

# Solid polymer electrolytes based on crosslinkable polyoctahedral silsesquioxanes (POSS) for room temperature lithium polymer batteries

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**Abstract** Solid polymer electrolytes (SPE), based on polyoctahedral silsesquioxanes (POSS) as a crosslinking agent, were prepared by radical polymerization. The ionic conductivity is greatly enhanced by introduction of crosslinkable POSS with multifunctional groups. The SPE prepared with 5 wt.% crosslinking agent shows an ionic conductivity of  $5.3 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature. The content of nonvolatile plasticizer, poly(ethylene glycol) dimethyl ether, in the SPE, could be raised to 95 wt.% without any leakage. The SPE is found to be electrochemically stable up to 5.3 V. Lithium polymer cell consisting of Li/SPE/LiCoO<sub>2</sub> exhibits 80% of initial discharge capacity even at the rate of 0.1 C at room temperature after 20 cycles, which is a substantial improvement for practical consideration of lithium polymer batteries at room temperature.

**Keywords** Solid polymer electrolyte · Crosslinking agent · Ionic conductivity · Electrochemical stability · Lithium polymer batteries

## Introduction

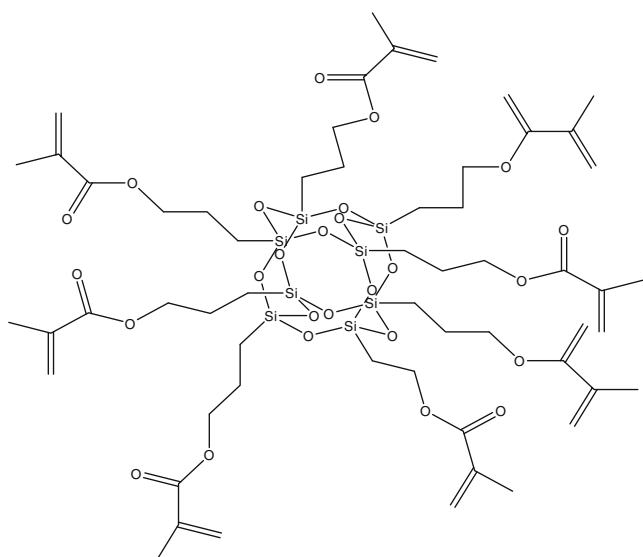
Over the last three decades, solid polymer electrolytes (SPE) have attracted a great deal of interest in the field of electrochemical devices owing to its potential application [1]. It can contribute to enhancing safety in lithium secondary batteries compared with their liquid electrolyte counterparts. In spite of this overwhelming advantage, it is still not applied commercially with complete success because of some limitations in electrochemical properties such as low ionic conductivity of electrolyte, especially at ambient temperature and also high interfacial resistance. To overcome these problems, many research efforts have been focused to improve the properties of polymer electrolytes in order to meet the requirements of lithium polymer batteries. Various polymer structure design stemming from poly(ethylene oxide) (PEO) [2–4] or introduction of inorganic fillers (such as SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.) to the PEO matrix are the representative approaches to enhance the ionic conductivity of SPE and also the interfacial stability between polymer electrolyte and lithium metal electrode [5, 6]. However, these approaches could not succeed in obtaining the commonly required ionic conductivity ( $>10^{-3} \text{ S cm}^{-1}$ ) for practical applications. It is because they could not attain sufficient chain mobility of polymer matrix without sacrificing the mechanical strength of SPE. Considering these barriers for practical application, we designed a new SPE system based on polymer nonwoven matrix which functions as a mechanical supporter [7, 8].

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**Fig. 1** Chemical structure of methacryl-POSS

The nonwoven matrix can create a large number of pores which functions as an ion-conductive region. A large amount of nonvolatile plasticizer could be also immobilized in the pores with maintaining mechanical strength of SPE.

To further enhance the ionic conductivities as well as mechanical properties of SPE, we introduce a new type of multifunctional crosslinking agent based on polyoctahedral silsesquioxanes (POSS). The preparation, electrochemical properties, and thermal properties of the SPE were discussed, and the cycle performances of lithium polymer cells composed of Li/SPE/LiCoO<sub>2</sub> were also evaluated at room temperature.

## Experimental

Polypropylene nonwoven matrix with 20 μm thickness was used as a mechanical supporting matrix after drying in vacuum at 80 °C for 24 h. Methacryl-POSS (POSS, Aldrich) as a crosslinking agent and poly(ethylene glycol) dimethyl ether (PEGDME, *M<sub>w</sub>*=250, Aldrich) as a nonvolatile plasticizer were stored over 4 Å molecular sieves prior to use. LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (LiTFSI, 3M) was also dried in a vacuum oven at 80 °C. Methyl benzoylformate (Aldrich) as a photoinitiator was used as received. All chemicals were handled in Ar-filled glove box.

