig. 1. <sup>1</sup>H NMR spectra of (a) SPP24 and (b) PE3.

25 °C and further dried under high vacuum at 80 °C for a week. The PE electrolytes were in viscous liquid-state.

#### 2.4. Electrochemical analysis

The ionic conductivities of the electrolytes were analyzed in a temperature range from 10 to 80 °C under a dry nitrogen condition using a ZAHNER IM-6ex impedance analyzer in the potentiostat mode with an AC amplitude of 10 mV over a frequency range from 100 mHz to 1 MHz. Composite electrolyte films (CEs) were sandwiched by two symmetrical stainless steel electrodes. The liquidstate PE3 and PE9.5 electrolytes were placed between two symmetrically aligned stainless steel electrodes in a Teflon cell. The samples were thermally equilibrated at each temperature for 30 min prior to taking the measurements. The ionic conductivity,  $\sigma$ , was calculated using the equation,  $\sigma = (1/R_b) \times (d/A)$ , where  $R_b$  is the bulk electrolyte resistance, d is the thickness of the electrolytes, and A is the cross-sectional area of the electrode. The real part of the impedance at the minimum of the imaginary part was used as the resistance to calculate the conductivity of the electrolytes. The electrochemical stability was evaluated by cyclic voltammetry of an inert stainless steel electrode in composite electrolytes using a potentiostat (WBCS3000, WonATech) at 25 °C. The counter electrode was a Li metal foil. The cells for CV measurements were assembled in an Ar-filled glove box ( $H_2O$  and  $O_2 < 0.1$  ppm).

#### 2.5. Characterizations

<sup>1</sup>H NMR spectra were recorded on an Ascend<sup>TM</sup> 400 spectrometer (300 MHz) using CDCl<sub>3</sub> (with a tetramethylsilane (TMS) reference) as the solvent at room temperature. Molecular weights ( $M_n$ ,  $M_w$ ) and polydispersity index (PDI) of SPPs and PEs were analyzed by gel permeation chromatography (GPC). Relative molecular weights were measured by GPC equipped with a Waters 515 HPLC pump and three columns including PLgel 5.0 µm guard, MIXED-C, and MIXED-D from Polymer Laboratories in series with a Viscotek LR125 laser refractometer. The system with a refractive index (RI) detector was calibrated using polystyrene standards from Polymer Laboratories. The resulting data were analyzed using

Omnisec software. GPC for the analysis of absolute molecular weights was performed using a Waters 515 HPLC pump equipped with three columns including PLgel 5.0 µm guard, MIXED-C, and MIXED-D from Polymer Laboratories in series with a Wyatt Technology MiniDAWN<sup>™</sup> triple-angle light scattering detector  $(\lambda = 690.0 \text{ nm})$  and a Wyatt Technology Optilab DSP interferomeric refractometer. The data were processed using Wyatt's ASTRA V software. HPLC grade THF (J. T. Baker) was used as the eluent at a flow rate of 1.0 mL min<sup>-1</sup> at 35 °C. The thermal transition behaviors of the SPP13, PEs, and CEs were examined by differential scanning calorimetry (DSC) using TA Instruments DSC-01000 under a nitrogen atmosphere. Samples with a typical mass of 3–7 mg were encapsulated in sealed aluminum pans. They were first heated to 150 °C and then quenched to -80 °C. This was followed by a second heating scan from -80 to 150 °C at a heating rate of 10 °C min<sup>-1</sup>. The heat of fusion  $(\Delta H_m)$  was calculated from the integral area between the baseline and each melting curve. The baseline was designated by connecting two points at which the instant value of its derivative curve becomes zero near the melting temperature  $(T_{\rm m})$ . The thermal stability of the SPP13, PEs, and CEs was investigated by thermogravimetric analysis (TGA) using TA Instruments TGA Q-5000IR under a nitrogen atmosphere. The samples were first heated to 130 °C and maintained at 130 °C for 10 min in order to evaporate residual water molecules, and then heated to 700 °C at a heating rate of 10 °C min<sup>-1</sup>.

