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Semi-interpenetrating solid polymer electrolyte based on thiol-ene cross-linker for all-solid-state lithium batteries



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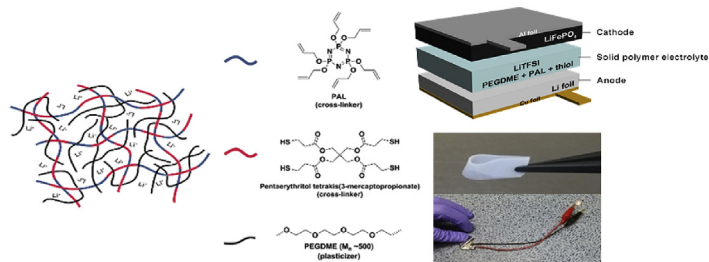
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HIGHLIGHTS

- A new cross-linker with allyl functional groups was synthesized.
- A novel semi-IPN SPE was prepared by *in-situ* radical polymerization.
- Solid polymer electrolytes exhibit very high ionic at ambient temperature.
- All-solid-state lithium battery have very good performance at ambient temperature.
- The cells exhibit stable electrochemical performance under severely wrinkled state.

GRAPHICAL ABSTRACT



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ABSTRACT

We developed highly promising solid polymer electrolytes (SPEs) based on a novel cross-linker containing star-shaped phosphazene with poly(ethylene oxide) (PEO) branches with very high ionic conductivity ($7.6 \times 10^{-4} \text{ S cm}^{-1}$), improved mechanical stability, and good electrochemical stability for all-solid-state lithium batteries. In particular, allyl groups were introduced at the ends of the cross-linker in order to overcome the easy self-polymerization of existing cross-linking acrylate end groups. A novel semi-interpenetrating network (semi-IPN) SPE was prepared by *in-situ* radical polymerization of a precursor solution containing lithium salt, poly(ethylene glycol) dimethyl ether as a plasticizer, and a mixture of pentaerythritol tetrakis(3-mercaptopropionate) and a synthesized hexakis(allyloxy)cyclo-triphosphazene (*thiol-ene* PAL) as the cross-linker. Batteries employing LiFePO₄ as the cathode, lithium foil as the anode, and the SPE thin film as the electrolyte were assembled and tested. At ambient temperature, the initial discharge capacity was 147 mAh/g at 0.1 °C and 132 mAh/g at 0.5 °C, and 97% of the capacity was retained at the 100th cycle. All-solid-state pouch-package lithium cells assembled with the SPEs exhibited stable electrochemical performance, even under a severely wrinkled state. These outstanding properties of SPEs based on *thiol-ene* PAL demonstrate feasibility for practical battery applications with improved reliability and safety.

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1. Introduction

Rechargeable lithium ion batteries (LIBs) have been widely developed for use in portable electronics, electric vehicles, and

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energy storage systems because of their high energy/power densities, high efficiency, and long life [1–3]. However, conventional LIBs containing a liquid electrolyte are at higher risk of fire or explosion because of the usage of a large amount of flammable electrolyte [4–6]. The most recent developments in LIB technology is directed toward the replacement of the liquid electrolytes with polymer electrolytes [7,8]. A polymer electrolyte based on alkali metal salt-doped poly(ethylene oxide) (PEO) was first reported by Wright in 1973 [9]. Since then, PEO-based solid polymer electrolytes (SPEs) have been regarded as promising solid electrolytes, and the number of contributions to the field of PEO-based SPEs has grown enormously due to their many advantages, including high ionic conductivity at high temperatures, high thermal and electrochemical stability, good safety, and excellent interface stability [10,11]. However, PEO-based SPEs have a critical problem for practical use in that the ionic conductivity is low, generally in the range from 10^{-8} to 10^{-7} S/cm at ambient temperature, which is caused by the high crystallinity of PEO polymers [12–14]. Moreover, these polymers have poor mechanical properties that may result in electrolyte leakage, allowing the electrodes to come into contact with the electrolyte and short-circuit the cell.

Various approaches have been used to suppress crystallization, increase the ionic conductivity and strengthen the mechanical properties of PEO-based SPEs [15]. Most of the approaches involve modifying PEOs with other monomers [16–18] such as star- or comb-branched polymers [19,20] and cross-linked networks [21] or the addition of other polymers, organic plasticizers, and inorganic nanoparticles, thus forming composite polymer electrolytes [22–25] to make SPEs mechanically and thermally stable with enhanced electrochemical performance. In our previous work, a cross-linker with acrylate end groups was applied to a semi-interpenetrating polymer network (semi-IPN), and enhanced ionic conductivity was observed [20,26]. Semi-IPN features the integration of both a mechanically stable cross-linked polymer network and a linear polymer as a small molecular ionic conductor [27]. However, the acrylate end groups easily self-polymerized in storage, and thus became difficult to handle for practical purposes.

In order to overcome the existing drawbacks, we synthesized a novel cross-linker with allyl functional groups, which have good storage stability. The cross-linker was made through the novel routes called “thiol-ene” system [28]. Thiol-ene polymerization is accomplished that the carbon double bonds of the allyl groups radically react with the thiol monomers to form thiol-ether cross-linking between the monomers [29]. It is a well-known, facile, and versatile polymerization process in which the thiol compound can be used in stoichiometric equivalence to the “ene” groups or as an additive in lower amounts under ambient conditions [28–35]. It is less sensitive to oxygen and forms structurally homogeneous polymer networks with reduced shrinkage and significantly simplified polymerization kinetics [36,37].