Solid polymer electrolytes were prepared by radical polymerization of a precursor solution composed of crosslinking agent (POSS), nonvolatile plasticizer (PEGDME), Li salt (LiTFSI), and photoinitiator (methyl benzoylformate). Li salt (LiTFSI) was added into SPE precursor at a concentration of [EO]:[Li]=20:1. The UV-curable SPE precursor was spread on the PP nonwoven matrix and was irradiated by UV for 5 min (8 mW cm<sup>-2</sup>, 365 nm).

The glass transition temperature (*T<sub>g</sub>*) of SPE was determined by using a differential scanning calorimeter (DuPont TA 2000 DSC) on samples sealed in hermetic aluminum pans. Each sample was scanned at a heating rate of 10 °C min<sup>-1</sup> within an appropriate temperature range under nitrogen atmosphere.

The polymer electrolyte film was sandwiched between two stainless steel electrodes for ionic conductivity measurements. This sample was vacuum-packed in an aluminum plastic pouch to avoid contamination. The ionic conductivities of SPE at temperatures ranging from -20 to 60 °C were evaluated from bulk resistance by alternating current (AC) complex impedance analysis using a Solartron 1455 frequency response analyzer in combination with a Solartron 1470 electrochemical interface over a frequency range of 1 Hz–1 MHz under an amplitude of 10 mV. The ionic conductivity ( $\sigma$ ) was calculated from the impedance data, using the relation  $\sigma = \frac{d}{RA}$ , where *d* and *A* are the thickness and area of prepared polymer electrolyte, respectively, and *R* is bulk resistance obtained from the AC impedance spectrum.

The electrochemical stability of SPE was determined by linear sweep voltammetry experiment performed on stainless steel electrode as a working electrode and lithium electrode as the reference electrode at a scanning rate of 1.0 mV s<sup>-1</sup>. The characteristics of the interface between SPE and lithium electrode were examined by monitoring the time dependence of the impedance of symmetrical Li/SPE/Li cells.

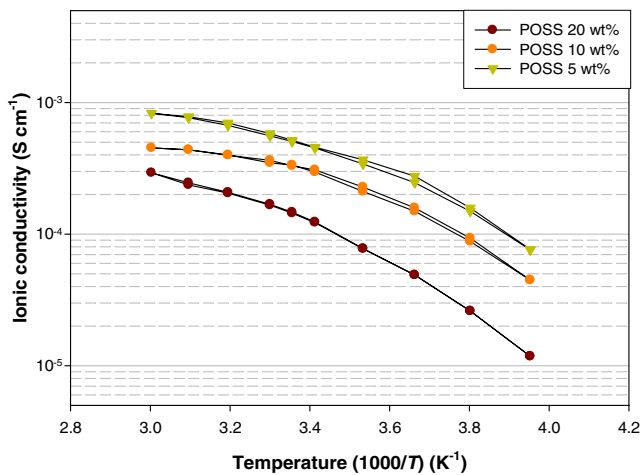
Charge–discharge characteristics were measured at room temperature with a battery tester (TOSCAT-3000U, Toyo System Co. Ltd.). The unit cell was assembled by sandwiching the SPE between Li anode and LiCoO<sub>2</sub> cathode (SK Mobile Energy). The cell was then sealed in an aluminum plastic pouch bag. All assemblies of the cells were carried out in a glove box filled with argon. The unit cell was cycled between 3.0 and 4.2 V at a constant current density.

## Results and discussion

The chemical structure of POSS as a crosslinking agent is shown in Fig. 1. POSS is a nanosized hybrid organic–

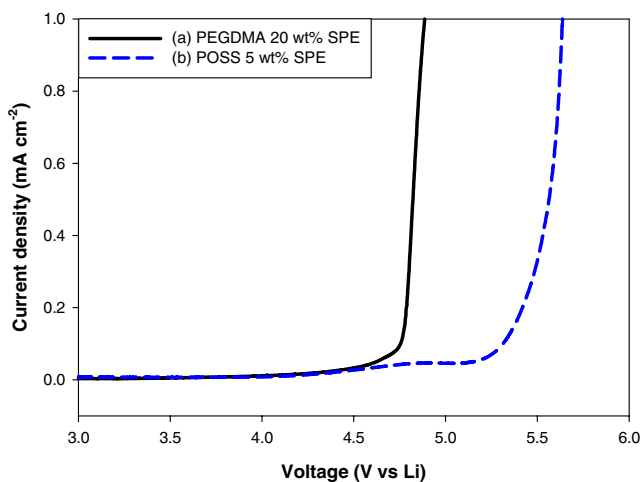
**Table 1** Ionic conductivity and glass transition temperature of SPE as a function of PEGDME content

