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A novel solid composite polymer electrolyte based on poly(ethylene oxide) segmented polysulfone copolymers for rechargeable lithium batteries

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ABSTRACT

It is a compelling challenge to develop solid polymer electrolyte membranes for rechargeable battery with both high ionic conductivity and superior mechanical performance. In this study, we first prepare a new type of all-solid-state composite polymer electrolyte from lithium bis-trifluoromethanesulphonimide (LiTFSI), succinonitrile (SN) and poly(ethylene oxide) segmented polysulfone copolymers (PSF-PEO) with various PEO contents in low molecular weight ($M_n=1500$ Da), which are synthesized by condensation polymerization. The optimized composite polymer electrolyte PSF-PEO35+LiTFSI+SN membrane exhibits a remarkable amorphous state; leading to its ionic conductivity of $1.6 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. Especially, the tensile strength of the PSF-PEO35+LiTFSI+SN electrolyte membrane is still more than 4.3 MPa at 80 °C, indicating its excellent mechanical property and high thermal stability in a wide temperature range. Li symmetric cell and Li/LiFePO₄ cell with the above electrolyte display low voltage polarization and good rechargeability. The test results indicate that the solid PSF-PEO35+LiTFSI+SN composite electrolyte membrane is a promising candidate for future applications in rechargeable lithium batteries.

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1. Introduction

All-solid-state polymer electrolytes avoid high volatility, liquid leakage and flammability of traditional liquid electrolytes or gel polymer electrolytes and allow for a safe and stable operation at temperatures exceeding 60 °C. They possess advantageous features of good mechanical properties, light weight, shape versatility and easy processability. Therefore, they are promising components in high energy density power sources, such as rechargeable lithium-sulfur batteries and lithium-air batteries. Potential applications for temperature-stable lithium batteries may widely include electrical vehicles (EVs), exploration vehicles in spaceflight, and measure-while-drilling tools used by the oil industry [1–5]. However, the batteries based on metallic lithium anode and solid polymer electrolytes have encountered the following problems: (i) a low ambient conductivity. (ii) side-reaction between electrolyte and lithium metal, giving rise to interface resistance increase and capacity loss during cycling. (iii) safety hazards caused by dendrite formation during cycling [6].

The conventional poly(ethylene oxide) (PEO)-based solid polymer electrolytes have been studied extensively due to the ability to form complexes with a wide variety of lithium salts [7]. In these electrolytes, the ether oxygen atoms interact with the cations and cause salt solvation. The cation transport is assisted

by segmental motion of the polymer chains. Recognizing the fact that ion conduction takes place in the amorphous phase of polyethylene oxide, considerable research has focused on tailoring a flexible host polymer chemical structure with larger proportion of amorphous phase such as PEO-based block copolymers [8,9], star-branched copolymers [10,11] and cross-linked network polymers [12]. Blending is also an effective method to improve the performance of PEO-based electrolytes. Polymer blend electrolytes based on PEO/Polyvinylidene fluoride [13], PEO/Polyacrylonitrile [14], PEO/Poly(methyl methacrylate) [15] and PEO/Polyurethanes [16] have been reported. But there is obvious phase separation in the PEO-based blend electrolytes because the compatibility of the PEO and others polymer is not good. In most cases, PEO-based electrolytes often have high degrees of crystallization and offer very low ionic conductivity at room temperature, limiting their potential for practical applications. The ionic conductivity of PEO-based polymer electrolytes can reach to the appreciable level (10^{-4} – $10^{-3} \text{ S cm}^{-1}$) to meet the requirement of battery application, when the operation temperature is higher than the melting point of the PEO (ca. 65 °C) [2,17]. Research efforts of these PEO-based electrolytes mainly focus on aliphatic polymers. There have been few attempts to prepare the solid polymer electrolytes from modified aromatic polymers. However, the mechanical properties and thermal stability of aliphatic polymers are poor above this temperature and they cannot be used as electrolytes without additional separator or reinforcing additives [18]. When the third component, such as solid non-ionic plastic crystal material [19,20] or inorganic fillers

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of silica, titanium, zeolites, aluminum oxides and others [21–24], was introduced into the PEO-based electrolytes to form the composite polymer electrolytes (CPEs), all of the above performances could be, more or less, improved. Therefore, development of amorphous PEO-based solid polymer electrolytes capable of combining high ionic conductivity with good mechanical property is the main goal of present research [25,26].

Succinonitrile (SN) is a typical molecule plastic crystal material and shows a phase transition at around $-40\text{ }^{\circ}\text{C}$, above which the material has a plastic-crystalline phase up to its melting temperature (approximately $60\text{ }^{\circ}\text{C}$) [19]. The SN has been employed as a solid solvent to dissolve lithium salts and SN-based plastic crystal electrolytes offer a high ionic conductivity of more than 10^{-4} S cm^{-1} at room temperature [19,27,28]. However, the SN-based plastic crystal electrolytes are excessively soft and susceptible to deform under low stress. Several attempts to improve the mechanical strength of SN-based plastic crystal electrolytes have been reported, which include the development of SN-based plastic crystal composite electrolytes (PCCEs) that exploit a polymer matrix as a mechanical reinforcing framework [20,29,30]. In PCCEs, there is a balance between their mechanical properties and electrochemical performance, which strongly depends on the composition ratio of the polymer matrix/SN. Although a high concentration of SN in the PCCEs is advantageous in delivering high ionic conductivity, deterioration of mechanical property is difficult to avoid.

