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Rational coating of $Li_7P_3S_{11}$ solid electrolyte on MoS_2 electrode for all-solid-state lithium ion batteries

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HIGHLIGHTS

- The $MoS_2/Li_7P_3S_{11}$ composite cathode is prepared by a solution method.
- The $Li_7P_3S_{11}$ layer on MoS_2 particles intimates the interfacial contract.
- The high performance is attributed to the interfacial architecture.

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ABSTRACT

Large interfacial resistance between electrode and electrolyte limits the development of high-performance all-solid-state batteries. Herein we report a uniform coating of $Li_7P_3S_{11}$ solid electrolyte on MoS_2 to form a $MoS_2/Li_7P_3S_{11}$ composite electrode for all-solid-state lithium ion batteries. The as-synthesized $Li_7P_3S_{11}$ processes a high ionic of 2.0 mS cm^{-1} at room temperature. Due to homogeneous union and reduced interfacial resistance, the assembled all-solid-state batteries with the $MoS_2/Li_7P_3S_{11}$ composite electrode exhibit higher reversible capacity of 547.1 mAh g^{-1} at 0.1 C and better cycling stability than the counterpart based on untreated MoS_2. Our study provides a new reference for design/fabrication of advanced electrode materials for high-performance all-solid-state batteries.

1. Introduction

Traditional liquid lithium ion batteries (LIBs) suffer from potential safety problems due to their flammable organic liquid electrolytes [1,2]. This greatly limits their applications and promotes the development of safe LIBs. Over the past decades, great efforts have been focused on developing safe all-solid-state (ASS) LIBs, which are considered as good candidates to replace liquid batteries because of their nonflammable solid electrolytes [3]. In addition, ASS LIBs offer many other advantages over liquid batteries such as high energy densities, excellent thermal/chemical stability and wide electrochemical stability widow [4–7]. Moreover, ASS LIBs are envisioned to be used as main power for portable devices, electronic vehicles and state grids owing to their high safety and high energy density.

Solid electrolytes can be divided into three categories: inorganic solid electrolytes, solid polymer electrolyte and composite solid electrolytes [8,9]. Among them, inorganic solid electrolytes are classified into oxide and sulfide electrolytes according to the types of active materials. Particularly, sulfide solid electrolytes have been widely investigated for ASS LIBs as they possess small grain boundary resistance, high lithium ionic conductivity of 1–10 mS cm^{-1} at room temperature and good electrochemical stability [10]. In 2005, Tatsumisago et al. [11] reported a fast lithium ionic conductor $Li_7P_3S_{11}$ with a high conductivity up to 3.2 mS cm^{-1} at room temperature. Inspired by his research, a growing number of works on sulfide solid electrolytes spring up. Recently, Kamaya et al. [12] reported a lithium superionic conductor $Li_{10}GeP_2S_{12}$ with an extremely high ionic conductivity of 12 mS cm^{-1} at room temperature, close to that of conventional liquid electrolytes. Among the explored sulfide electrolytes, $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ shows an exceptionally high conductivity of 25 mS cm^{-1} at room temperature [13]. The lithium ionic conductivity of the solid electrolyte is approaching the demand of ASS LIBs.

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However, due to the point contacts at the interface of ASS LIBs, the number of electrochemical active sites tends to little accompanied by large interface resistance [14]. And the large interface resistance between electrodes and electrolyte lead to the degradation of the battery performance.

