

# Long Cycle Life All-Solid-State Sodium Ion Battery

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**Supporting Information** 

**ABSTRACT:** All-solid-state sodium ion batteries (ASIBs) based on sulfide electrolytes are considered a promising candidate for large-scale energy storage. However, the limited cycle life of ASIBs largely restricts their practical application. Cycling-stable ASIBs can be achieved only if the designed cathode can simultaneously address challenges including insufficient interfacial contact, electrochemical and chemical instability between the electrode and electrolyte, and strain/stress during operation , rather than just addressing one or part of these challenges. Chevrel phase  $Mo_6S_8$  has inherent high electronic conductivity and small volume change during sodiation/desodiation, and is chemically and electrochemically stable with the sulfide electrolyte, and therefore the only challenge of using  $Mo_6S_8$  as the cathode for ASIBs is the insufficient contact between  $Mo_6S_8$  and the solid electrolyte (SE). Herein, a thin layer of SE is coated on  $Mo_6S_8$  using a solution method to achieve an intimate contact between  $Mo_6S_8$  and the SE. Such a SE-coated  $Mo_6S_8$  cathode enabled an ASIB with a high cycling performance (500 cycles), even much better than that of the liquid-



electrolyte batteries with the  $Mo_6S_8$  cathode. This work provides valuable insights for developing long-cycle life ASIBs. **KEYWORDS:** all-solid-state, sodium ion batteries, electrode design, interphase, cycling stability

# INTRODUCTION

Sodium-ion batteries (SIBs) utilizing ubiquitous sodium sources have shown great promise in large-scale energy storage applications for renewable energy and smart grids where low cost is a more important consideration than high energy density. Remarkable progress has been made in developing room temperature SIBs based on organic liquid electrolytes.<sup>1</sup> However, these SIBs suffer from safety problems arising from the volatile and flammable liquid electrolytes. In this regard, replacing the liquid electrolyte with a nonflammable, inorganic solid electrolyte (SE) to prepare all-solid-state sodium ion batteries (ASIBs) is attracting intense research interests.<sup>6-19</sup> Considerable efforts have been devoted to develop high sodium-ion conductive SEs, and the ionic conductivities of some electrolytes have approached or even surpassed 10<sup>-3</sup> S cm<sup>-1,12,16,20-28</sup> Among all these SEs, sulfide-based materials  $(Na_2S-P_2S_5 and other derivatives)$  have attracted the most attention because high ionic conductivity can be achieved by simple cold pressing.<sup>6,29</sup> Despite these achievements, ASIBs using these sulfide electrolytes still suffer poor performance. To our best knowledge, the cycle life of all reported ASIBs using sulfide electrolytes is limited, regardless of the type of electrodes used. The limited cycle life of ASIBs significantly restricts their application in large-scale energy storage systems.

The limited cycle life of ASIBs is strongly related with the degradation of electrodes. However, the exact mechanism for

the capacity decay of electrodes is still under debate. It is generally believed that the cycling performance of ASIBs is mainly limited by the following challenges: (i) limited ionic and electronic conduction of the electrode arising from the insufficient interfacial contact between the SE, carbon, and active material,<sup>30,31</sup> (ii) electrochemical and chemical stability between the electrode and electrolytes, <sup>28,31</sup> and (iii) strain/ stress in the electrode composites generated by the volume change of the active material during charge and discharge.<sup>32,33</sup> However, most of the previous efforts focused on merely one or part of these challenges, limiting the electrochemical performance. Ideally, a high-performance electrode should address all these challenges simultaneously, although the exact approach for different battery systems may be different depending on the properties of the electrolyte and electrodes used.