Content of PEGDME (wt.%)	$\sigma$ (S cm <sup>-1</sup> at 25°C)	<i>T<sub>g</sub></i> (°C)
0	$5.8 \times 10^{-6}$	-43.2
80	$1.4 \times 10^{-4}$	-75.3
90	$3.4 \times 10^{-4}$	-79.5
95	$5.3 \times 10^{-4}$	-82.7

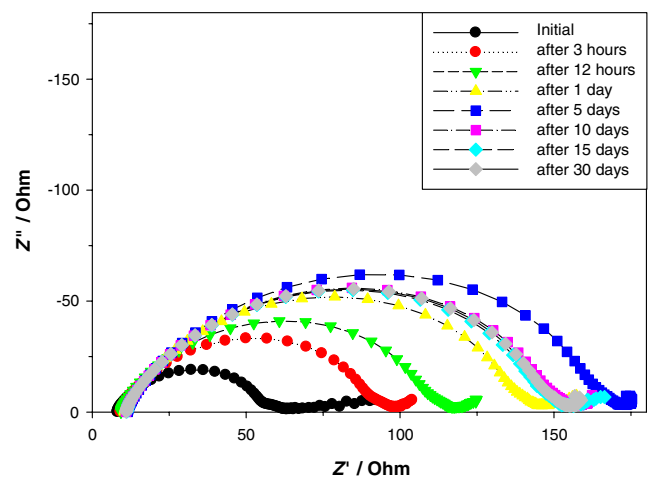


**Fig. 2** Ionic conductivities of SPE with different crosslinking agent (POSS) contents as a function of temperature. POSS 20 wt.% (maroon-colored circle), POSS 10 wt.% (orange-colored circle), and POSS 5 wt.% (olive green-colored inverted triangle)

inorganic material, which consists of a silica cage in the center with functional groups attached at the cage corners, having the general formula  $(RSiO_{1.5})_n$  therein R is H, alkyl, alkylene, aryl, aromatic alkylene, or their derivative groups [9]. Generally, it is known that POSS with reactive functionalities are suitable for polymerization, crosslinking, grafting, or surface bonding. The incorporation of these nanoparticle reinforcing agents into polymeric materials can improve the properties such as thermal and oxidation resistance, surface hardening, and flammability reduction [10]. In this work, methacryl-POSS was used as a cross-linking agent for SPE based on polymer mechanical supporter. SPE based on POSS were expected to exhibit



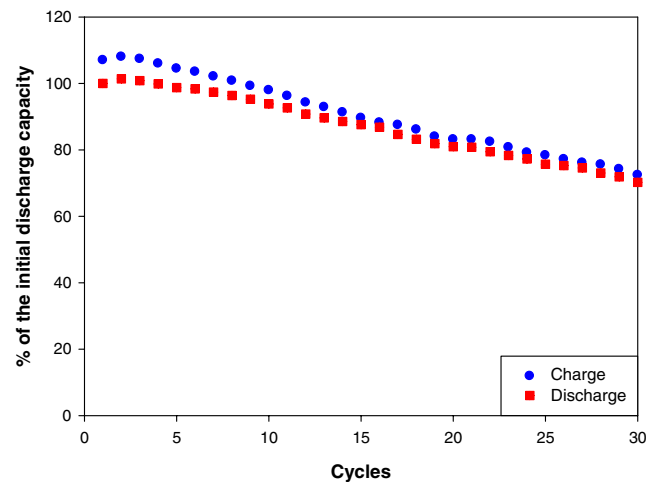
**Fig. 3** Electrochemical stability of SPE with 20 wt.% PEGDMA and 80 wt.% PEGDME (a) and 5 wt.% POSS and 95 wt.% PEGDME (b; scan rate of  $1 \text{ mV s}^{-1}$ )



**Fig. 4** Impedance plots showing the interfacial resistances of SPE with 5 wt.% POSS and 95 wt.% PEGDME stored at room temperature as a function of time

higher ionic conductivities at ambient temperature because POSS can entrap sufficient amount of nonvolatile plasticizer within SPE without leakage and loss in the mechanical property due to its eight acrylate groups. The functionalized  $\text{SiO}_2$  particles (POSS) as fillers in polymer electrolytes were also expected to improve the electrochemical stability and mechanical properties. Good dispersion of functionalized  $\text{SiO}_2$  particles in the polymer matrix can yield more charge carriers available for conduction [5, 11]. With these reasons, methacryl-POSS is chosen as a candidate for crosslinking of SPE in this work.

