



A new branched copolyether-based polymer electrolyte for lithium batteries

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ABSTRACT

A series of novel branched copolyethers, poly((1,3-dioxolane)-co-((2-(2-methoxyethoxy)methyl)oxirane)) (P(DXL-co-MEMO)) and poly((1,3-dioxolane)-co-((2-(2-(2-methoxyethoxy)ethoxy)methyl)oxirane)) (P(DXL-co-ME₂MO)), were synthesized via cationic polymerization, and the structures of these copolymers were characterized by ¹H NMR and GPC. Ionic conductivities of copolyether/lithium bis(trifluoromethanesulphonyl) imide (LiTFSI), polyethylene oxide (PEO)/LiTFSI and PEO/copolyether/LiTFSI were investigated via electrochemical impedance spectroscopy. The results showed that the ionic conductivity of the P(DXL-co-MEMO)/LiTFSI polymer electrolyte was higher than that of the P(DXL-co-ME₂MO)/LiTFSI polymer electrolyte, and the room temperature ionic conductivity of the P(DXL-co-MEMO)/LiTFSI polymer electrolyte was up to $2.2 \times 10^{-4} \text{ S cm}^{-1}$. Compared with the PEO/LiTFSI polymer electrolyte, the ionic conductivities of the PEO/copolyether/LiTFSI composite polymer electrolytes had a great improvement, but their thermal stabilities did not obviously reduce.

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1. Introduction

Lithium secondary batteries are widely used in communications, transportation, military and household application because of their advantages of long cycle life, high energy density, very low self-discharge rate and low weight. Since the polymer electrolyte based on polyethylene oxide (PEO) was first reported by Wright in 1973 [1,2], PEO-based polymer electrolyte has attracted a great attention due to its good comprehensive performance including high ionic conductivity at high temperature region, good electrochemical stability and good mechanical properties. However, the polymer electrolyte based on linear polyethylene oxide (PEO) has lower ionic conductivity ($10^{-8} \text{ S cm}^{-1}$) at room temperature because the PEO chains are easy to crystallize at room temperature which affects the migration of carriers. Therefore, the practical use of PEO-based polymer electrolyte is seriously impeded [3,4]. How to improve the room temperature ionic conductivity of the polymer electrolyte based on linear PEO has become a focus of contemporary research.

As a result, many methods are used to inhibit the formation of crystalline poly(ethylene oxide), such as copolymerization with other monomer [5–7], star and dendritic structures [8] and cross-linking [9–12], or addition of other polymer, organic plasticizer and inorganic

nano-particles forming composite polymer electrolytes [13,14]. Watanabe [15,16] reported that comb-polymer P(EO/MEEGE) and cross-linking comb-polymer P(EO/MEEGE/AGE) were used as solid polymer electrolytes. Because introduction of short ether side chain decreased the crystallization and promoted the segmental mobility, the room temperature ionic conductivities of these polymer electrolytes were higher than that of the linear PEO-based polymer electrolyte.

An ideal polymer electrolyte not only should contain a large fraction of oxygen to promote salt dissociation, but also has a low glass transition temperature to increase segment mobility and ion transport [17] because poly(1,3-dioxolane) not only have a large fraction of oxygen relative to polyoxyethylene, but also does not crystallize even when the temperature is as low as -50 °C [18]. In addition, considering that high branched chain is conducive to reducing the glass transition temperature and increasing segment mobility, the copolymer of 1,3-dioxolane with substituted ethylene oxide can be used as a kind of new polymer electrolyte matrix.

In recent years, the composite polymer electrolyte has received increasing attention due to its higher room temperature ionic conductivity, easy preparation and low cost. The composite polymer electrolytes can be made of different polymers and lithium salt. Because blends of linear PEO and other polymer are beneficial to inhibiting crystallization of linear PEO, some polymers with functional groups and similar structure including poly(methyl methacrylate) (PMMA) [19], poly(vinylidene fluoride) (PVDF) [13,20], poly(acrylonitrile) (PAN) [21,22] and poly(ethylene glycol) (PEG) were chosen to form the PEO-based composite

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polymer electrolytes. Good compatibility between these polymers and PEO matrix can evidently promote ion migration. The new type of branched copolymer synthesized by the copolymerization of 1,3-dioxolane with substituted ethylene oxide should have good compatibility with PEO. Therefore, in this work, new types of branched copolyethers, P(DXL-co-MEMO) and P(DXL-co-ME₂MO), were firstly designed and synthesized via cationic polymerization. The polymer electrolytes including P(DXL-co-MEMO)/LiTFSI, P(DXL-co-ME₂MO)/LiTFSI, PEO/LiTFSI and PEO/P(DXL-co-MEMO)/LiTFSI were prepared, and the relationship between the ionic conductivity and the content of comonomer in the copolymers and the content of lithium salts was investigated.

2. Experimental

2.1. Materials

Epichlorohydrin, 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol and 1,3-dioxolane (Aladdin, China) were used as received; Sodium hydroxide, sodium chloride, hexane and chloroform were purchased from Beijing Chemical Works; Tetrabutylammonium hydrogen sulfate (J&K, China) and boron trifluoride etherate (Alfa Aesar, China) were used without further purification; Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, 99%, Aladdin, China) was dried under vacuum at 80 °C for 24 h before use.

