



Enhanced ionic conductivity of sulfide-based solid electrolyte by incorporating lanthanum sulfide

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Abstract

Solid electrolyte is the key point for developing all-solid-state lithium-ion battery with good recyclability and no safety problem. Here, a crystalline phase of lanthanum sulfide (La_2S_3) was incorporated into glassy sulfide-based solid electrolytes ($\text{Li}_2\text{S}-\text{SiS}_2$ or $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$) to form two composite systems $\text{Li}_2\text{S}-\text{SiS}_2-x\text{La}_2\text{S}_3$ and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5-y\text{La}_2\text{S}_3$. The results demonstrated that La_2S_3 has the ability to suppress the crystallization of $\text{Li}_2\text{S}-\text{SiS}_2$ or $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ during the synthetic process. The lithium-ion conductivities of the designed composites can be improved by more than one order of magnitude in comparison with the pristine samples. And both of these two composites have a wide electrochemical window of more than 8 V vs. Li^+/Li .

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1. Introduction

Traditional liquid electrolytes used in lithium-ion battery contain toxic and flammable solvents, which bring serious problems such as leakage, inflammability and narrow operating temperature range. For safety concerns and particular applications, the next-generation lithium-ion batteries have been heading for replacing the traditional liquid electrolytes with solid electrolytes [1]. However, the solid electrolytes have not been widely used because their ionic conductivities are still much lower than those of the liquid electrolytes. To meet the requirements of high performance solid-state batteries, advanced solid electrolytes having similar ionic conductivity with the liquid electrolyte are highly required. Many inorganic solid electrolytes have been investigated among which sulfide-based electrolytes show great promising prospects.

Sulfide-based electrolytes have much higher lithium-ion conductivity than oxide-based electrolytes owing to their higher polarization ability of S^{2-} than O^{2-} . $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ [2–5], $\text{Li}_2\text{S}-\text{SiS}_2$ [6–8] and $\text{Li}_2\text{S}-\text{GeS}_2$ [9–11] are currently the most studied sulfide-based electrolytes. In these systems, P_2S_5 , SiS_2 or GeS_2 serve as network former and Li_2S is network modifier. It is well known that the lithium-ion conductivities of these sulfide electrolytes can be improved by reducing the crystallinity to form poorly-crystallized or amorphous phases. Unfortunately, these systems usually have low-melting points and are easy to form good crystalline phase. So it is very important to develop strategies to stabilize the glassy phase of sulfide-based electrolytes. Although remarkable progress has been made in the preparation of the glassy systems by doping oxides, sulfides, lithium halides or other chemical materials to improve ionic conductivities, an effective strategy still represents a big challenge [6,12–19]. In this paper, we propose a facile route to improve the ionic conductivities of $\text{Li}_2\text{S}-\text{SiS}_2$ and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ systems by incorporating lanthanum sulfide (La_2S_3). The La_2S_3 in the composites can suppress the crystallization of $\text{Li}_2\text{S}-\text{SiS}_2$ or $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$, and the ionic conductivities of these composites can be significantly enhanced.

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2. Experimental details

La_2S_3 , SiS_2 , P_2S_5 and Li_2S were used as the starting materials. All the raw materials were stoichiometrically synthesized in our lab, and the purities were confirmed by X-ray diffraction. For the incorporation of La_2S_3 into $\text{Li}_2\text{S}-\text{SiS}_2$, the molar ratio of Li_2S , SiS_2 and La_2S_3 was controlled as 6: 3: x ($x=0, 0.1, 0.3, 0.5, 0.75$ and 1.0). For the addition of La_2S_3 into $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$, the molar ratio of Li_2S , P_2S_5 and La_2S_3 was controlled as 4: 1: y ($y=0, 0.1, 0.2, 0.3$ and 0.5). The fully mixed precursors were loaded into evacuated and sealed silica tubes. The tubes were placed into the furnace, heated at $750\text{ }^\circ\text{C}$ for 10 h and then quenched in water. The final products were collected and ground into fine powders.

X-ray diffraction (XRD) analysis was carried out with an X-ray diffractometer (Rigaku D/Max 2550V, 40 kV 40 mA) with $\text{CuK}\alpha$ radiation in the 2θ range from 20° to 60° .

For ionic conductivity measurement, powder sample was cold-pressed into a $\phi 10 \times 1$ mm pellet and both sides of the pellet were attached with indium plates as current collectors. Then the measurement was conducted in a dry argon flow by complex impedance on an impedance analyzer (Chenhua 660B) in the frequency range of 0.1 Hz and 0.1 MHz over the temperature range from 30 to $210\text{ }^\circ\text{C}$.

DC polarization measurement was carried out to determine the electronic conductivity. Indium foil was used as blocking electrode and lithium plate as unblocking electrode. Time dependence of the electrical current was measured under a constant voltage 1 V for 1600 s.

Cyclic voltammogram (CV) of the asymmetric Li/sample/Pt cell was performed on Chenhua 660B to evaluate the electrochemical stability of the electrolytes at the scan rate of 10 mV s^{-1} . The Lithium plate and Pt plate in the cell are serve as the reference/counter and working electrodes, respectively.

