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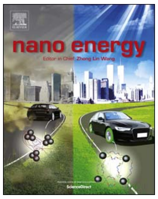

Full paper

Amorphous modified silyl-terminated 3D polymer electrolyte for high-performance lithium metal battery

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ABSTRACT

Polymer electrolyte has been considered to eliminate the safety issue that caused by the lithium dendrite growth in the liquid electrolyte for the high-energy lithium metal battery. However, the practical applications of polymer electrolyte are still impeded by the low Li ionic conductivity, weak interfacial compatibility, low thermal stability and narrow electrochemical window. In this study, we have proposed a novel modified silyl-terminated polyether based polymer electrolyte by a cross-linking fabrication method. With a three-dimensional network structure, the amorphous polymer electrolyte has high ionic conductivity (~ 0.36 mS cm^{-1}) at room temperature, much higher thermal stability (T_m = 379 °C), high lithium ion transference number (~ 0.65), stable electrochemical window up to 5.0 V (*vs.* Li^+/Li) and an excellent compatibility to the electrode. With $LiFePO_4$ cathode and this polymer electrolyte, the lithium metal battery delivers the high specific capacity of ~ 130 mA h g^{-1} at 1 C rate over 300 cycles, and ~ 105 mA h g^{-1} at 3 C rate with a superb cycling stability over 600 cycles at room temperature. We believe that this polymer electrolyte is a promising candidate for the practical applications and brings a new way to develop the high performance electrolyte for the lithium metal battery.

1. Introduction

With the high theoretical specific capacity of metallic Li anode (3860 mA h g^{-1}), the rechargeable Li-metal batteries (LMBs) have re-ignited the researchers' passions in recent years to meet the demands of high energy density and long lifetime of electric devices [1–10]. Nevertheless, there are still many obstacles for the further development of LMBs using liquid electrolyte, especially the safety issue that caused by the Li dendrite growth [7–14]. In order to improve the security and cycling stability of LMBs, the polymer electrolyte (PE) and inorganic solid electrolyte (ISE) have been developed to avoid the leakage and flammability of the liquid electrolyte [15–41]. Different from the ISE with the high sensitivity to moisture/oxygen and the rigid interfacial contacts with the electrodes, the PE has good flexibility and strong adhesion to the electrodes, and been considered as the promising candidate for the high performances LMBs [21–28]. Among the various PE, the poly (ethylene oxide) (PEO) as the earliest system, has been explored extensively because of several advantages [42–51]. However, with the high crystallinity of PEO, the lithium ions (Li^+) migration has been restrained seriously, which causes the low ionic conductivity at room temperature [44–46]. Furthermore, PEO-PE is still suffered from narrow electrochemical window and weak interfacial compatibility to the electrodes, which extremely hinder their further applications in LMBs. Even worse, there were almost involving a lot of volatile organic solvent that may make a chemical waste and cause environmental problems for fabricating the PEO-PE when the solid powders as the reactive precursor [43–49]. Although plenty of modifications have been exploited for reducing or eliminating the crystallinity of PEO chains, it still cannot meet the requirements of high flexibility, high thermal stability, high ionic conductivity, and wide electrochemical window for the LMBs.

It has been reported that the polysiloxane (PSI)-PE has high ionic conductivity, low glass transition temperature (T_g) and high flexibility because of the amorphous structure caused by the -[Si-O-] segments, which offer sufficient Li^+ diffusion pathway [52–54]. However, most of the PSI-PE are liquids/gels at room temperature, which are not easy to be operated for the battery assembling. Inspired by the PEO- and PSI-PE, herein, we demonstrated a novel modified silyl-terminated polyether (MSTP)-PE with cross-linked network, which has been prepared *via* the facile polymerization from the MSTP monomer with lithium bis (trifluoromethanesulfonyl)imide (LiTFSI) as the Li salt and the tetraethylene glycol dimethyl ether (TEGDME) as the plasticizing agent.

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Unlike solid material as the precursor, the MSTP monomer is liquid that no need to be dissolved in the organic solvent. Moreover, the backbone of monomer has the silyl with [-Si-O-] on both terminals. Accordingly, the MSTP-PE can be obtained by the polymerization of terminal silyl without any change of the backbone chains, and has [-Si-O-] as the cross-linking parts that similar to the PSI, which facilitates the fast Li^+ migrations [53]. Therefore, the amorphous structure of the MSTP-PE (arises from the polymerization of silyl) and the additive of the plasticizing agent have improved its ionic conductivity and the interfacial compatibility (the flexibility of the PE) to the electrodes, which are beneficial for improving the electrochemical performances of LMBs. Furthermore, there was no chemical release of organic solvent, UV-photo polymerization or hot pressing during the fabrication process, which can be defined as "Green Synthesis" for the PE. As a result, this amorphous MSTP-PE has a high ionic conductivity (~ 0.36 mS cm^{-1}) at room temperature, much higher thermal stability (T_m = 379 °C), high lithium ion transference number (~ 0.65), stable electrochemical window up to 5.0 V (*vs.* Li^+/Li) and a good adhesion to the electrode. In addition, the polymer LMB with a $LiFePO_4$ cathode can deliver the high specific capacity of ~ 130 mA h g^{-1} at 1 C rate over 300 cycles, and a specific capacity of ~ 105 mA h g^{-1} at 3 C rate with excellent cycling stability over 600 cycles at room temperature. Therefore, the MSTP-PE reported in this study is a promising candidate for the practical applications in high performances polymer LMBs.

