



# One-pot preparation of new copolymer electrolytes with tunable network structure for all-solid-state lithium battery



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## HIGHLIGHTS

- One-pot preparation of new electrolytes with tunable network structure.
- The influence factors on the ionic conductivity are systematically investigated.
- The new electrolytes present excellent electrochemical and mechanical properties.
- The all-solid LiFePO<sub>4</sub>/Li battery exhibits excellent cell performance under 60 °C.

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## ABSTRACT

A new class of copolymer electrolytes with tunable network structure is successfully designed and prepared via a facile one-pot reaction. The trimethylolpropane triglycidyl ether (TMPEG) is cross-linked with poly (ethylene glycol) diamine (NPEG) to create well-defined solid network polymer electrolyte (SNPE). The network structure could be tuned by changing the molar ratio of TMPEG and NPEG or the molecular weight of NPEG. The effects of molecular weight of NPEG and molar ratio of EO/Li<sup>+</sup> on the ionic conductivity are systematically investigated. The optimal electrolyte TMPEG-NPEG4K[2:1]-16:1 presents a maximum conductivity of  $1.10 \times 10^{-4} \text{ S cm}^{-1}$  under 30 °C, and an 18-fold ionic conductivity enhancement in that of PEO-based electrolyte. Furthermore, it also exhibits wide electrochemical window (0–5.4 V), excellent compatibility with metallic Li, and superior mechanical properties. The all-solid-state lithium batteries LiFePO<sub>4</sub>/Li are assembled with TMPEG-NPEG4K[2:1]-16:1 electrolyte, and present good cycling and rate performance under 60 °C. The initial discharge specific capacities of the batteries are 161.7 mAh g<sup>-1</sup> at 0.2 C and 132.7 mAh g<sup>-1</sup> at 1 C, and the capacity retention ratio can be retained at 90.6% and 90.5% after 100 cycles. This new copolymer electrolyte may become a promising candidate for applications in all-solid-state lithium battery.

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## 1. Introduction

Lithium ion batteries (LIBs) are one of the most attractive energy storage devices due to their acceptable energy density, environmentally benignity, and long cycling life [1,2]. The LIBs technologies have been first introduced into the consumer electronics market by Sony in 1991. However, safety problems that could lead to the leakage and flammability caused by organic liquid electrolyte, became obvious with increasing battery size for vehicle application.

These LIBs raise safety concerns due to containing flammable small molecule electrolyte [3]. Several incidents such as the fires in the LIB unit of Tesla vehicles and a Boeing 787 airplane have raised questions about the inherent safety advantages of LIBs with organic liquid electrolyte [4]. Furthermore, the low energy density of these traditional LIBs has been pointed out as one of the roadblocks for the ultimate replacement of internal combustion vehicles by electric vehicles.

Lithium (Li) metal is an ideal negative electrode for rechargeable batteries to enhance the energy density due to its extremely high theoretical specific capacity (3860 mAh g<sup>-1</sup>), low density (0.59 g cm<sup>-3</sup>) and the lowest negative electrochemical potential (−3.04 V vs. the standard hydrogen electrode) [5]. Unfortunately, rechargeable batteries based on Li negative electrodes have not yet

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been commercialized. However, there are two main challenges hindering the development of LIBs. Firstly, the growth of Li dendrites results in serious safety issue owing to potential internal short circuits. Secondly, the electrochemical instability of Li electrode during repeated charge/discharge processes causes the poor cycle life in rechargeable batteries. Therefore, replacing flammable electrolytes and enhancing the energy density of LIBs technologies are the forefront of research in both academia and industry [6,7].

Solid polymer electrolytes exhibit excellent electrochemical stability and favorable mechanical properties, and can be operated over a wide temperature window. They are regarded as the most promising materials for developing secondary batteries using metallic Li as negative electrode [8,9]. Moreover, solid polymer electrolytes also avoid the presence of flammable organic solvents. It brings a new perspective to research on LIBs, enabling high-energy battery chemistry with an intrinsically safe cell design.

It is well known that polymer electrolyte used in LIBs is usually based on poly (ethylene oxide) (PEO). Lithium ion migration around the PEO segments, due to the local motion of the ethylene oxide (EO,  $-\text{CH}_2\text{CH}_2\text{O}-$ ) chains in the amorphous region, depends on the strong dipole interaction of the ether groups and metal cations [10,11]. Additionally, PEO has a high dielectric constant and strong  $\text{Li}^+$  solvating ability. However, their further applications are limited by their low ionic conductivity ( $10^{-6} \sim 10^{-7} \text{ S cm}^{-1}$  at room temperature), poor mechanical property and narrow electrochemical stability window [12,13].

Prevalingly, PEO is a semi-crystalline polymer, and the amorphous phase with activated chain segments (above  $T_g$ ) has an overwhelming influence on ion transportation [14]. For instance, PEO crystallization is detrimental to ion transport due to the slowed down polymer chain dynamics upon crystallization [15]. The suppression of PEO crystallinity is generally regarded as the design criterion for PEO-based electrolytes to increase the percentage of the amorphous phase of PEO for ion transport.

So far, various strategies and approaches such as the addition of a plasticizer [16] or nano-filler [17], polymer blends [18], grafting short PEO oligomers onto polymer backbones or cross-linking PEO based polymers [19], and block copolymer [20] have been widely investigated to enhance the ionic conductivity of PEO-based electrolytes.