On the other hand, aromatic polysulfone (PSF) is one of the most common thermoplastic polymeric materials widely used in the manufacture of synthetic polymer membranes because of its outstanding thermal stability, good film forming ability, toughness and superior mechanical properties. This amorphous polymer has been utilized as a membrane material in such applications as gas separation [31], ultra-filtration [32], ion-exchange membranes [33], polymer electrolyte membrane fuel cell [34] and so on. There have been several attempts to prepare the solid polymer electrolytes from modified polysulfone [35,36].

In the present study, we synthesized a series of amorphous PSF-PEO segmented copolymers via a simple random copolymerization. These copolymers consisting of two chemically dissimilar polymer segments: aromatic polysulfone segment ensures excellent mechanical strength and high thermal stability, while the low molecular weight PEO segment exhibits high flexibility, low degree of crystallization. Then, we prepared a new self-standing composite polymer electrolyte membrane consisting of a high content of PSF-PEO matrix and low content SN with lithium bis-trifluoromethanesulphonamide (LiTFSI). It is an effective approach to enhance the conductivity of the solid polymer electrolyte and maintain its excellent mechanical properties at the same time. The mechanical and electrochemical properties of the PSF-PEO composite polymer electrolytes, such as stress-strain, ionic conductivity, and interfacial stability, are investigated. Finally, a Li/LiFePO₄ cell using the optimized polymer electrolyte was assembled and tested.

2. Experimental

2.1. Materials

4,4'-Dichlorodiphenyl sulfone (DCDPS) was purchased from Aldrich and purified by recrystallization from ethanol before use. Poly(ethylene glycol) (PEG) oligomer with the number-averaged molecular weight of 1500 Da was purchased from Acros. 4,4'-Dihydroxybiphenyl (DHBP) was purchased from TCI. Other materials were obtained from Sino harm Chemical Reagent Company. N, N-dimethylacetamide (DMAc) was distilled under reduced pressure and dried over molecular sieve 4 Å. Anhydrous potassium carbonate was further dried at $160\text{ }^{\circ}\text{C}$ for 10 h in vacuum before use. Poly(ethylene oxide) was purchased from Aldrich (average molecular weight of 6×10^5). Succinonitrile (SN, Aldrich) was sublimated twice to remove impurities. Lithium bis-trifluoromethanesulphonamide (LiTFSI, purity: 99%, Aladdin) was heated at $100\text{ }^{\circ}\text{C}$ under vacuum prior to electrolyte preparation. Other materials, such as PEG and DHBP, were used as received. The LiFePO₄ cathode material with 2 wt.% carbon was from Phostech Lithium Company. Its particle size was ca. 200 nm.

2.2. Synthesis of PSF-PEO copolymers

The PSF-PEO copolymers with different content of PEO were synthesized according to a previously reported method [37]. The schematic of PSF-PEO synthesis procedure is illustrated in Fig. 1. In a typical reaction, 1.8201 g (6.338 mmol) DCDPS, 1.5639 g (1.000 mmol) chlorine-end-capped poly(ethylene oxide) (PEO-Cl₂), 1.3664 g (7.338 mmol) DHBP, 1.2 g (8.870 mmol) K₂CO₃, 10 ml DMAc and 8 ml toluene were added to a 100 ml dry three-neck flask equipped with a magnetic stirrer, an argon inlet, and a Dean-Stark trap with a condenser. The reaction mixture was magnetically stirred and heated to reflux, and toluene and water were evaporated and collected in the Dean-Stark trap. When water was completely evaporated from the flask, the reaction temperature rose to $160\text{ }^{\circ}\text{C}$ and the reaction was kept at this temperature for 20 h. After cooling to room temperature, the resulting highly viscous-solution mixture was poured into water and the white fiber-like precipitate was collected by filtration, thoroughly washed with deionized water and dried in vacuum.

2.3. Preparation of composite polymer electrolyte membrane

The composite polymer electrolytes were prepared via the traditional solution casting technique. The PSF-PEO polymer used was 0.4 g. The molar ratio of PEO: LiTFSI was 8:1 and the exact weight ratio of PSF-PEO: SN: LiTFSI was 50:35:15. Predetermined amounts of PSF-PEO, LiTFSI and SN were dissolved into tetrahydrofuran, and then were stirred at room temperature until the mixture appeared to be homogeneous. The mixture was cast on

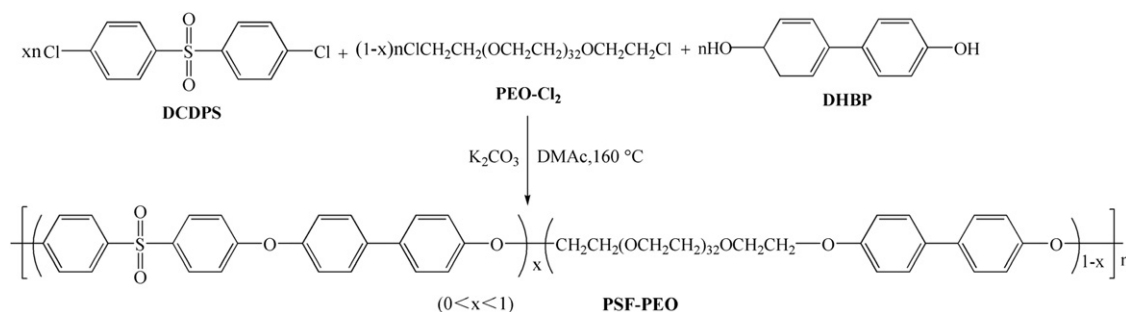


Fig. 1. Schematic synthesis procedure of PSF-PEO segmented polysulfone copolymers.

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