We demonstrate a long cycle life ASIB based on the sulfide electrolyte utilizing the SE-coated  $Mo_6S_8$  as the model cathode. Chevrel phase  $Mo_6S_8$  was selected as the cathode material because of the following reasons: (1)  $Mo_6S_8$  has fast reaction kinetics for Na<sup>+</sup> intercalation/deintercalation and high electronic conductivity,<sup>34–36</sup> (2) the sodiation/desodiation

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Figure 1. Schematic diagram of a bulk-type ASIB enabled by a SE-coated Mo<sub>6</sub>S<sub>8</sub> cathode.

potential of  $Mo_6S_8$  is ~1.4 V (vs Na/Na<sup>+</sup>) which limits the electrochemical decomposition of the Na<sub>3</sub>PS<sub>4</sub> electrolyte and the electrochemical reaction between  $Mo_6S_8$  and  $Na_3PS_4$ , <sup>19</sup> (3) the Mo<sub>6</sub>S<sub>8</sub> cathode and Na<sub>3</sub>PS<sub>4</sub> electrolyte are chemically stable because they both are sulfides, and (4) the volume change of  $Mo_6S_8$  during intercalation/deintercalation of  $Na^+$  is small. The only challenge of using Mo<sub>6</sub>S<sub>8</sub> as the cathode for the ASIB is the insufficient interfacial contact between Mo<sub>6</sub>S<sub>8</sub> and the SE. In this study, a solution method was used to coat a thin layer of the SE on the surface of Mo<sub>6</sub>S<sub>8</sub> to achieve intimate contact between  $Mo_6S_8$  and the SE, and thus a long cycle life. Figure 1 shows the schematic of such a Na–Sn/Na<sub>3</sub>PS<sub>4</sub>/Mo<sub>6</sub>S<sub>8</sub> ASIB with an improved interface between Mo<sub>6</sub>S<sub>8</sub> and the SE and high conductivities for both electron and Na<sup>+</sup>. The intimate interfacial contact also helps to improve the utilization (capacity) of the  $Mo_6S_8$  active material by increasing the active sites for the charge transfer reaction. The SE-coated Mo<sub>6</sub>S<sub>8</sub> cathode enabled an ASIB to be stably charged/discharged for 500 cycles at 60 °C, representing the best cycling performance for all of the reported ASIBs based on sulfide SEs. The cycling performance of the Mo<sub>6</sub>S<sub>8</sub> cathode in the ASIB is even much better than that in the liquid-electrolyte batteries because of the improved interface between the electrode and electrolyte.

#### EXPERIMENTAL SECTION

Material Synthesis. Chevrel phase Mo<sub>6</sub>S<sub>8</sub> powders were obtained by leaching Cu from the Chevrel phase Cu<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub>.<sup>37</sup> To prepare Cu<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub>, copper sulfide (CuS, Sigma-Aldrich), molybdenum (Mo, Sigma-Aldrich), and molybdenum disulfide (MoS<sub>2</sub>, Sigma-Aldrich) powders with the corresponding stoichiometric ratio were ball milled for 0.5 h, and pressed into pellets under 10<sup>6</sup> Pa. The pellets were then sealed in stainless steel Swagelok to be heated at 900 °C for 24 h under argon. After this, the prepared Cu<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> powders were stirred in 6 M HCl solution with  $O_2$  flow for 12 h to completely remove Cu. The precipitates were then collected, washed with distilled water several times, and then dried at 100 °C overnight under vacuum to obtain Mo<sub>6</sub>S<sub>8</sub>. To prepare the SE-coated Mo<sub>6</sub>S<sub>8</sub> cathode, 0.1425 g of Na<sub>3</sub>PS<sub>4</sub> was dissolved in 3 mL N-methylformamide (NMF),<sup>24</sup> and then 0.19 g of Mo<sub>6</sub>S<sub>8</sub> powders were dispersed into the solution under magnetic stirring for 12 h. All processes were performed in an Ar-filled glovebox. The mixed solution was dried at 150 °C under vacuum in a Schlenk flask, and the collected powders were heated at 270 °C for 1 h under Ar to obtain the SE-coated Mo<sub>6</sub>S<sub>8</sub>. Na<sub>3</sub>PS<sub>4</sub> SE powders were prepared through a mechanical ball-milling process followed by heat treatment.<sup>14,20</sup> Sodium sulfide (Na<sub>2</sub>S, Sigma-Aldrich) and phosphorus pentasulfide ( $P_2S_5$ , Sigma-Aldrich) with a molar ratio of 3:1 were ball milled in a zirconia vial at 510 rpm for 20 h. The ball-milled powders were then annealed in an argon atmosphere at 270 °C for 1 h.