To minimize the interfacial resistance between electrodes and electrolyte, a large amount of interfacial processing techniques have been explored and some progresses have been achieved. For example, Tatsumisago et al. [15] developed an interface modification method by depositing gold thin films and the results showed that the gold films decreased the interfacial resistance and improved the chemical stability. Aso et al. [16] reported a highly conductive $80Li_2S-20P_2S_5$ solid electrolyte and its coating on NiS particles to form intimate solid − solid contacts between NiS and solid electrolyte. The ASS batteries with the $80Li_2S-20P_2S_5$ coated composite exhibited better cycle performance than the cell with the uncoated one. In addition, Yao et al. [17] fabricated a general interfacial architecture that $Li_7P_3S_{11}$ electrolyte particles anchored on cobalt sulfide nanosheets by an in-situ liquid-phase approach, which intimated the contact between electrolyte and active materials and improved the electrochemical performance of ASS LIBs. These results indicate that interface modifications are effective in reducing the interfacial resistance and enhancing the performance of ASS LIBs.

MoS_2 has been widely studied as an active material due to its high capacity (670 mAh g^{-1}), good chemical stability, and low toxicity [18–24]. However, the utilization of active MoS_2 materials is limited by the large interfacial resistance between electrode and solid electrolyte. In this present work, we report a $MoS_2/Li_7P_3S_{11}$ composite electrode synthesized by a solution method. The $Li_7P_3S_{11}$ layer is coated on MoS_2 particles to intimate the contact between the electrode and solid electrolyte. An ASS battery with the $MoS_2/Li_7P_3S_{11}$ composite electrode shows better cycling stability and rate performance than the counterpart based on untreated MoS_2. The interface modification of electrode for ASS LIBs is a very effective method for enhancing the efficiency of lithium ion transport, leading to excellent electrochemical properties.

2. Experimental

2.1. Materials synthesis

$Li_7P_3S_{11}$ coated MoS_2 electrode was prepared by a solution method. Li_2S (99.9%, Alfa Aesar), P_2S_5 (99.9%, Alfa Aesar) and MoS_2 (99%, Alfa Aesar) powders were used as the starting materials. Firstly, 5.0 mmol MoS_2 was added in 40 ml acetonitrile (99.8%, Alfa Aesar) solvent and stirred for 2 h at room temperature. To prepare the $Li_7P_3S_{11}$ coated MoS_2 electrode, 1.4 mmol Li_2S and 0.6 mmol P_2S_5 powders were dissolved in the above solution. The solution was stirred for 24 h at room temperature to ensure sufficient reaction and then dried at 80 °C to remove the organic solvent. The obtained powder was further heated at 250 °C for 2 h to enable the crystallization of the $Li_7P_3S_{11}$ glass. Finally, the powder was ground and the $MoS_2/Li_7P_3S_{11}$ composite was obtained. The $Li_7P_3S_{11}$ solid electrolyte is also prepared by the same solution method mentioned above. 11.7 mmol Li_2S and 5.0 mmol P_2S_5 powders were dissolved in 40 mL acetonitrile under stirring at room temperature for 24 h. After that, the solution was dried at 80 °C to evaporate the solvent. The obtained powder was heated at 250 °C in argon atmosphere for 2 h. All the preparation processes performed in a dry glove box (O_2 < 0.1 ppm, H_2O < 0.1 ppm).

The working electrode of solid-state cell was prepared by grinding in an agate mortar under argon atmosphere. It consists of $MoS_2/Li_7P_3S_{11}$ composite, $Li_7P_3S_{11}$ solid electrolyte and acetylene carbon black (AB) with a weight ratio of 30: 60: 10, namely $MoS_2/Li_7P_3S_{11}$ composite electrode (the net weight ratio of MoS_2 in the composite is 24%). For comparison, the $MoS_2-Li_7P_3S_{11}-AB$ composite was also prepared by the same procedure mentioned above except without the $Li_7P_3S_{11}$ coating on MoS_2 particles, namely untreated MoS_2 electrode.

2.2. Materials characterizations

The X-ray diffraction (XRD) patterns of the as-synthesized products were recorded on an X'Pert PRO instrument with copper Kα radiation from 10° to 80°. The morphologies and microstructures of the materials were examined using a Hitachi S-4800 field-emission scanning electron microscope (SEM) and a TecnaiG^2 F20 field emission transmission instrument (TEM). The ionic conductivity of the solid electrolyte was measured by a PARSTAT MC multi-channel electrochemical workstation.