#### 3. Results and discussion

#### 3.1. Synthesis of organic/inorganic hybrid star-shaped polymers and PEG-functionalized POSS derivatives

Star-shaped P(PEGMA-*r*-MA-POSS) (SPP) was synthesized via ATRP using OBPS as an octafunctional core initiator in the presence of CuBr/PMDETA catalyst (Scheme 1(a)). Fig. 1(a) shows the <sup>1</sup>H NMR spectrum with the assignments of the respective peaks of the star-shaped polymer (SPP24). Resonance peaks corresponding to P(PEGMA) and P(MA-POSS) segments were found in the spectrum, attesting to the formation of the expected structure. Proton peaks observed at  $\delta = 0.76$ , 1.24, and 1.73 ppm were clearly assigned to the



Scheme 1. Preparation of (a) organic/inorganic hybrid star-shaped polymers (SPP) via atom transfer radical polymerization and (b) PEG-functionalized POSS (PE) via hydrosilylation reaction.

cyclohexyl protons ( $\delta = 0.76$  ppm, cyclohexyl-CH, 1.24 ppm, cyclohexyl-CH<sub>2</sub>, and 1.73 ppm, cyclohexyl-CH<sub>2</sub>) of P(MA-POSS) segments. The proton peaks from the PEG side chains ( $\delta = 3.5-4.1$  ppm, CH<sub>2</sub>-CH<sub>2</sub>-O and 3.41 ppm, CH<sub>3</sub>-O) indicate the inclusion of PEGMA in the polymers. The proton peaks from the methacrylate backbone ( $\delta = 0.7-2$  ppm) and OBPS ( $\delta = 0.18$  ppm, (CH<sub>3</sub>)<sub>2</sub>-Si) were poorly resolved due to the abundance of protons in the POSS and PEG side chains.

The absolute and relative molecular weights of the star-shaped polymers were obtained by GPC using a multi-angle laser light scattering (MALLS) detector and a refractive index (RI) detector, respectively (Table 1). The relative molecular weights of the polymers obtained using the RI detector are much smaller than the corresponding absolute molecular weights obtained using the MALLS detector. This should have resulted from the smaller hydrodynamic volume of the star-shaped polymer compared to that of the linear polymer, even with the same absolute molecular weight [30]. The observed discrepancy between the relative and absolute molecular weights also could have resulted from the use of linear polystyrene (PS) standards for GPC-RI calibration. The hydrodynamic radius of the polymers in this study should differ from that of the PS due to their different chemical structures. PEG chains can have relatively smaller hydrodynamic volume than PS in THF, which could result in smaller relative molecular weights than absolute molecular weights [31]. All SPPs in this study have more or less uniform size distribution as indicated by the small PDI values less than 1.27.

In order to evaluate the effect of PEG chain length of PEGfunctionalized POSS (PE) on the properties of composite electrolytes, PEs were prepared with different numbers of ethylene oxide (EO) units; 3 and an average of 9.5. The content of EO units in PE3 is smaller than that in the matrix polymer, SPP13, while the content of EO units in PE9.5 is larger than that in SPP13 (Table 1). PEs were synthesized using the hydrosilylation reaction of OHPS with allyl-PEGs in the presence of Pt(dvs) catalyst (Scheme 1(b)). As shown in Fig. 1(b), proton peaks observed at  $\delta = 3.38 - 3.66$  ppm (methyl (- $O-CH_3$ ) and oxymethylene ( $-O-CH_2-$ ) moieties) of PEG indicate that allyl-PEGs were incorporated in the POSS molecules. The presence of POSS core was confirmed by the proton peaks at  $\delta = 0.18$  ppm ((CH<sub>3</sub>)<sub>2</sub>-Si). The proton peaks from the allyl groups  $(\delta = 5.89, 5.24, \text{ and } 4.04 \text{ ppm for CH}_2=CH-, CH_2=CH-, \text{ and CH}_2=$ CH–CH<sub>2</sub>O–, respectively) of Allyl-PEG and Si–H groups ( $\delta$  = 4.74 ppm) of OHPS were not observed after the reaction, suggesting that stoichiometric reaction between the Si-H and allyl groups (1:8 molar feed ratio of [OHPS]:[Allyl-PEG]) was attained. The absolute molecular weights of PEs (2800 and 4800 g mol<sup>-1</sup> for PE3 and PE9.5, respectively) obtained with GPC using the MALLS detector were quite close to their calculated molecular weights (2660 and 4950 g mol<sup>-1</sup> for PE3 and PE9.5, respectively). The PDI values slightly larger than 1 could arise from the coupling reaction of OHPS in the presence of water molecules, resulting in higherorder condensation products [26].

