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$Li_7P_3S_{11}$/poly(ethylene oxide) hybrid solid electrolytes with excellent interfacial compatibility for all-solid-state batteries

Xiaoyan Xu[a], Guangmei Hou[a], Xiangkun Nie[a], Qing Ai[a], Yang Liu[b], Jinkui Feng[a], Lin Zhang[a], Pengchao Si[a], Shirui Guo[a], Lijie Ci[a,*]

[a] *SDU& Rice Joint Center for Carbon Nanomaterials, Key Laboratory for Liquid-Solid Structural Evolution & Processing of Materials (Ministry of Education), School of Materials Science and Engineering, Shandong University, Jinan, 250061, China*
[b] *Energy Storage Material & Device Lab, School of Materials Science and Engineering, University of Jinan, China*

HIGHLIGHTS

- A hybrid solid electrolyte of $Li_7P_3S_{11}$/PEO is synthetized via a facile method.
- The $Li_7P_3S_{11}$/PEO hybrid solid electrolyte presents higher ionic conductivity.
- The $Li_7P_3S_{11}$/PEO electrolyte shows better interfacial stability with lithium foil.
- The batteries with $Li_7P_3S_{11}$/PEO exhibit excellent electrochemical performance.

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ABSTRACT

Low ionic conductivity and poor interfacial compatibility between lithium electrodes and $Li_7P_3S_{11}$ sulfide solid electrolytes are the greatest challenges for all-solid state lithium-sulfur batteries. Herein, we introduce a hybrid solid electrolyte with $Li_7P_3S_{11}$ being wrapped with polyethylene oxide-$LiClO_4$ (PEO-$LiClO_4$). As served as conductive bridge between $Li_7P_3S_{11}$ particles, PEO-$LiClO_4$ would provide Li^+ transition paths between $Li_7P_3S_{11}$ particles, thus successfully improve its ionic conductivity. Moreover, the polymer layer of PEO-$LiClO_4$ can isolate lithium metal and $Li_7P_3S_{11}$ solid electrolyte, suppressing the reaction between lithium electrode and $Li_7P_3S_{11}$ electrolyte. Therefore, hybrid solid electrolyte $Li_7P_3S_{11}$-PEO-$LiClO_4$ shows excellent interfacial compatibility with lithium foil. Lithium-sulfur battery with the hybrid electrolyte $Li_7P_3S_{11}$-PEO-$LiClO_4$ exhibits much improved electrochemical performance with better cycling stability and higher Coulombic efficiency.

1. Introduction

All-solid-state batteries have been considered as one of the promising candidates to meet the growing application demands in large scale energy storage devices and electric vehicle with improved safety and higher energy density [1–3]. Solid electrolyte (SE) is the key to the all-solid-state battery, and the sulfide solid electrolyte has captured much attention due to its high ionic conductivity and wide electrochemical window at room temperature [4–8]. The $Li_7P_3S_{11}$ (LPS) glass-ceramic has higher ionic conductivity, and can be prepared by the solution synthesis method, which is facile and easy-control compared with ball milling or melting-quenching methods [9–12]. Therefore, LPS is considered as one of the most promising SE for solid-state batteries in practical application.

Lithium metal is expected to be used in all solid-state battery as the anode to further improve the energy density [13,14]. However, issues of large interfacial resistance between LPS and lithium metal could restrict their widely application in lithium ion battery [15,16]. It was also reported that the glass-ceramic LPS electrolyte could react with lithium metal [17,18], causing an increase of the interfacial resistance, which lead to fast capacity fading and low Coulombic efficiency for all-solid-state Li—S battery. Therefore, a favorable and stable solid – solid interfaces between lithium and LPS is crucial to achieve excellent cycling performances for Li—S battery. To improve the interface stability between lithium and sulfide electrolyte LPS, Li—In alloy was used as the anode in substitution of pure Li for Li—S batteries [19,20]. Xu et al. also reported that the interface reaction could be suppressed by using Li_3PO_4-doped LPS electrolyte [21].

A hybrid electrolyte combining the merits of organic and inorganic electrolytes is another strategy to solve interface problems between Li

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[*] Corresponding author.
E-mail address: lci@sdu.edu.cn (L. Ci).

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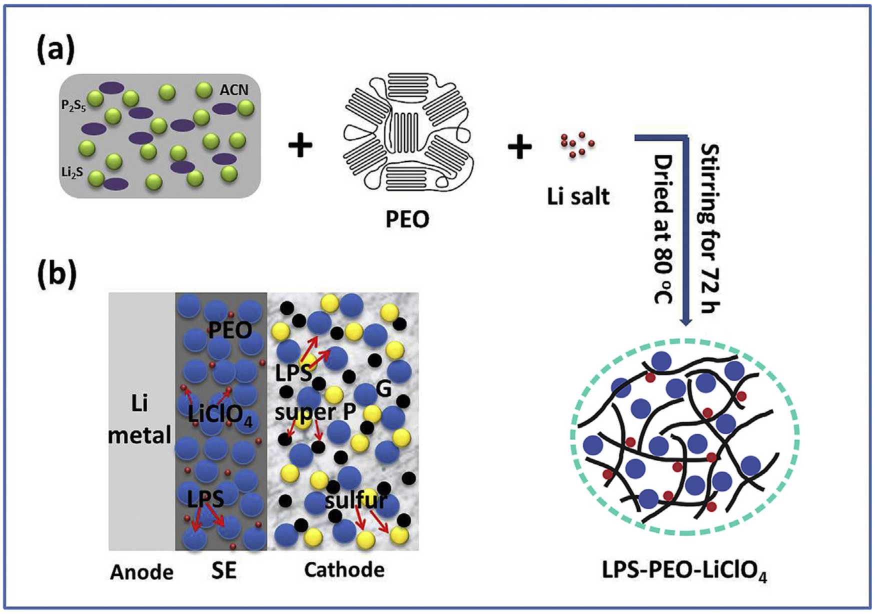