2.3. Electrochemical evaluation

The ionic conductivity of the solid electrolyte was tested through electrochemical impedance spectroscopy (EIS) using a blocking symmetric $In/Li_7P_3S_{11}/In$ cell. The as-synthesized $Li_7P_3S_{11}$ powder was cold-pressed between two indium foils in a die (10 mm in diameter) at a pressure of 380 MPa. The EIS measurements were carried out for the assembled cell at frequencies from 1 MHz to 1 Hz with the amplitude of 10 mV. A non-blocking $Li/Li_7P_3S_{11}/Li$ cell was assembled to further determine the ionic conductivity of the solid electrolyte through a chronoamperometry test.

All-solid-state cells were assembled in a dry argon-filled glovebox by using the $MoS_2/Li_7P_3S_{11}$ composite as the working electrode, $Li_7P_3S_{11}$ as electrolyte and lithium foil as the counter electrode. 80 mg of $Li_7P_3S_{11}$ solid electrolyte was placed in a 10 mm die and cold-pressed at a pressure of 380 MPa. Subsequently, 3–5 mg $MoS_2/Li_7P_3S_{11}$ working electrode was placed on the top of the electrolyte pellet. The formed two-layer pallet was cold-pressed at 380 MPa for 3 min. After that, a lithium foil was placed on the other side of the solid electrolyte as a counter and reference electrode and again cold-pressed at 120 MPa. And two stainless steel disks were attached to the both sides of the cell as current collectors.

Electrochemical performances of the assembled all-solid-state cells were investigated using a LAND battery test system. The galvanostatic charge-discharge tests were carried out in the voltage window of 0.1 V–3.0 V at room temperature. Cyclic voltammetry (CV) measurements were conducted on a CHI 600D electrochemistry workstation from 0.1 to 3.0 V (vs. Li/Li^+) at 0.1 mV s^{-1}. The EIS of the cells was tested on a PARSTAT MC multi-channel electrochemical workstation.

3. Results and discussion

Fig. 1 shows the schematic illustration of the preparation process of $MoS_2/Li_7P_3S_{11}$ composite electrode. First, MoS_2 as the active material was dissolved in the acetonitrile solvent separately. Li_2S (70 mol%) and P_2S_5 (30 mol%) as the raw materials for preparing $Li_7P_3S_{11}$ solid electrolyte layer were then added into the solution and stirred for 24 h. During the mixing process, there are no apparent precipitation could be observed. Then, the solution was dried at 80 °C to remove the organic solvent. The solid electrolyte coating on MoS_2 is amorphous, which needs to be further heat-treated at 250 °C for 2 h to enable the crystallization. The heating process was designed to crystallize the $Li_7P_3S_{11}$ glass for enhancing the ionic conductivity of the solid electrolyte layer. And then the composite of $Li_7P_3S_{11}$ glass-ceramic coated MoS_2 was obtained. The $MoS_2/Li_7P_3S_{11}$ composite, $Li_7P_3S_{11}$ electrolyte and AB were mixed uniformly to as the working electrode, which processes both high ionic and electronic conductivity.

An XRD pattern of the as-synthesized $MoS_2/Li_7P_3S_{11}$ composite is shown in Fig. 2. The main diffraction peaks in the XRD pattern for the composite (2θ = 14.4°, 39.4°, 44.2° and 49.8°) is assigned to the $2H-MoS_2$ phase [25,26]. In addition, it can be demonstrated from the magnified pattern from 10° to 35° that the characteristic peaks of $Li_7P_3S_{11}$ phase (2θ = 18.0°, 19.7°, 21.8°, 23.7° and 25.9°) [27–29] confirm the successful preparation of $MoS_2/Li_7P_3S_{11}$ composite. Because the $Li_7P_3S_{11}$ coating is thin on the MoS_2 particles and the peak