2. Experimental section

2.1. Fabrication of polymer electrolyte

The modified silyl-terminated polyether (MSTP) monomer used in this work was purchased from Aldrich. The lithium bis(trifluoromethane sulfonyl imide) (LiTFSI, 99%) and the tetraethylene glycol dimethyl ether (TEGDME, 99%) were supplied by Macklin Company. The di-*n*-butyltin bis(2,4-pentanedionate) as the catalyst was obtained from Aldrich.

MSTP-PE was fabricated by a solution-casting method. Typically, MSTP (1.5 g), LiTFSI (1 g) and TEGDME (2 mL) were added into the glass bottle in sequence under intense stirring to form a homogeneous solution. Subsequently, the catalyst (5 μL) was added into the solution and stirred for 30 min. Then the homogeneous solution was poured into the Whatman® filter (100% borosilicate glass fiber) on the PTFE plate followed by the polymerization in a vacuum oven at 60 °C for 3 h and then 80 °C for 3 h. Pristine PEO polymer electrolyte (PEO-PE) was fabricated *via* similar method without the filter supporting matrix.

2.2. MSTP-PE characterization

The morphology of the sample was characterized by a field emission scanning electron microscope (SEM, Hitachi S-4800). The thickness of the PE was also tested by the SEM. DSC (Perkin Elmer) was carried out to measure the thermal property of the polymer electrolyte from 25 to 800 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. XRD (Bruker D8 Advance) were recorded in the range of 10–60 °.

2.2.1. Electrochemical evaluation

Ionic conductivity of the solid polymer electrolytes was tested by EIS using an VersaSTAT 3 system at varied temperatures ranging from 0 to 80 °C. The polymer electrolyte membranes were sandwiched between two stainless-steel (SS) plate electrodes and the spectra were recorded in the frequency range of 0.1–10^5 Hz with an AC amplitude of 10 mV. The bulk resistance (R_b) of membrane was determined from the impedance spectrum. The ionic conductivity (σ) was calculated from Eq. (1)

$$\sigma = L/R_b S \tag{1}$$

where R_b is the bulk resistance and *L* and *S* are the thickness and area of the polymer electrolyte, respectively. The electrochemical stability window was investigated by linear sweep voltammetry (LSV) performed on a working electrode of stainless steel, Li metal as the counter and reference electrode of MSTP electrolyte at a scan rate of 1.0 mV s^{-1} between 0 and 6.0 V. The lithium-ion transference number ($t_{Li}{}^+$) was calculated by the chronoamperometry test on the Li/MSTP-PE/Li battery with an applied voltage of 0.01 V and was determined by following equation:

$$t_{Li}^{+} = \frac{I_{ss}}{I_0} \times \frac{V - I_0 R_0}{V - I_{ss} R_{ss}} \tag{2}$$

where I_0 and I_{ss} are the initial and steady-state currents, and R_0 and R_{ss} are the first and last resistances, respectively. The tests were completed by EIS measurements taken before and after the polarization scans over a frequency range of 0.1–10^5 Hz with a 10 mV amplitude in the room temperature.

The mechanical property of the MSTP-PE was investigated by a tensile machine (UTM4304) at a stretching speed of 10 cm min^{-1} for the sample with the width of about 1 cm and length of 8 cm.

2.3. Battery test

The $LiFePO_4$ or $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) cathode was composed of 80 wt% $LiFePO_4$ /NCA, 10 wt% PVDF, and 10 wt% carbon black. Areal density of obtained $LiFePO_4$ (NCA) cathode was 1.2–3.0 mg cm^{-2}. The $LiFePO_4$/MSTP-PE/Li battery was charged and discharged between 2.5 and 4.0 V at varied current densities. The C rates in all of the electrochemical measurements are defined based on 1 C = 170 mA g^{-1}. The battery was assembled in an argon-filled glove box, with oxygen content less than 5 ppm and H_2O content less than 1 ppm. The galvanostatic charge/discharge tests of coin-type battery (CR2032) were conducted on LAND testing system (Wuhan LAND electronics Co., Ltd.) at 25 °C. The battery with the $LiFePO_4$ cathode using 1 M $LiPF_6$-EC/DMC liquid electrolyte was also assembled and tested in the same condition.

3. Results and discussion

3.1. Synthesis of MSTP-PE

MSTP-PE was fabricated by a facile cross-linked casting method. As shown in Fig. 1**a**, for the typical fabrication process, the liquid MSTP monomer, Li salt and a certain amount of plasticizing agent were added into a glass bottle simultaneously, followed by the intense stirring to form a homogeneous solution. Subsequently, the solution was poured into the filter paper on the PTFE plate and then dried for polymerization in a vacuum oven [26]. Fig. 1**a** also shows the schematic diagram of the precursor and the corresponding cross-linked network structure of MSTP-PE after fully polymerization. For the detail, the MSTP monomer has the polyether backbone with the silyl on both terminals (Fig. 1**b**). After polymerization of terminal silyl, the MSTP-PE can be obtained without any change of the backbone chain, in which the [-Si-O-] as the cross-linking part (the red area in Fig. 1**a** and **b**). For comparison, the pristine PEO-PE was also prepared *via* similar method without any modification.

3.2. SEM, XRD and thermal stability analyses of MSTP-PE

The surface and cross-section of as-prepared MSTP-PE have been revealed by the scanning electron microscopy (SEM). From Fig. 2**a**, it can be found that the surface of PE is smooth and homogenous, which is beneficial for the strong adhesion to the electrodes with superb interfacial contact. The cross-section SEM image of MSTP-PE (the inset of Fig. 2**a**) demonstrates that the pores of the fibrous matrix in filter paper were fully filled by the PE, and the thickness of MSTP-PE is ~ 210 μm (Fig. S1). With the favorable mechanical property, the continuous and