



Dendrite-free Li metal deposition in all-solid-state lithium sulfur batteries with polymer-in-salt polysiloxane electrolyte



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ABSTRACT

Replacement of solid polymer electrolyte (SPE) to routine liquid electrolyte is highly desirable for high-energy-density lithium sulfur batteries due to its low volatility, high safety and the ability to suppress shuttle effect. Herein, a polymer-in-salt polysiloxane SPE was fabricated with bi-grafted polysiloxane copolymer, lithium bis(trifluoromethanesulfonyl)imide and poly(vinylidene fluoride), which shows higher ionic conductivity ($7.8 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C). To obtain the satisfactory ionic conductivity and high mechanical property of solid electrolyte simultaneously, cellulose acetate matrix was combined as a rigid substrate to prepare composite polymer electrolyte (CPE) that possesses high ionic conductivity ($4.0 \times 10^{-4} \text{ S cm}^{-1}$), enhanced mechanical strength (6.8 MPa), wide electrochemical stability window (4.7 V vs. Li^+/Li), and high ion transference number (0.52) at ambient temperature. In addition, the CPE effectively inhibits the growth of lithium dendrites and diffusion of polysulfides. The assembled lithium sulfur battery with CPE exhibits good room-temperature cycling performance at 1C, which indicates that such polymer-in-salt polysiloxane based composite electrolyte membranes can be applied to ambient temperature all-solid-state lithium sulfur batteries.

1. Introduction

The sustainable development of electric vehicles and large-scale storage grids has caused a strong demand for advanced high-energy-density storage systems [1]. A lithium sulfur (Li-S) battery possesses high theoretical capacity (1672 mAh g^{-1}) and energy density (2600 Wh kg^{-1}), with additional benefits such as natural abundance, low cost and non-toxicity [2]. Despite the considerable advantages, their practical applications have been limited by low electrical conductivity of sulfur, notorious shuttle effect, along with safety issues due to dissolution of polysulfides into liquid electrolytes and the formation of lithium dendrites [3]. In order to overcome these challenges, replacement of solid polymer electrolyte (SPE) to routine organic liquid electrolyte is highly desirable for all-solid-state Li-S batteries [4]. SPE can not only potentially impede the lithium dendrites growth [5,6] and diffusion of polysulfides between the cathode and anode [7], but also improve the safety and cycling performance of batteries [8]. In recent years, various polymer electrolytes have been explored, such as poly(ethylene oxide) (PEO) [9,10], polyacrylonitrile [11,12], poly(propylene carbonate) [13], polyimide [14], and polysiloxane solid electrolytes [15,16]. Among these polymer systems, polysiloxane electrolyte has been proved to be one of the most promising one for rechargeable batteries [17,18].

Polysiloxane electrolyte possesses superior thermal and electrochemical stabilities, but low ionic conductivities and poor mechanical properties at ambient temperature [19]. The ionic conductivities of polysiloxane electrolytes can be improved by the molecular structure design of polymer matrix. The Si-H bond has high reactivity with C=C double bond, which renders the cyclic propylene carbonate or ethylene oxide chain segment be conveniently linked to the polymer molecules by block copolymerization [20], grafting [21,22], and cross-linking [23] methods. The cyclic carbonate is commonly used as the solvent for liquid electrolytes due to its high dielectric constant, which is beneficial to promote dissociation of the lithium salts, and thus increasing the charge carrier number [21]. The ethylene oxide is considered as an efficient lithium ion conduction function [24,25]. Consequently, the ionic conductivities of polysiloxane electrolytes can be obviously enhanced. Another method proposed to obtain polysiloxane electrolytes with high ionic conductivities involves the use of high content lithium salt (exceeding 50 wt %) in SPE, which have been firstly described as “polymer-in-salt” [26,27]. In the conventional SPE, the content of lithium salt in polymer is relatively low and the polymer is the main component, so the SPE can be named “salt-in-polymer” and shows relatively low ionic conductivities. Conversely, in polymer-in-salt electrolyte systems, the high content lithium salt is helpful to improve

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the ionic conductivity of SPE [28,29]. However, as the ionic conductivity is elevated, the mechanical property of electrolyte is declined instead [30,31]. It is clear that the electrolytes with poor mechanical properties could not effectively suppress the dendrites growth [32,33], especially, the Li-S battery with low voltage that a lithium metal anode is required [34]. In order to obtain excellent ionic conductivity and mechanical property at the same time, composite polymer electrolyte (CPE) prepared with high ionic conductive polymer electrolytes and rigid non-woven fabric is an effective strategy [35,36].

In this paper, we prepared a polymer-in-salt SPE membrane with the polysiloxane (BPSO) electrolyte, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and poly(vinylidene fluoride) (PVDF), which exhibits high ionic conductivities. CPE membranes were fabricated by employing cellulose acetate membranes as the backbones and polymer-in-salt polysiloxane copolymers as the ionic conductive materials. The CPE membranes not only possess satisfactory ionic conductivities and mechanical properties, but also can block the growth of lithium dendrites and dissolution of polysulfides. All-solid-state Li-S batteries fabricated with CPE membranes exhibit good electrochemical performance at ambient temperature.

2. Experimental section

2.1. Materials

3-(Allyloxy)-1,2-propanediol and vinyl tris(2-methoxyethoxy)silane were commercially purchased from Tokyo Chemical Industry. Diethyl carbonate and potassium carbonate were both analytical reagent grade and supplied by Beijing Chemical Agent Co. (China). Polymethylhydrosiloxane (M_w : 1500~1900) and elemental S were Alfa Aesar products. Karstedt catalyst solution was offered by Aladdin. LiTFSI and cellulose acetate (CA, M_w : 50,000) were obtained from Sigma-Aldrich. multi-walled carbon nanotube (MWCNT) was supplied by Shenzhen Nanotech Port Co, Shenzhen, China. All solvents were used as received without further purification.

