



In-situ preparation of poly(ethylene oxide)/Li₃PS₄ hybrid polymer electrolyte with good nanofiller distribution for rechargeable solid-state lithium batteries

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HIGHLIGHTS

- Li₃PS₄ nanofillers present excellent distribution in PEO-matrix.
- In-situ and mechanical-mixing preparation methods are compared and investigated.
- In-situ prepared electrolyte shows better conductivity and electrochemical stability.
- All-solid-state LiFePO₄/Li battery exhibits decent cell performance under 60°C.

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ABSTRACT

Nano-sized fillers in a polymer matrix with good distribution can play a positive role in improving polymer electrolytes in the aspects of ionic conductivity, mechanical property and electrochemical performance of Li-ion cells. Herein, polyethylene oxide (PEO)/Li₃PS₄ hybrid polymer electrolyte is prepared via a new in-situ approach. The ionic conductivities of the novel hybrid electrolytes with variable proportions are measured, and the optimal electrolyte of PEO-2%vol Li₃PS₄ presents a considerable ionic conductivity of $8.01 \times 10^{-4} \text{ S cm}^{-1}$ at 60 °C and an electrochemical window up to 5.1 V. The tests of DSC and EDXS reveal that the Li₃PS₄ nanoparticles with better distribution, as active fillers scattering in the PEO, exhibit a positive effect on the transference of lithium ion and electrochemical interfacial stabilities. Finally, the assembled solid-state LiFePO₄/Li battery presents a decent cycling performance (80.9% retention rate after 325 cycles at 60 °C) and excellent rate capacities with 153, 143, 139 and 127 mAh g⁻¹ at the discharging rate of 0.1 C, 0.2 C, 0.5 C and 1 C at 60 °C. It is fully proved that it is an advanced strategy to preparing the new organic/inorganic hybrid electrolytes for lithium-ion batteries applications.

1. Introduction

Rechargeable lithium-ion batteries, as an essential component for energy storage devices, has gained popular application in mobile phones, laptops, tablets and other digital electronic products [1,2]. In recent years, as the most promising candidates for energy storage, lithium-ion batteries are widely used in the applications of electric mobiles, smart grids, uninterruptible power supplies (UPS) etc. However, the development is restricted by lots of shortcoming such as poor anti-disturbance from environment, terrible thermal stability after long

operation time, explosion hazards, leakage or internal short circuit because of nonaqueous liquid electrolytes in the conventional lithium-ion batteries [3,4]. With this current challenge, solid polymer electrolytes (SPEs) are regarded as one of the most considerable solutions to solving security problems for lithium-ion batteries because they possess several advantages such as fire resistance, no-leakage, light weight, flexible geometry, convenient processability, outstanding stability in electrochemistry [5,6]. Amongst all the research categories of polymer electrolytes, poly(ethylene oxide) (PEO) based SPEs have attracted extensive attention in academic field and practical application which is

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ascribed to their excellent Li-ion solvating properties and easy-forming repeated ethylene oxide-lithium (EO/Li⁺) complexes [7]. Nevertheless, there is lots of crystalline phase in pure PEO, which inhibited Li-ion transfer, leading to low ionic conductivity of 10^{-7} S cm⁻¹ at ambient temperature [8]. Hence, it's important to make great efforts to bring down the crystallinity for the sake of enhancement of the ionic conductivity.

A great quantity of work has been done to improve and enhance SPEs based on PEO [9–16], including but not limited to the following three points: (I) synthesis of cross-linked structure, random, block or comb-like copolymers, (II) addition of plasticizers to enhance the flexibility of the SPEs, (III) taking advantage of inorganic ceramics, in order to break the crystallinity of the polymer. Of these alternates, dispersing inorganic ceramics including SiO₂, TiO₂, Al₂O₃, or LiAlO₂ in the polymer matrix has attracted a great interest owing to their special properties, for instance, enhanced mechanical strength and thermodynamic stability [17], fire retardance [18] and improved ionic conductivity in comparison to that of the pristine polymer. The addition of inorganic ceramics is considered to inhibit reorganization of structured arrangement in polymer crystallization and enhance free volume, which is in favor of high lithium ion conduction [19]. However, most of the metal oxide fillers studied so far are passive, i.e., they do not contribute to the ionic conductivities of the hybrid polymer electrolytes by only providing migration pathways, or by acting as a source of charge carries. Therefore, several Li⁺ conductors, for instance, Li_{1.4}Al_{0.4}Ge_{1.7}(PO₄)₃ (LAGP), Li_{0.33}La_{0.557}TiO₃ (LLTO) and Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP) etc. have been selected to incorporate into the PEO-matrix recently, which drastically increase ionic conductivities, electrochemical stability and mechanical properties in these hybrid polymer electrolytes [20–22]. Normally, these hybrid polymer electrolytes are prepared by mechanical-mixing to achieve adequately dispersing the inorganic fillers in the polymer matrix. Whereas, physical mixtures by mechanical-mixing the organic polymers with inorganic fillers are likely to result in inhomogeneous dispersion in microscopic distribution and existing considerable amount of polymer crystallization regions. Besides, most of the reported Li⁺ conductors are oxides with micron-sized particles, while a lot of reports have well proven that nano-sized fillers are much more effective in improving ionic transport properties than micron-sized fillers due to their large specific surface areas [23,24]. However, it also important to note that nano-sized ceramics will give rise to agglomeration which could weaken polymer-ceramic interaction and mechanical properties of the resulting materials, running more challenges to further improving of ionic conductivity.