#### 3.2. Preparation of composite electrolytes

A series of CEs with various contents of SPP13 and PEs were prepared to investigate the effect of blend composition on the dimensional stability, thermal behavior, and ionic conductivity of the CEs (Table 2). The composite electrolytes were designated as CE#-*x*, where # is the number of EO units in PEs, and *x* is the weight percentage of PEs in the electrolytes. When the content of PEs (PE3 and PE9.5) in CEs was smaller than 20 wt%, the CEs showed freestanding film state, while when the content of PEs was larger than 30 wt%, the CEs became sticky and flimsy (Fig. S1). Fig. 2 shows the flexible, transparent, dimensionally-stable electrolyte films prepared from the CEs and lithium salts.

Table 2Thermal properties of SPP13, PEs, and CEs.

Sample <sup>a</sup>	$T_{g}^{f}(^{\circ}C)$	$T_{m}^{f}(^{\circ}C)$	$\Delta H_{\rm m}^{\rm f}$ (J g <sup>-1</sup> )	$T_{d,5\%,10\%}^{g}$ (°C)	Char yield <sup>h</sup> (%)
SPP13	-60.9	-	_	285, 308	1.2
CE3-10 <sup>b</sup>	-62.4	_	-	293, 314	2.8
CE3-20 <sup>c</sup>	-62.8	-	-	291, 314	7.5
CE9.5-10 <sup>d</sup>	-62.8	-0.3	1.3	283, 306	1.8
CE9.5-20 <sup>e</sup>	-64.5	-3.6	19.6	275, 301	2.0
PE3	-	-	-	306, 360	32.3
PE9.5	-	5.5	71.6	223, 249	18.2

<sup>a</sup> Samples without lithium salt. Free-standing films could be prepared from the SPP13, CE3-10, CE3-20, CE9.5-10, and CE9.5-20 with and without lithium salt.

<sup>b</sup> Weight ratio of SPP13:PE3 = 90:10.

<sup>c</sup> Weight ratio of SPP13:PE3 = 80:20.

<sup>d</sup> Weight ratio of SPP13:PE9.5 = 90:10.

<sup>e</sup> Weight ratio of SPP13:PE9.5 = 80:20.

<sup>f</sup> Obtained by DSC equipped with RCS at a heating rate of 10 °C.

 $^{\rm g}$  Decomposition temperatures,  $T_{\rm d,5\%,10\%}$  are defined as 5 and 10 wt% loss, respectively.

<sup>h</sup> Char yield (in wt%) at 700 °C.

The morphologies of CEs were analyzed by transmission electron microscopy (TEM) (Fig. S2). The contrast in the TEM micrograph originates from the differences in the diffraction and mass thickness between dissimilar domains [32]. Since the POSS moiety, which contains silicon, has a higher electron density than the PEG moiety, the domain composed of aggregated P(MA-POSS) appears darker than the P(PEGMA) domain [33]. Therefore, the presence of aggregated POSS domains can be identified without any additional staining step. Polymers with randomly distributed MA-POSS and PEGMA moieties have been known to exhibit homogeneous morphology without the aggregation of POSS moieties [33]. Phase separation between the POSS and PEG moieties in both CE3s and CE9.5s was not observed, although the PEs were introduced to the SPP13 matrix, indicating that homogeneous composite electrolytes were fabricated by the simple solution casting, possibly due to the similarity of their chemical structures [34].