2.2. Preparation of bi-grafted polysiloxane

The bi-grafted polysiloxane was obtained by two reactions according to a previously reported method [37]. Firstly, the cyclic [(allyloxy)methyl]ethylene ester carbonic acid (CECA) was synthesized by transesterification of 3-(allyloxy)-1,2-propanediol with diethyl carbonate. Potassium carbonate catalyst (21.7 mmol) was added to a mixture of 3-(allyloxy)-1,2-propanediol (18.9 mmol) and diethyl carbonate (64.3 mmol). After continuous stirring for 24 h at 120 °C, the mixture was filtered to discharge the solid phase. Then, the obtained solution was distilled at 155 °C, and the product was collected under 10 mmHg reduced pressure. Secondly, BPSO was prepared by the hydrosilylation reaction of Si-H with C=C under an argon atmosphere. Polymethylhydrosiloxane (Alfa Aesar, M_w : 1500~1900, 4.0 g) was dissolved in anhydrous toluene (10 mL). Vinyl tris(2-methoxyethoxy)silane (6.8 g), CECA (5.0 g), and the Karstedt catalyst solution (0.02 mL) were added to the polymethylhydrosiloxane solution. The mixture was kept at 110 °C for 24 h under stirring and reflux. After the solvent was evaporated at 80 °C under vacuum, the remainder was purified by repeated precipitation in the mixed solvent of cyclohexane and acetone (9:1 v/v) and dried under vacuum. A transparent product BPSO was obtained.

2.3. Solid electrolyte fabrication

The SPE membranes were prepared by the solution-casting technique. Firstly, various stoichiometric mass ratios of BPSO (1.0 g), LiTFSI, PVDF and dimethylformamide (DMF, 5.0 mL) were mixed by stirring for 3 h at ambient temperature. The mixture was poured onto teflon dishes, and then heated under vacuum condition for 24 h at

100 °C to remove DMF. Finally, a solid and thin film with the thickness of ca. 120 μm was obtained. To enhance the mechanical properties of SPE, CA was used as the framework. The rigid CA frameworks were fabricated by the electro-spinning technique. Firstly, the as-spun membranes were prepared by electro-spinning the as-prepared solution (10 wt% CA, 60 wt% dimethylacetamide and 30 wt% acetone) at a high voltage of 20 kV at 25 °C. Secondly, the membranes were infiltrated in the mixed solution of ethanol and lithium hydroxide (1 mol L⁻¹) for 24 h, and washed with ethanol for many times and dried for 12 h at 60 °C. The CPE membranes were obtained by mixing appropriate amounts of BPSO, LiTFSI, PVDF, and DMF at 25 °C for 3 h. The mixture was then casted on CA framework. After evaporation of the DMF solvent, A solid, flexible and self-standing film (~120 μm) was obtained.

2.4. Materials characterizations

Fourier Transform infrared spectroscopy (FTIR) were collected with a thermo Nicolet 6700 instrument operating in a diffuse reflectance model. The ¹H Nuclear Magnetic Resonance (NMR) spectra were recorded in chloroform-d with tetramethylsilane as internal reference using a spectrometer FT NMR Bruker Avance 300II. The mechanical properties of electrolytes were measured on an Inston-3300 electronic universal testing machine (USA) at a stretching speed of 1.66 mm s⁻¹ at 25 °C. The thermal stability was evaluated with a TA 2920 modulated instrument. The samples were heated under N₂ flow at a rate of 10 °C min⁻¹ from 25 to 600 °C. The morphologies and component analyses of samples were examined by scanning electron microscope (SEM, JSM-6330) and energy dispersive x-ray spectroscopy.

2.5. Electrochemical measurements

The ionic conductivities of solid electrolytes were measured with oscillation amplitude of 5 mV over the frequency range from 100 kHz to 0.1 Hz in the temperature range between 15 and 85 °C on a solartron electrochemical station (1260+1287). The linear sweep voltammetry (LSV) was measured in a stainless steel | electrolyte | Li coin cell at a scan rate of 1.0 mV s⁻¹ from 0 to 6 V at 25 °C. The lithium ion transference number (t_+) was evaluated at 25 °C with the method of direct current (DC) polarization/alternating current (AC) impedance in a symmetrical lithium coin cell. The t_+ was calculated by the Eq. (1):

$$t_{Li^+} = \frac{I_s(\Delta V - I_0 R_i^0)}{I_0(\Delta V - I_s R_i^s)} \quad (1)$$

where I_0 and I_s are the initial current and steady current during direct current (DC) polarization process, R_i^0 , R_i^s are the charge-transfer resistances of lithium symmetric cell before and after DC polarization, ΔV is the applied voltage (10 mV). The interface stabilities of the electrolyte membranes against lithium electrode were measured by recording the values of interfacial resistance of lithium symmetric cell for different storage times at 25 °C or by a galvanostatic cycling of a symmetric cell with charging for 1 h and discharging for 1 h at a current density of 0.5 mA cm⁻².

2.6. Battery assembly and measurements

The multi-walled carbon nanotube/sulfur (MWCNT@S) composite materials were fabricated with a typical thermal infusion strategy, as previously reported [38,39]. Elemental S and MWCNTs (80:20 w/w) were mixed by ball milling for 5 h. Afterward, the mixture was sealed in a polytetrafluoroethylene container and treated at 155 °C for 24 h under argon atmosphere. The cathodes were prepared by mixing MWCNT@S, BPSO-30% LiTFSI electrolyte, carbon black, PVDF (5:2:2:1 by weight) were mixed in a mortar. After that, the mixture was dispersed in N-methyl pyrrolidone and thoroughly stirred. The

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