**Material Characterization.** X-ray diffraction (XRD) patterns were obtained using a D8 ADVANCE X-ray diffractometer (Bruker AXS, WI, USA) with Cu K $\alpha$  line as a radiation source. Scanning electron microscopy (SEM) images and transmission electron microscopy (TEM) images were acquired with a Hitachi SU-70 field emission scanning electron microscope and a field emission transmission electron microscope (JEOL2100F).

Electrochemistry. The all-solid-state batteries were fabricated using cubic Na<sub>3</sub>PS<sub>4</sub> as the SE and the Na-Sn-C composite as the counter and reference electrode. The Na-Sn-C composite was obtained based on the previous report.<sup>20</sup> To prepare the cathode composite, the SE-coated Mo<sub>6</sub>S<sub>8</sub> powders were mixed with additional Na<sub>3</sub>PS<sub>4</sub> powders and acetylene black (Soltex, Inc.) by grinding in a mortar. The weight ratio of the Mo<sub>6</sub>S<sub>8</sub>/coated SE and additional  $Na_3PS_4$ /acetylene black is 38:57:5. In order to identify the effect of SE coating on the electrochemical performances, the cathode composite consisting of bare Mo<sub>6</sub>S<sub>8</sub>, Na<sub>3</sub>PS<sub>4</sub>, and acetylene black with the weight ratio of 38:57:5 was also prepared by hand grinding. To assemble allsolid-state batteries, the as-obtained SE-coated Mo<sub>6</sub>S<sub>8</sub> or bare Mo<sub>6</sub>S<sub>8</sub> composite powders (5 mg) were put on one side of the  $Na_3PS_4$ electrolyte (120 mg) in a PTFE tank with a diameter of 10 mm as the cathode, whereas Na-Sn-C powders were put on the other side. The triple layers were then cold pressed together under 360 MPa between two stainless steel rods, which function as current collectors. The cells were tested for galvanostatic discharge-charge cycles and the electrochemical impedance spectroscopy (EIS) test. The galvanostatic discharge-charge cycles were conducted on a battery cycler (LAND CT-2001A, China) within a voltage of 0.9-1.9 V at 60 °C and at room temperature. EIS measurements were conducted using an electrochemistry workstation (Solatron 1287/1260) within a frequency range from 1 MHz to 0.1 Hz, with an ac amplitude of 20 mV. To compare the electrochemical properties of Mo<sub>6</sub>S<sub>8</sub> in liquidelectrolyte sodium batteries, 80 wt %  $Mo_6S_8$  active material, 10 wt % polyvinylidene fluoride binder, and 10 wt % carbon black were dissolved in the N-methyl-2-pyrrolidone solvent to form a slurry, which was coated on an aluminum foil. The mass loading of the active material was about 2 mg cm<sup>-2</sup>. After being dried at 80 °C under vacuum for one day, the coated aluminum foil was cut into discs. The discs were used as the working electrode for the coin cell (2032) with sodium as the counter and reference electrode, glass microfibers from Whatman GF/F as the separator, and 1 M NaClO<sub>4</sub> in a mixture of fluoroethylene carbonate-dimethyl carbonate (1:1 by volume) as the liquid electrolyte. The coin cells were tested for galvanostatic discharge-charge cycles in a voltage range of 1.2-2.2 V at 60 °C and at room temperature.