Consequently, in this work, a new approach is put forward to prepare inorganic-polymer hybrid SPEs by in-situ synthesis of Li₃PS₄ nanoparticles within PEO-matrix which possess good distribution of nanofillers. As illustrated in Fig. 1, PEO/Li₃PS₄ hybrid polymer

electrolytes were prepared via in-situ synthesis in solvent, sequentially casting on the Teflon plate and annealed. β-Li₃PS₄ glass-ceramic is a Li superionic conductor with a conductivity beyond 10^{-4} S cm⁻¹ at RT and has a relatively stable electrochemical property in Li₂S-P₂S₅ binary systems [25]. Therefore, in-situ synthesis of Li₃PS₄ glass-ceramics in PEO shows a unique opportunity for investigating the interplay between Li₃PS₄ and PEO host at the interphase. The properties of the hybrid polymer electrolytes with two different preparation methods containing in-situ preparation and mechanical-mixing preparation are compared. Their properties are systematically investigated. Finally, all-solid-state lithium batteries were fabricated and investigated as well.

2. Experiment section

2.1. Preparation of hybrid polymer electrolyte

Li₂S (Idemitsu Kosan, 99.9%) and P₂S₅ (Sigma-Aldrich, 99%) were dissolved in the acetonitrile (ACN, Aladdin, 99.8%) solvent with molar ratio of 3:1 and stirred for 5 h (h) at 25 °C. Then, the polyethylene oxide (PEO, M_w = 6 × 10⁵, Aldrich) and bis(trifluoromethane)sulfonilimide (LiTFSI, 99.9%, Aldrich, EO:Li⁺ = 18:1) were dissolved in the above solution and stirred overnight to get a uniform slurry. The slurry was casted on the Teflon plate, volatiled solvent for 48 h at room temperature (RT) and annealed at 230 °C for 4 h, successively. Finally, the hybrid electrolyte membranes with Li₃PS₄ glass-ceramics were stripped off from the Teflon plate and tailored into 19 mm-diameter round membranes for further characterization. All of above experimental operations were performed in glove boxes that filled with high purity argon atmosphere (moisture and oxygen below 0.5 ppm). Herein, this preparation is remarked as in-situ preparation method.

As a contrast, PEO/Li₃PS₄ hybrid electrolytes were prepared via mechanical-mixing as well. Li₃PS₄ with different volume fractions (1% vol, 2%vol, 3%vol, 4%vol, and 5%vol) and PEO were mechanical-mixed in the ACN solvent, then the slurry was casted on the Teflon plate and dried for 48 h at RT. It should note that the Li₃PS₄ glass-ceramics were synthesized from ACN solvent instead of traditional ball-milling method. Li₂S and P₂S₅ with a stoichiometry of 3 to 1 were mixed in ACN at 25 °C. After stirring for 24 h and vacuum distillation, the precipitate was heat-treated at 80 °C to remove the ACN. This precursor was calcined at 230 °C for 4 h to obtain the sample of Li₃PS₄.

Fig. 2 shows the process schematic of mechanical-mixing and in-situ preparation method for comparison.

2.2. Characterization and instruments

Field emission scanning electron microscopy (FESEM, Hachi S-4800) with energy dispersive X-ray spectroscopy (EDXS) was used to confirm the morphology of the Li₃PS₄ and corresponding element

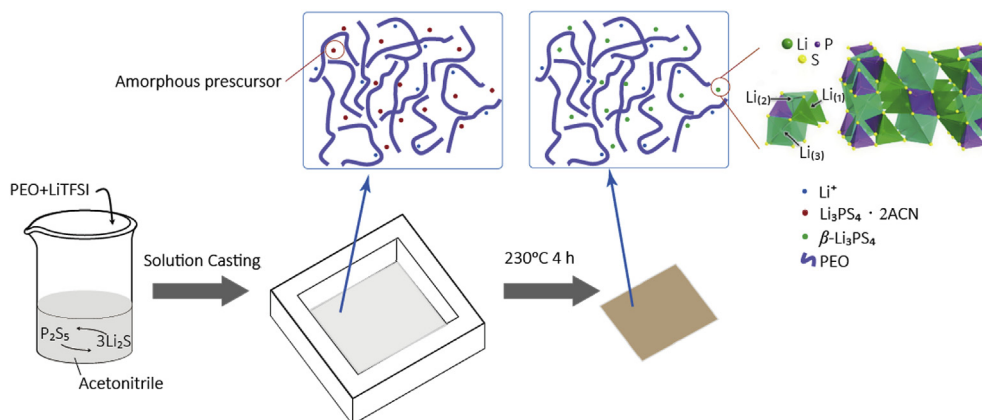


Fig. 1. The process flow diagram of in-situ preparation of PEO/Li₃PS₄ hybrid polymer electrolytes.

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