Among these aforementioned approaches, cross-linking is considered as the most key factor to improve both the ionic conductivity and mechanical properties of polymer electrolyte. In addition, cross-linking, which is based on a well-developed polymer network structure, can stabilize the amorphous state of linear PEO below the crystallization temperature. Liu et al. [21] fabricated a cross-linked polymer electrolyte by a solvent-free hot-pressing method for all-solid-state LIBs. The ionic conductivity of the electrolyte is  $5.1 \times 10^{-5} \text{ S cm}^{-1}$  at  $30^\circ\text{C}$ , and the decomposition potential is 4.87 V, which is thermally stable up to  $230^\circ\text{C}$  in argon atmosphere. Coates et al. [22] prepared a polymer composed of stiff semi-crystalline PE chains covalently cross-linked by PEO segments using a ring-opening metathesis polymerization (ROMP) route. The cross-linked polymer electrolyte exhibits both high ionic conductivity and excellent resistance to dendrite growth. Most importantly, it with the low-modulus ( $G' \approx 1.0 \times 10^5 \text{ Pa}$  at  $90^\circ\text{C}$ ) presents remarkable dendrite growth resistance contrary to the theoretical predictions, and identify that a high-modulus polymer electrolyte is not a requirement for the control of dendrite proliferation.

In this paper, quite different from the most previous reported cross-linked polymer electrolyte by complicated procedures [22–24], a new class of network polymer electrolytes were prepared via a facile one-pot reaction. The network structures of them could be tuned by changing the molar ratio of TMPEG and NPEG or the molecular weight of NPEG. Scheme 1 illustrates the cross-

linked chemical procedure to prepare the two types of network structures, TMPEG-NPEG[1:1] and TMPEG-NPEG[2:1]. As shown in Scheme 1, the comonomer TMPEG is cross-linked by an end-functionalized amido-PEG (NPEG) to create a well-defined SNPE. When the molar ratio of epoxy groups in TMPEG and amine groups in NPEG is 1/1, the network structure named as TMPEG-NPEG[1:1]; while the molar ratio of epoxy groups in TMPEG and amine groups in NPEG is 2/1, the network structure named as TMPEG-NPEG[2:1]. This chemistry is confirmed to be an attractive method for solid electrolyte preparation due to its high efficient and yielding networks with few defects, and can accommodate a wide variety of precursor polymers [25,26]. The effects of NPEG with different molecular weight and molar ratio of EO/ $\text{Li}^+$  on the ionic conductivity and mechanical property were investigated, respectively. The conductivity, phase behavior and electrochemical stability of the new prepared SNPEs were also systematically characterized. Finally, all-solid-state lithium batteries  $\text{LiFePO}_4/\text{Li}$  were assembled and characterized with the optimal electrolyte TMPEG-NPEG4K [2:1]-16:1 (“16:1” means a molar ratio of EO/ $\text{Li}^+$  is 16:1).

## 2. Experimental

### 2.1. Materials

All the materials have been dried prior to use and the experiments were carried out in glove box ( $\text{H}_2\text{O}$  and  $\text{O}_2 < 0.1 \text{ ppm}$ ) under argon atmosphere. TMPEG, NPEG and Tetrahydrofuran (THF) were purchased from Sigma-Aldrich. PEO ( $M_w = 6 \times 10^5$ , Aladdin), trimethylolpropane triglycidyl ether (TMPEG) and poly (ethylene glycol) diamine (NPEG) were dried at  $50^\circ\text{C}$  under vacuum for 24 h (h) prior to use. THF was distilled from sodium/benzophenone to obtain the anhydrous THF. Lithium bis(trifluoromethane)sulfoniimide (LiTFSI, Sigma-Aldrich) and  $\text{LiFePO}_4$  (Dyanonic) were also dried at  $110^\circ\text{C}$  under vacuum for 24 h prior to use.

### 2.2. Preparation of SNPEs

Four molecular weights of NPEG (1500, 4000, 6000, and 10000  $\text{g mol}^{-1}$ , abbreviated as NPEG1.5K, NPEG4K, NPEG6K and NPEG10K, respectively) were selected to cross-linking with TMPEG to create two types of copolymers TMPEG-NPEG[1:1] and TMPEG-NPEG[2:1] as shown in Scheme 1.

In typical procedure, for the preparation of TMPEG-NPEG1.5K [2:1]-16:1 copolymer electrolyte, TMPEG ( $M_n = 302.36 \text{ g mol}^{-1}$ , 181.42 mg) and NPEG ( $M_n = 1500 \text{ g mol}^{-1}$ , 675 mg), were dissolved in 2 mL anhydrous THF and stirred at  $60^\circ\text{C}$  for 8 h to form a homogeneous solution. After the solution was cooled to the room temperature, the LiTFSI ( $M_n = 287.09 \text{ g mol}^{-1}$ , 266.45 mg, EO/ $\text{Li}^+ = 16$  by mole) was added into the solution and stirred for another 2 h. Afterwards, the resulting solution was cast onto a Teflon plate and kept in the oven under  $90^\circ\text{C}$  for 12 h, and then it was heated under  $110^\circ\text{C}$  for 2 h to make sure all the epoxy groups were reacted with amine groups completely. Finally, the electrolyte membrane was peeled off from the Teflon plat and punched into circles with diameters 19 mm and 10 mm for further measurements. All the procedures were conducted in an argon-filled glove box.

In addition, for the preparation of TMPEG-NPEG1.5K[1:1]-16:1, 90.71 mg of TMPEG and 675 mg of NPEG1.5K should be weighted and reacted according to the reaction described in Scheme 1(a), and 266.45 mg of LiTFSI was added into it to maintain the molar ratio of EO/ $\text{Li}^+ = 16$ . In this paper, the molar ratio of EO/ $\text{Li}^+$  will be selected from 14, 16, 18 and 20. Therefore, the weight of LiTFSI should be changed accordingly.

Similarly, the other cross-linked electrolytes based on TMPEG-

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