# RESULTS AND DISCUSSION

The SE-coated Mo<sub>6</sub>S<sub>8</sub> was prepared by mixing Mo<sub>6</sub>S<sub>8</sub> into a Na<sub>3</sub>PS<sub>4</sub> solution with NMF as the solvent, followed by drying at 150 °C under vacuum and annealing at 270 °C for 1 h under Ar. NMF has been used as a solvent to prepare Na<sub>3</sub>PS<sub>4</sub> from a liquid-phase process.<sup>24</sup> Na<sub>3</sub>PS<sub>4</sub> SE (Figure S1) was prepared using the previous reported procedure.<sup>14</sup> Figure 2 shows the XRD patterns of the as-prepared Mo<sub>6</sub>S<sub>8</sub> and SE-coated Mo<sub>6</sub>S<sub>8</sub>. All diffraction peaks of SE-coated Mo<sub>6</sub>S<sub>8</sub> can be attributed to



Figure 2. XRD patterns of as-prepared  $\rm Mo_6S_8$  (a) and SE-coated  $\rm Mo_6S_8$  (b).

 $Mo_6S_8$  and the  $Na_3PS_4$  electrolyte, indicating the  $Na_3PS_4$  SE is chemically stable with  $Mo_6S_8$ .

Figure 3 shows the morphologies of  $Mo_6S_8$  and SE-coated  $Mo_6S_8$ . The bare  $Mo_6S_8$  particles show an irregular shape with



**Figure 3.** SEM images of bare  $Mo_6S_8$  (a) and SE-coated  $Mo_6S_8$  (b). The inset shows the EDS spectra of SE-coated  $Mo_6S_8$ . (c) SEM image and elemental mappings of Mo and Na in SE-coated  $Mo_6S_8$ .

a particle size from 200 to 1  $\mu$ m (Figure 3a). The surface of the sample becomes rough after being coated with the Na<sub>3</sub>PS<sub>4</sub> SE (Figure 3b). The EDS analysis indicates that the SE-coated Mo<sub>6</sub>S<sub>8</sub> mainly consists of Mo, S, Na, P, and a slight amount of O. O present in the electrode could come from the slight amount of Na<sub>3</sub>POS<sub>3</sub><sup>24</sup> formed in the precipitated SE and from the air contamination when the sample is transferred for the SEM test. A homogenous distribution of Na could be observed from the elemental mappings (Figure 3c), suggesting that the Na<sub>3</sub>PS<sub>4</sub> SE was uniformly coated on Mo<sub>6</sub>S<sub>8</sub>. Elemental mappings of P and S are provided in Figure S2. The thickness of the coating layer is estimated to be around 20 nm from the

TEM result (Figure S3). Also, the ionic conductivity of this coating layer was tested to be  $1.1 \times 10^{-5}$  S cm<sup>-1</sup> at 60 °C (Figure S4).

The electrochemical performance of  $Mo_6S_8$  and SE-coated  $Mo_6S_8$  cathodes were evaluated in ASIBs using cubic  $Na_3PS_4$  (Figure S1) as the SE and Na–Sn–carbon composite (Figure S5) as the anode. The usage of the Na–Sn–carbon composite instead of Na metal stems from the better interfacial stability between Na–Sn and  $Na_3PS_4$  SEs.<sup>14,38</sup> The carbon (acetylene black) in the composite acts as a buffer to accommodate the volume change of the anode during cycling.<sup>11,14</sup> The capacity of the Na–Sn–carbon anode is excess. Figure 4 shows the



**Figure 4.** Charge/discharge curves of the  $Mo_6S_8$  (a) and SE-coated  $Mo_6S_8$  (b) cathodes in ASIBs at 5 mA g<sup>-1</sup> at 60 °C. (c) Cycling performance of the  $Mo_6S_8$  and SE-coated  $Mo_6S_8$  cathodes in ASIBs at 5 mA g<sup>-1</sup>. Both cells were tested within a voltage range of 0.9–1.9 V. All of the current densities and capacities were calculated based on the weight of  $Mo_6S_8$  in the electrode composites.