Recently, attempts to apply the thiol-ene system to SPEs have been addressed [31,38,39], but it ended up only synthesis and characterization of new materials. In this study, we synthesized star-shaped hexakis(allyloxy)cyclotriphosphazene (PAL) with allyl functional groups and then cross-linked PAL through the semi-IPN polymerization method via thiol-ene chemistry to make a free-standing solid film with outstanding ionic conductivity at near room temperature, a wide electrochemical window, and sufficient dimensional stability to be applied to lithium ion batteries.

2. Experimental

2.1. Materials

Allyl alcohol (Kanto Chemical, Japan), sodium hydride (dry, 95%,

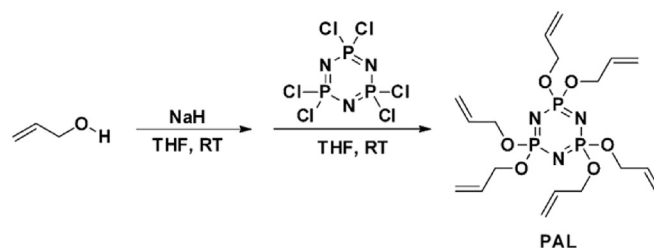
Sigma-Aldrich, USA), 2-allyloxyethanol (98%, Sigma-Aldrich, USA) phosphonitrilic chloride trimer (99%, Sigma-Aldrich, USA), pentaerythritol tetrakis(3-mercaptopropionate) (>95%, Sigma-Aldrich, USA), tetrahydrofuran (THF, anhydrous, $\geq 99.9\%$, Sigma-Aldrich, USA), poly(ethylene oxide) (PEO, Sigma-Aldrich, USA), acetonitrile (anhydrous, 99.8%, Sigma-Aldrich, USA), cyclohexanone (99.8%, Acros-Organics, USA), and LiFePO_4 (LFP, Hanwha Chemical, Korea) were purchased and used as received. *t*-Butyl peroxyvalerate (*t*-BPP, Seki Arkema Co., Japan) was purchased and used as received; it was kept in cold storage in an Ar-filled glove box. Poly(ethylene glycol) dimethyl ether (PEGDME, Mn \approx 500, Sigma-Aldrich, USA) was purchased and used after drying until the moisture level was less than 5 ppm by heating under vacuum and using molecular sieves. Bis(trifluoromethane)sulfonamide (LiTFSI, 99.95%) was supplied by Sigma-Aldrich and used after drying at 120 °C in a vacuum oven for 48 h before use.

2.2. Synthesis of hexakis(allyloxy)cyclotriphosphazene (PAL)

Scheme 1 shows the synthetic route of the star-shaped PAL cross-linker. Allyl alcohol (4.54 g, 77.66 mmol) was added dropwise into a solution of sodium hydride (1.86 g, 77.66 mmol) in ice bath-cooled THF (100 mL). The reaction mixture was stirred at room temperature until all the sodium hydride was consumed. Then, a solution of phosphonitrilic chloride trimer (3 g, 8.63 mmol) in THF (50 mL) was added to the allyl alcohol and sodium hydride in THF solution and stirred at 50 °C for 1 day. After the reaction was completed, precipitated salts were removed by filtration. The remaining filtrate was extracted with ethyl acetate and deionized (DI) water, and the organic layer was dried with magnesium sulfate. The residue was purified with column chromatography with a mixture of ethyl acetate and hexane (1:5 v/v). ^1H NMR (Avance DRX 300, Bruker, Germany) (CDCl_3 , ppm): δ 4.456–4.462 (t, 2H), 5.190 (dd, 1H, $J = 0.9$ Hz, 0.9 Hz), 5.338 (dd, 1H, $J = 1.2$ Hz, 1.2 Hz), 5.898–5.993 (m, 1H), ^{13}C NMR (Avance 500, Bruker, Germany) (CDCl_3 , ppm): δ 66.541, 117.208, 133.126, 133.148, 133.170, 133.192, ^{31}P NMR (Avance II 500 with Cyro, Bruker, Germany) (CDCl_3 , ppm): δ 18.311 (s).

2.3. Preparation and characterization of solid polymer electrolytes

The SPEs were prepared by *in-situ* thermal cross-linking of a homogeneous precursor solution composed of thiol-ene cross-linkers, (pentaerythritol tetrakis(3-mercaptopropionate) and hexakis(allyloxy)cyclotriphosphazene (PAL) (6:4 w/w), a plasticizer (PEGDME), lithium salt (LiTFSI), and a thermal initiator (*t*-BPP). All components were mixed together without using any solvent and stirred until the solution became clear. The weight ratio between thiol-ene cross-linker and the plasticizer with 3:7 and the amount of thermal radical initiator was fixed at 2 wt% with respect to the amount of the cross-linker. The concentration of lithium salt was adjusted such that the $[\text{EO}]/[\text{Li}^+]$ molar ratio of the polymer



Scheme 1. Synthetic routes of the star-shaped PAL cross-linker.

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