#### 3.3. Thermal properties

The thermal stability of CEs without lithium salt was examined by thermogravimetric analysis (TGA). For all of the CEs, thermal decomposition occurred above 200 °C (Fig. S3), indicating that the CEs have sufficient thermal stability for use as the SPEs in lithium

(a) er Chemistry Lab.	(b) er Chemistry Lab.
Seoul National Univ.	Seoul National Univ.
lymer Chemistry Lab.	olymer Chemistry Lab.
Seoul National Univ.	Seoul National Univ.
(c) ner Chemistry Lab.	Seoul National Univers
C IN C IN .	Seou Vational Univers
Seoul National Univ.	Seoul Val nal Univers
olvmer Chemistry Lab	Seoul N ion Univers
enginer enemistry Ede.	Seoul National ver
Seoul National Univ.	Seoul National Univ

**Fig. 2.** Photographs of composite electrolyte films containing LiTFSI ([Li]/[EO] = 0.06) prepared by a solution casting method: (a) SPP13, (b) CE3-20, and (c) CE9.5-20.

batteries even at the elevated temperature. The thermal decomposition temperatures at 5 and 10% weight loss ( $T_{d,5\%}$  and  $T_{d,10\%}$ , respectively) and char yield data of the samples are summarized in Table 2. The  $T_{d,5\%,10\%}$  values of CE3s are larger than those of SPP13, whereas  $T_{d,5\%,10\%}$  values of CE9.5s are smaller than those of SPP13. This should have resulted from the higher and lower thermal stabilities of PE3 and PE9.5, respectively, than that of the SPP13 matrix polymer. Since PEG moieties have lower decomposition temperature than POSS moieties [20,22], PE3 with smaller PEG content exhibited higher thermal decomposition temperature than PE9.5 with larger PEG content. The char yield of CEs increased as the PE contents increased due to the larger silsesquioxane content in PEs than in SPP13.

The thermal transition behaviors of SPP13 and CEs with and without lithium salt were investigated by differential scanning calorimetry (DSC). As shown in Fig. 3, the glass transition temperature  $(T_g)$  of P(PEGMA) segments in SPP13 was observed at -60.9 °C, with no melting transition ( $T_{\rm m}$ ) peak, indicating that SPP13 is an amorphous polymer without any crystalline phase. It was reported in our previous work that SPPO without MA-POSS moieties showed both  $T_g$  and  $T_m$  of P(PEGMA) segments at -63.9 and -6.8 °C, respectively (Fig. S4) [20]. However, the formation of crystalline domains of P(PEGMA) segments in SPP13 should be disturbed by the randomly distributed P(MA-POSS) segments so that the melting behavior of P(PEGMA) segments was not observed in SPP13 [20,33]. Although SPP13 can form dimensionally-stable free-standing film, the P(PEGMA) segments in the film still have high enough mobility at room temperature, as estimated by its  $T_{g}$ of -60.9 °C, which is much lower than room temperature. The  $T_{g}$ behavior of P(PEGMA) segments in SPP13 with POSS moieties could be affected by two factors. One is the increase in the free volume of the polymer due to the large volume of POSS resulting in the decrease of  $T_{\rm g}$  [24]. The other is the rigidity of POSS, which decreases the mobility of the chains, resulting in the increase of  $T_{g}$ [21,22]. The combined effect of these two competing factors led to the slight increase in the  $T_g$  value of SPP13 compared to that of SPP0 [20].

For both CE3s and CE9.5s, the  $T_g$  values decrease with the increase in the contents of PE3 and PE9.5 because the mobility of P(PEGMA) segments of SPP13 was increased by the plasticization effect of liquid-state PEs [29]. CE9.5s were found to have smaller  $T_g$  values than CE3s when they had the same PE contents, which could be ascribed to the larger content of flexible PEG segment in PE9.5 than in PE3. Among the CEs, CE9.5-20 exhibited the lowest  $T_g$  at -64.5 °C, indicating that CE9.5-20 has the highest P(PEGMA)



Fig. 3. DSC traces of SPP13 and CEs without lithium salt.

segmental mobility. Since lithium ions are transferred through the mobile amorphous phase of PEG chains, the low  $T_g$  value is an imperative factor to achieve high ionic conductivity [5]. Melting transition peaks from PEG moieties in CE9.5s were observed, because PE9.5 in CE9.5s has relatively long PEG moieties, and exhibit semi-crystalline domains (Table 2 and Fig. S5). It is note-worthy that the CEs have very low glass transition temperatures, and can form free-standing electrolyte films.