Fig. 1. (a) Schematic of fabrication process of LPS-PEO-$LiClO_4$ hybrid solid electrolyte. (b) Schematic illustration of an all solid-state Li—S battery structure based on LPS-PEO-$LiClO_4$ hybrid solid electrolyte.

metal and LPS solid electrolyte. Recently, PEO based SE has attracted much attention because of its favorable interface compatibility with lithium foil and its great flexibility [22–24]. Here, we introduce a hybrid electrolyte of LPS and PEO-$LiClO_4$. The coating of PEO-$LiClO_4$ on LPS particles improves the ionic conductivity of LPS and the interfacial compatibility with lithium foil. The Li—S battery based on the hybrid electrolyte showed excellent electrochemical performance with improved cycling stability and higher Coulombic efficiency.

2. Experimental

2.1. Materials synthesis

The Li_2S and P_2S_5 (the mole ratio of Li_2S and P_2S_5 is 7:3) was mixed with PEO-$LiClO_4$ (the mole ratio of ether oxygen to lithium ratios is 8:1, $M_{w\ PEO}$ = 100000) with different mass ratio (1%, 2%, 3% and 4%) in acetonitrile solvent under stirring at 50 °C for 72 h. After that, it was dried at 80 °C for overnight. Then the powder was further heat-treated at 250 °C for 1 h and the hybrid electrolytes were obtained. Here, the heat treatment has an important effect on the sulfide solid electrolyte phase, thus influencing its ionic conductivity. After annealed at 250 °C for 1 h, a pure phase $Li_7P_3S_{11}$ was obtained with high ionic conductivity up to 10^{-3} S/cm. A too high annealing temperature would form an impurity phase of $Li_4P_2S_6$ which has a much lower ionic conductivity, while low heat-treatment temperature was difficult to crystallize. All preparation processes were performed in an argon atmosphere with water and oxygen content below 0.1 ppm $Li_7P_3S_{11}$ electrolyte was synthesized with the same method mentioned above in the absence of PEO-$LiClO_4$. It was further used as the electrolyte in cathode layers.

The cathode of all-solid-state LSBs consisted of sulfur powder, LPS solid electrolyte and carbon black. Firstly, the sulfur and graphene (1:1 mass ratio) was ball milling for 2 h using a planetary ball mill apparatus. Then the powder was heated to 155 °C at a rate of 5 °C/min in air and kept for 10 h to get S/G composites. Finally, the cathode composites was obtained after the S/G composites, LPS and super P was mixed in a ratio of 50:40:10 (mass ratio) and was ball milling at 580 rpm for 24 h in Ar ambient at room temperature.

2.2. Material characterization

The crystalline structure of samples was characterized using a Miniflex 600 instrument with copper Ka radiation between 10 and 50°. Microstructure was investigated using a transmission electron microscope (JEOL JEM-2100 F). The mass ratio of sulfur in S/G cathode was measured by thermogravimetric analysis (Mettler-Toledo TGA2) in N_2 ambient from 30 °C to 800 °C at a heating rate of 5 °C/min. Raman spectra were recorded by a Renishaw in Via micro-Raman microscope. The X-ray photoelectron spectroscopy (XPS, ESCALAB 250) analysis was performed with Al Kα as the X-ray source.

2.3. Electrode fabrication and electrochemical measurements

Ionic conductivity of solid electrolytes was measured after they were cold pressed at 300 MPa with 10 mm of diameter. Indium foils were used as the current collectors on both sides of the pellets for EIS tests. S/G/LPS/C composites were used as cathode and the lithium metal as negative electrodes. For assembly of the all solid-state batteries, the composite cathode (~2.0 mg cm^{-2}) and solid electrolytes powders were sequentially put in a 10 mm die and then cold pressed at a pressure of 300 MPa. Then the lithium foil (75 μm) was attached on the other side of the solid electrolyte surface and it was pressed under 120 MPa. The stainless steel disks were used as current collector for cell test.

All electrochemical measurements were carried out by using an Autolab analyzer (PGSTAT302 N). Stainless steel and Li were served as the working and reference/counter electrodes for cyclic voltammogram when it was measured at a scan rate of 1 mV s^{-1} between 5.0 and −0.2 V. The impedances were characterized by AC impedance measurements in the frequency range of 10^6 Hz–1 Hz from 25 °C to 80 °C. The galvanostatic charge/discharge test was carried out on a Land battery testing instrument.

3. Results and discussion

As illustrated in Fig. 1a, the hybrid electrolyte with a different mass ratio of LPS and PEO-$LiClO_4$ was in-situ prepared with a facile and straight forward strategy. Li_2S, P_2S_5, PEO and $LiClO_4$ with appropriate ratio were mixed in acetonitrile (ACN) solvent. After stirring for 72 h,

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