3. Results and discussion

XRD patterns of $6\text{Li}_2\text{S}-3\text{SiS}_2-x\text{La}_2\text{S}_3$ with various La_2S_3 contents are shown in Fig. 1. It can be seen that Li_4Si_4 was obtained at $x=0$ [8]. With the increasing of La_2S_3 , the peaks indexed to La_2S_3 appear and become stronger gradually. The unchanged phase of La_2S_3 before and after the synthetic process indicates that there is no reaction between La_2S_3 and Li_2S or SiS_2 . Since the melting temperature of Li_4Si_4 is around $750\text{ }^\circ\text{C}$, the quenching process should result in the poor crystallinity of Li_4Si_4 . And it can be observed that the peaks indexed to Li_4Si_4 become relatively weaker with the increasing of x and almost disappeared at $x=1.0$. The poor-crystal Li_4Si_4 transforms into amorphous state step by step, implying that the added La_2S_3 can efficiently suppress the crystallization of Li_4Si_4 during the preparation process.

Usually, the coordination number of La^{3+} is six to nine, while Si^{4+} is 4-coordinated in Li_4Si_4 . Considering other conditions, such as the reaction temperature, reaction time and especially the big difference of atomic radius between La^{3+} and Si^{4+} , the possibility of substitution of Si^{4+} by La^{3+} is very low. So it can be concluded that the final samples can be

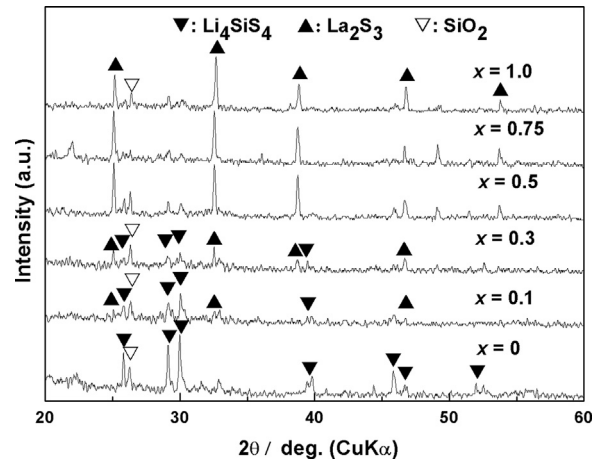


Fig. 1. X-ray diffraction patterns for the samples $3\text{Li}_4\text{Si}_4-x\text{La}_2\text{S}_3$.

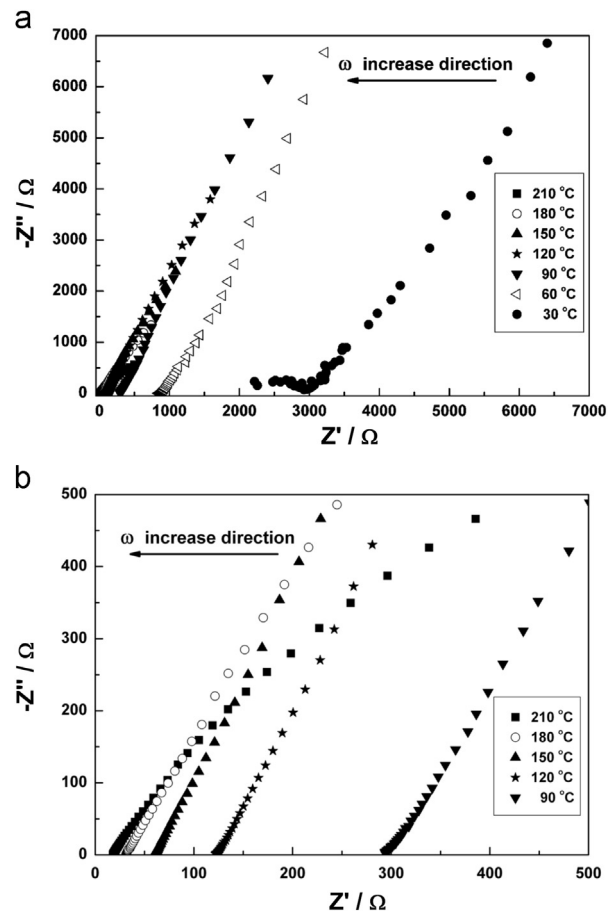


Fig. 2. Complex impedance plots for $3\text{Li}_4\text{Si}_4-x\text{La}_2\text{S}_3$ with $x=0.3$. (a) Complex impedance plots. (b) Enlarged plots from 0 to 500 Ω .

recognized as a kind of composite, poor-crystallized Li_4Si_4 /well-crystallized La_2S_3 ($3\text{Li}_4\text{Si}_4-x\text{La}_2\text{S}_3$).

Ionic conductivities of the obtained samples were examined through the AC impedance spectroscopy. Fig. 2 shows the impedance plots of $3\text{Li}_4\text{Si}_4-x\text{La}_2\text{S}_3$ with $x=0.3$ at various temperatures. A semicircle in the high-frequency range with a spike in the low frequency range was observed at $30\text{ }^\circ\text{C}$. As typical ionic conductor, the semicircle is interpreted as a

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