Fig. 4 shows the thermal transition behaviors of CE9.5-20 with various lithium salt concentrations ([Li]/[EO] = 0.00-0.12). The melting transition peak of CE9.5-20 without lithium salt at  $-3.6 \degree$ C disappeared when the CE9.5-20 was mixed with the lithium salt, indicating that the crystalline domains disappear after the addition of lithium salt into CE9.5-20. The formation of crystalline domains of PEG moieties in CE9.5-20 could be prevented by the complexation of lithium ions with the PEG moieties [29,35]. In addition, the  $T_{\rm g}$  of P(PEGMA) segments in CE9.5-20 increases with increasing lithium salt concentration. It is known that lithium ions restrict the chain mobility of P(PEGMA) segments because they interact with the PEG moieties [20,33].

#### 3.4. Ionic conductivity

The ionic conductivities of CEs were investigated as a function of LiTFSI concentration ([Li]/[EO] = 0.03-0.12) to obtain the optimized lithium salt concentration for CEs, as shown in Fig. 5. Maximum ionic conductivities at 20 °C were observed at a [Li]/[EO] ratio of 0.06 for all the CEs. The ionic conductivity behavior exhibiting a maximum value at a certain lithium salt concentration can be explained with the following equation:

$$\sigma = \sum n \times q \times \mu \tag{5}$$

The ionic conductivity is related to the number of charge carriers and their mobility according to this equation, where *n* is the number of charge carriers, *q* is the charge on the charge carrier, and  $\mu$  is the mobility of the charge carrier [36]. When the salt concentration ([Li]/[EO]) is smaller than 0.06, the increase in conductivity is ascribed to the increase in the number of lithium ions. The subsequent decrease in ionic conductivity when the salt concentration is larger than 0.06 can be explained by the decrease in the chain mobility of ion-conducting P(PEGMA) segments, as confirmed by the increased  $T_g$  values of CEs with increasing lithium salt concentration (Fig. 4). The lithium salt in CEs restricts the segmental motion of the polymer matrix by intra- and/or inter-molecular



Fig. 4. DSC traces of CE9.5-20 with various LiTFSI concentration.



Fig. 5. Ionic conductivities of SPP13 and CEs containing LiTFSI with various concentrations ([Li]/[EO] = 0.03-0.12) at 20 °C.

coordination with the oxygens in the PEG moieties [19,35]. This behavior has been observed for most polyether-based electrolytes containing lithium salts [19,35,37].

The temperature dependence of ionic conductivities for SPP, PE, and CE electrolytes at a ratio of [Li]/[EO] = 0.06 is presented in Fig. 6. The PE electrolytes in a liquid-state show higher ionic conductivities than SPP13 electrolyte in a solid-state, because the liquid-state can provide higher lithium ionic mobility than the solid-state [3.11.12]. Therefore, the ionic conductivity of CEs increased as the content of the liquid-state PEs in CEs increased. CE9.5s with longer PEG moieties were found to exhibit higher conductivities than the CE3s with shorter PEG moieties, which could be attributed to the higher mobility of ion-conducting P(PEGMA) segments in CE9.5s, as estimated by the  $T_g$  values (Fig. 3 and Fig. S6). The lower  $T_g$  value is the key factor for increasing the ionic conductivity of SPEs, because lithium ions in the polymer matrix are transferred by the segmental motion of polymer chains [5]. In addition, the CE9.5s contain a larger amount of lithium salt (in wt%) than the CE3s, because PE9.5 contains a larger content of EO units than PE3 (Table 1), although the salt concentration based on EO units (in mol%) is identical for both electrolytes. As the ionic conductivity is proportional to the number of charge carriers (equation (5)), the larger amount of lithium salt in CE9.5 compared



Fig. 6. Temperature dependence of ionic conductivities of SPP0, SPP13, PEs, and CEs containing LiTFSI ([Li]/[EO] = 0.06).

to that in CE3 could also contribute to the higher ionic conductivity [20].