The ionic conductivities of SPE with different ratios of crosslinking agent (POSS) to nonvolatile plasticizer



**Fig. 5** Cycle life characteristics for the unit cell of Li/SPE (with 5 wt.% POSS)/LiCoO<sub>2</sub> at room temperature (current density =  $0.2 \text{ mA cm}^{-2}$ )

(PEGDME) are listed in Table 1. The increase of ionic conductivities with the content of PEGDME is closely related to the decrease in glass transition temperature. It was observed that ionic conductivity of SPE is gradually increased with the increase of the PEGDME content. The highest value of ionic conductivity was measured to be  $5.3 \times 10^{-4} \text{ S cm}^{-1}$  at the 5 wt.% POSS, 95 wt.% PEGDME. This ionic conductivity value seems to be high enough considering the SPE with the sufficient mechanical strength for practical applications [7, 8].

An Arrhenius plot of ionic conductivities of SPE with different POSS contents is shown in Fig. 2. The temperature was varied from  $-20$  to  $60$  °C at a step of  $10$  °C and then cycled back to  $-20$  °C. It is found that the ionic conductivities of SPE were maintained at each temperature under thermal stress during cycled heat treatment between  $-20$  and  $60$  °C. This indicates that the SPE has dimensional stability up to 5 wt.% of crosslinking agent content within the above operating temperature range.

Electrochemical stability of SPE is also of importance for its practical application. Decomposition of SPE can cause a drastic decrease of the capacity on cycling and give rise to safety problems. The electrochemical stability of the SPE containing 5 wt.% POSS is shown in Fig. 3. It is clear from the figure that our SPE is stable up to 5.3 V. We have already reported on the electrochemical stability of the system based on PEGDMA crosslinking system without containing nanosized ceramic fillers [7]. It is demonstrated that the electrochemical stability of this system is far better than the above system. The enhancement of electrochemical stability of SPE-based POSS by 0.5 V is conjectured to originate from addition of nanosized filler [12].

To obtain high performance of lithium polymer battery at room temperature, the electrolyte should have high ionic conductivity and low interfacial resistance with the electrode [13]. The interfacial stability of the lithium electrode and SPE was evaluated by monitoring the AC impedance of a symmetric Li/SPE/Li cells stored at room temperature under the open circuit condition for 30 days. Figure 4 shows the AC impedance spectra of the symmetric Li/SPE/Li cells in which the first interception at high frequency is related to bulk resistance, and a semicircle in the medium frequency range represents the interfacial resistance. It is observed that interfacial resistance increases with the storage time. The initial increase of interfacial resistance is attributed to the formation of a passive film on the surface of the lithium electrode caused by the reaction of the electrode with polymer electrolyte or residual impurities. The SPE generates interfacial resistances about  $140 \Omega$  after a few days. This value is rather lower compared with previously reported values, and we conducted the charge and

discharge tests at 0.1-C rate [14, 15]. This indicates that nanosized filler (POSS) is helpful to form a compact and stable passive film quickly [16, 17].

The unit cell consisting of Li/SPE/LiCoO<sub>2</sub> was cycled at room temperature. The charge and discharge tests were repeatedly performed at 0.1 C between 3.0 and 4.2 V. The discharge characteristics of the cells are shown in Fig. 5. The discharge capacity of the unit cell shows about 80% of the initial discharge capacity after 20 cycles. This seems to be quite an advanced result for lithium polymer batteries based on SPE operating at room temperature. However, it is necessary to further tune the structure of SPE and also develop an electrode binder which is more compatible with SPE in order to enhance cycle performance.

## Conclusions

The SPE based on multifunctional crosslinking agent POSS acting as a hybrid nanofiller have been successfully prepared by UV curing method. The new SPE has enhanced electrochemical and thermal properties, and it could hold more plasticizer in the electrolyte compared to conventional SPE owing to high crosslinking density of methacryl-POSS. As a result, the unit cell based on Li/SPE/LiCoO<sub>2</sub> could be cycled even at room temperature. This seems to be a forward step toward the realization of lithium rechargeable batteries based on SPE at room temperature.

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