2.2. Synthesis of copolymer

2.2.1. Synthesis of MEMO and ME₂MO

Tetrabutylammonium hydrogen sulfate (0.02 mol), epichlorohydrin (0.9 mol) and aqueous sodium hydroxide (36 g, 50 wt.%) were added to 250 ml single-necked flask and stirred in ice-water bath. Then, 2-methoxyethanol (0.3 mol) or 2-(2-methoxyethoxy)ethanol (0.3 mol) was slowly added to the reaction solution. The reaction mixture was stirred for 3 h at room temperature. After the reaction completed, the product was extracted with chloroform, and washed to neutral with saturated salty water. The organic fraction was dried over anhydrous sodium sulfate for 24 h and then filtered, and the solvent of filtrate was evaporated under reduced pressure to obtain product. Before polymerization, the product needed to be dried again with calcium hydride [23–26].

2.2.2. Synthesis of P(DXL-co-MEMO) and P(DXL-co-ME₂MO)

In a typical experiment, 5 ml DXL and 2.5 ml MEMO or 2.5 ml ME₂MO were added to 50 ml three-necked flask, and the flask was degassed by three freeze–pump–thaw cycle. Then, the flask was placed in a preheated oil bath at 70 °C, and 1.5 mol% BF₃·OEt₂ was injected in 30 s by a micro-injector. After reaction for 4 h, the product was washed with hexane and dried in a vacuum oven to obtain the viscous liquid copolymer.

2.3. Preparation of polymer electrolytes

First, an appropriate amount of P(DXL-co-MEMO) or P(DXL-co-ME₂MO) and LiTFSI were added to acetonitrile, and strongly stirred with high speed to form a homogeneous solution. Then, the solution was poured into a Teflon mold and volatilized at room temperature. Finally, the polymer electrolytes were dried in a vacuum oven for 24 h at 60 °C. The obtained polymer electrolytes were viscous liquid.

The above procedure was used to obtain PEO/LiTFSI and PEO/P(DXL-co-MEMO)/LiTFSI solid polymer electrolyte.

2.4. Characterization

¹H NMR spectra were determined on a Bruker Avance 400 spectrometer at room temperature with deuteriochloroform (CDCl₃) as solvent and tetramethylsilane as internal standard. Gel permeation

chromatography (GPC) measurements were performed using PL-GPC50 equipped with differential refractometer at room temperature with THF as eluent at a flow rate of 1.0 ml min⁻¹.

Differential scanning calorimetry (DSC) measurements were performed on Q2000 instrument under nitrogen atmosphere. The heating rate was 10 °C min⁻¹ ranging from -90 °C to 150 °C. The data were collected on the second heating cycle.

X-ray diffraction (XRD) measurements were measured on a Shimadzu-6000 X-ray diffractometer with CuKα radiation in the 2θ range of 5–70° at a scanning rate of 5° min⁻¹.

Impedance spectroscopy used a Solartron SI 1287 electrochemical interface and a Solartron 1255B frequency response analyzer, AC amplitude of 10 mV, and a frequency range of 1 Hz–1000 kHz. The ionic conductivity of the polymer electrolyte was calculated from the following equation:

$$\sigma = L/AR_b$$

Here, L is the distance between the two electrodes, A is the area of the polymer electrolyte contacted with the stainless steel electrodes, and R_b is the bulk resistance.

3. Results and discussion

3.1. Synthesis of copolyether

As we know, the linear poly(ethylene oxide) was easy to crystallize at room temperature. Therefore, two substituent ethylene oxides containing ethylene oxide units were designed and synthesized by the reaction of epichlorohydrin with 2-methoxyethanol or 2-(2-methoxyethoxy)ethanol. The copolymers P(DXL-co-MEMO) and P(DXL-co-ME₂MO) used for the polymer electrolyte were prepared by cationic polymerization of 1,3-dioxolane and the above obtained substituent ethylene oxide. Because impurity had a great influence on cationic polymerization, the purity of monomer must be sufficiently high, and monomer must be re-dried before use. The synthetic route of two new copolymers was shown in Scheme 1.

Tables 1 and 2 summarized the experimental conditions and results of the prepared copolymers. As can be seen from Tables 1 and 2, the molecular weight distributions of the prepared copolymers were narrow. With the increase of the contents of comonomer MEMO or ME₂MO in the feed, the contents of comonomer in the copolymer increased, but the molecular weight and molecular weight distribution of the copolymers decreased. It might be because the comonomer ME₂MO or MEMO with large substituent group existed as a large steric hindrance during the copolymerization of 1,3-dioxolane and the comonomer ME₂MO or MEMO. With the increase of the content of the comonomer, copolymerization ability of 1,3-dioxolane and the comonomer decreased, which could lead to a lower degree of polymerization.

3.2. The analysis of ¹H NMR spectra

The ¹H NMR assignments of MEMO or ME₂MO (Fig. 1a) were as follows: the peaks at 2.4 ppm, 2.6 ppm and 3.0 ppm were the characteristic absorption peaks of the protons of the epoxide ring. The peak at 3.3 ppm belonged to the characteristic absorption peak of the protons of OCH₃. The integrated area ratio of the 3.0 ppm and 3.3 ppm bands (A_{3.3}/A_{3.0} = 3) indicated clearly the preparation of MEMO or ME₂MO. The ¹H NMR spectrum of P(DXL-co-MEMO) or P(DXL-co-ME₂MO) was presented in Fig. 1b, the peak occurred at 3.4 ppm corresponding to the characteristic peak of the branched terminal methyl, and the peak at 4.7 ppm was assigned to the characteristic absorption peak of the protons of O–CH₂–O. The copolymer composition could be calculated from Fig. 1b (n_{comonomer}/n_{DXL} = A_{3.4}/A_{4.7}).

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