Among the CEs, the CE9.5-20 exhibited the highest ionic conductivity over the range of temperatures. Although the ionic conductivity of the film-state CE9.5-20 is lower than that of the liquidstate PE electrolytes, it is about three times of magnitude higher than that of the SPP13 electrolyte without PEs at room temperature. Moreover, the ionic conductivities of solid-state CE9.5-20 were found to be close to those of wax-state SPPO electrolyte with only P(PEGMA) segments, although the CE9.5-20 contains a smaller amount of lithium salt than the SPPO electrolyte due to the smaller content of EO units in the composite. This could be ascribed to the lower glass transition temperatures of the polymeric matrix in CE9.5-20 than in SPPO electrolyte (Fig. 4, Figs. S4 and S6) and the high ionic conductivity of PE9.5 in CE9.5-20 (Fig. 6). The maximum ionic conductivities of CE9.5-20 were 5.4  $\times$   $10^{-4}$  and 4.5  $\times$  10  $^{-5}$  S cm  $^{-1}$  at 80 and 30  $^\circ\text{C},$  respectively. Therefore, the introduction of PEs into the SPP13 still maintained dimensional stability, while providing a larger amount of mobile lithium ions, resulting in enhanced ionic conductivity. Also, the ionic conductivity value obtained for the CE9.5-20 was about two orders of magnitude larger than that for conventional SPEs based on the linear PEO homopolymer [8–10].

#### 3.5. Electrochemical stability and cell performance

Fig. 7 shows typical cyclic voltammograms of an inert stainless steel electrode in a cell with different SPEs and a lithium metal counter electrode. All the SPEs exhibited similar cyclic voltammetric behaviors between +2.5 and +5.0 V (vs. Li/Li<sup>+</sup>), although the SPP13 electrolyte showed slightly wider electrochemical stability window than CEs. The anodic currents from oxidation of CEs were observed at voltages higher than about 4.2 V, indicating that the CEs are electrochemically stable up to +4.2 V without decomposition. Thus, the CEs can be applied to 4 V class lithium batteries. These potential windows of CEs are comparable to or slightly wider than that of the conventional linear PEO-based electrolyte [38]. This could be ascribed to the presence of electrochemically stable inorganic POSS moieties in CEs, in which the POSS moieties could be in contact with the electrode to form the interface [39].

All-solid-state lithium cells of Li/SPP13 or CE9.5-20 ([Li]/ [EO] = 0.06)/V<sub>2</sub>O<sub>5</sub> were fabricated, and their charge–discharge capacities were investigated. The electrolyte films had enough dimensional stability to separate the electrodes in the cells. Thus, we did not use the separator to assemble the cells in this study,



Fig. 7. Cyclic voltammograms of stainless steel electrodes in SPP13 and CEs containing LiTFSI ([Li]/[EO] = 0.06) at 25 °C.

in contrast to lithium ion batteries containing liquid electrolytes. The preliminary results of the charge–discharge cycle tests of the Li/SPP13 or CE9.5-20/V<sub>2</sub>O<sub>5</sub> cells at 60 °C in the potential range of 2–4 V are shown in Fig. S7. The discharge capacities (normalized by the mass of V<sub>2</sub>O<sub>5</sub>) of the Li/CE9.5-20/V<sub>2</sub>O<sub>5</sub> cell are larger than those of the Li/SPP13/V<sub>2</sub>O<sub>5</sub> cell during the cycles. The larger capacity of the cell with CE9.5-20 should be attributed to the higher ionic conductivity of CE9.5-20 than that of SPP13 (Fig. 6). The facile ionic transport of CE9.5-20 is expected to alleviate the ohmic polarization loss of the cell, leading to the larger capacity [40].

Although these results clearly reveal the possible applications of the CEs as solid-state electrolytes for lithium-ion batteries, the cycling performance of the cells with CEs needs to be improved for practical applications. Discharge capacities for both cells gradually decreased with increasing cycle number. In addition to the high ionic conductivity of SPEs, other factors such as stable contact of the porous cathode with the SPEs during charge-discharge cycles and microstructure of the cathode are also very important to obtain good cyclability in lithium ion batteries [41]. In addition, corrosion of the aluminum current collector could occur at elevated temperatures in the presence of the LiTFSI used in this study, resulting in the deterioration of battery performance [42]. Therefore, the improvement of the charge-discharge cycle life of the all-solidstate batteries with CE9.5-20 is a major challenge to be examined in future studies. Efforts are under way to optimize the fabrication process of the composite cathode, the interfacial contact between the electrodes and CE9.5-20, and the choice of proper lithium salts.

#### 4. Conclusions

Organic/inorganic hybrid star-shaped polymers (SPP13) containing 87 mol% PEGMA and 13 mol% MA-POSS monomeric units were prepared via ATRP and used as the polymer matrix for composite electrolytes (CEs). PEG-functionalized POSS derivatives with different numbers of EO units in PEG moieties (PE3 and PE9.5) were prepared by hydrosilylation reaction to investigate the effects of the PE contents and PEG chain length of PEs on the properties of CEs when they were applied as plasticizers. A series of CE films with different compositions of SPP13 and PEs could be prepared by a simple solution casting method, and they were found to be flexible, transparent, and dimensionally stable enough to separate the electrodes in batteries. The  $T_{g}$  values of ion-conducting P(PEGMA) segments in CEs were found to be smaller than that in SPP13, indicating that P(PEGMA) segments in CEs have higher mobility than those in SPP13. The CE9.5-20 composed of 80 wt% SPP13 and 20 wt% PE9.5 showed ionic conductivity value ( $4.5 \times 10^{-5}$  S cm<sup>-1</sup> at 30 °C) about three times of magnitude larger than that of the SPP13 electrolyte ( $1.5 \times 10^{-5}$  S cm<sup>-1</sup> at 30 °C). This could be attributed to the higher lithium ionic mobility and larger amount of lithium ions in the CE9.5-20. The CEs were electrochemically stable up to +4.2 V. suggesting that they are applicable to the 4 V class lithium ion batteries. The all-solid-state lithium cell with CE9.5-20 exhibited larger discharge capacity than that with SPP13 at 60 °C and C/10 rate, which could be ascribed to the higher ionic conductivity of CE9.5-20 than that of SPP13. We believe that this composite electrolyte is a promising candidate material for use in all-solid-state lithium batteries. Ongoing studies are being conducted to enhance the charge-discharge cycle life of the all-solid-state batteries with CE9.5-20.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.polymer.2013.08.049.

#### References

- [1] Tarascon JM, Armand M. Nature 2001;414:359-67.
- Scrosati B. Chem Rec 2005;5:286-97. [2]
- Scrosati B, Garche J. J Power Sources 2010;195:2419–30. [3]
- [4] Agrawal RC, Pandey GP. J Phys D Appl Phys 2008;41:223001-18.
- [5] Meyer WH. Adv Mater 1998;10:439-48.
- [6] Stephan AM, Nahm KS. Polymer 2006;47:5952–64.
- [7] Arico AS, Bruce P, Scrosati B, Tarascon JM, van Schalkwijk W. Nat Mater 2005;4:366-77.
- [8] Fenton DE, Parker JM, Wright PV. Polymer 1973;14:589.
- [9] Kelly IE, Owen JR, Steele BCH. J Power Sources 1985;14:13–21.
  [10] Gray FM, MacCallum JR, Vincent CA. Solid State Ionics 1986;18–19:282–6.
- [11] Rossi NAA, Zhang Z, Schneider Y, Morcom K, Lyons LJ, Wang Q, et al. Chem Mater 2006:18:1289-95.
- [12] Zhang L, Zhang Z, Harring S, Straughan M, Butorac R, Chen Z, et al. J Mater Chem 2008:18:3713-7.
- [13] Capuano F, Croce F, Scrosati B. J Electrochem Soc 1991;138:1918-22. [14] Tominaga Y, Asai S, Sumita M, Panero S, Scrosati B. J Power Sources 2005;146:
- 402 6[15] Soo PP, Huang B, Jang YI, Chiang YM, Sadoway DR, Mayes AM. J Electrochem
- Soc 1999;146:32-7.
- [16] Panday A, Mullin S, Gomez ED, Wanakule N, Chen VL, Hexemer A, et al. Macromolecules 2009;42:4632-7.
- [17] Oh B, Vissers D, Zhang Z, West R, Tsukamoto H, Amine K. J Power Sources 2003:119-21:442-7.
- [18] Kim SK, Ko T, Kim K, Choi SW, Park JO, Kim KH, et al. Macromol Res 2012;20: 1181-90.

- [19] Jeon JD, Kwak SY, Cho BW. J Electrochem Soc 2005;152:A1583-9. [20] Kim DG, Sohn HS, Kim SK, Lee A, Lee JC. J Polym Sci Part A Polym Chem 2012;50:3618-27.
- [21] Ryu HS, Kim DG, Lee JC. Polymer 2010;51:2296–304.
- [22] Ryu HS, Kim DG, Lee JC. Macromol Res 2010;18:1021–9.
- [23] Dong F, Ha CS. Macromol Res 2012;20:335–43.
- [24] Wu J, Haddad TS, Mather PT. Macromolecules 2009;42:1142–52.
- [25] Inoue K. Prog Polym Sci 2000;25:453–571.
- [26] Maitra P, Wunder SL. Chem Mater 2002;14:4494-7.
- [27] Maitra P, Wunder SL. Electrochem Solid-State Lett 2004;7:A88–92.
- [28] Zhang H, Kulkarni S, Wunder SL, J Electrochem Soc 2006;153:A239–48.
   [29] Zhang H, Kulkarni S, Wunder SL, J Phys Chem B 2007;111:3583–90.
- [30] Matyjaszewski K, Miller PJ, Pyun J, Kickelbick G, Diamanti S. Macromolecules 1999:32:6526-35.
- [31] Taton D, Cloutet E, Gnanou Y. Macromol Chem Phys 1998;199:2501-10.
- [32] Zheng L, Hong S, Cardoen G, Burgaz E, Gido SP, Coughlin EB. Macromolecules
- 2004:37:8606-11. [33] Kim SK, Kim DG, Lee A, Sohn HS, Wie JJ, Nguyen NA, et al. Macromolecules 2012:45:9347-56
- [34] Brandrup J, Immergut EH, Grulke EA, Abe A, Bloch DR. Polymer handbook. 4th
- ed, vol. 2. United States of America: A Wiley-Interscience Publication; 1999. [35] Niitani T, Amaike M, Nakano H, Dokko K, Kanamura K. J Electrochem Soc 2009;156:A577-83.
- [36] Every HA, Zhou F, Forsyth M, MacFarlane DR. Electrochim Acta 1998;43: 1465 - 9
- [37] Ghosh A, Kofinas P. J Electrochem Soc 2008;155:A428-31.
- [38] Armand MB, Duclot MJ, Rigaud P. Solid State Ionics 1981;3-4:429-30.
- [39] Lee J, Lee Y, Bhattacharya B, Nho YC, Park JK. J Solid State Electrochem 2010;14:1445-9
- [40] Ha HJ, Kil EH, Kwon YH, Kim JY, Lee CK, Lee SY. Energy Environ Sci 2012;5: 6491-9.
- [41] Niitani T, Shimada M, Kawamura K, Dokko K, Rho YH, Kanamura K. Electrochem Solid-State Lett 2005;8:A385-8.
- [42] Mun J, Yim T, Choi CY, Ryu JH, Kim YG, Oh SM. Electrochem Solid-State Lett 2010:13:A109-11.