electrochemical performance of Mo<sub>6</sub>S<sub>8</sub> and SE-coated Mo<sub>6</sub>S<sub>8</sub> cathodes at 60 °C. Two plateaus could be observed at ~1.4 and  $\sim 1.3$  V for the discharge process and at  $\sim 1.3$  and  $\sim 1.5$  V for the charge process, suggesting a two-step sodiation/ desodiation of Mo<sub>6</sub>S<sub>8</sub>. The two-step reaction agrees very well with the sodiation/desodiation of  $Mo_6S_8$  in the conventional liquid electrolyte.<sup>32,36</sup> The SE-coated  $Mo_6S_8$  exhibits a smaller voltage hysteresis during charge and discharge and delivers a much higher revisable capacity for the first cycle than those of the bare  $Mo_6S_8$  cathode. Moreover, the SE-coated  $Mo_6S_8$  also exhibits much higher capacity retention than bare Mo<sub>6</sub>S<sub>8</sub>. After 50 cycles, the capacity of the SE-coated  $Mo_6S_8$  cathode is stabilized at 89 mA h  $g^{-1}$ , whereas the capacity for the bare  $Mo_6S_8$  cathode decreases to 54 mA h g<sup>-1</sup>. In addition, we also studied the electrochemical performance of Mo<sub>6</sub>S<sub>8</sub> cathodes after being coated with different amounts of the SE (Figure S6). The results indicate that there is an optimized amount of the coating layer. If the coating layer is too thin, the sufficient interfacial contact cannot be ensured, and if the coating layer is too thick, the electronic conductivity of the cathode composite will be decreased.

Figure 5a,b show the rate behaviors of the  $Mo_6S_8$  and SE-coated  $Mo_6S_8$  electrode in ASIBs at 60 °C. The SE-coated  $Mo_6S_8$  electrode delivers high capacities of 90, 86, 82, 67, and



**Figure 5.** Charge–discharge profiles of the  $Mo_6S_8$  (a) and SE-coated  $Mo_6S_8$  (b) cathodes in ASIBs at various current densities from 5 to 60 mA g<sup>-1</sup> at 60 °C. The cells were discharged and charged for three cycles at each current density, and the second charge–discharge profiles were provided. (c) Rate performance of the  $Mo_6S_8$  and SE-coated  $Mo_6S_8$  cathodes in ASIBs. Both cells were tested within a voltage range of 0.9–1.9 V. (d) Impedance profiles of the ASIBs using  $Mo_6S_8$  and SE-coated  $Mo_6S_8$  as cathodes. The EIS plots were measured at fully discharged states.

61 mA h g<sup>-1</sup> at current densities of 5, 10, 15, 30, and 60 mA g<sup>-1</sup>, whereas the bare Mo<sub>6</sub>S<sub>8</sub> electrode only provides 75, 62, 60, 48, and 33 mA h g<sup>-1</sup> at the same currents of 5, 10, 15, 30, and 60 mA g<sup>-1</sup>. The enhanced rate performance of SE-coated Mo<sub>6</sub>S<sub>8</sub> (Figure 5c) demonstrates that Na<sub>3</sub>PS<sub>4</sub> coating of Mo<sub>6</sub>S<sub>8</sub> improves the reaction kinetics, which is also supported by a much smaller interfacial resistance in the EIS of SE-coated Mo<sub>6</sub>S<sub>8</sub> (Figure 5d). The EIS spectra were fitted with an equivalent circuit shown in Figure S7, and the fitting result indicates that the interfacial resistance between the cathode and electrolyte was reduced from 1125 to 654  $\Omega$  after coating a thin layer of the SE on the cathode surface. Even at room temperature, the SE-coated Mo<sub>6</sub>S<sub>8</sub> electrode also shows much higher cycling stability and better rate performance than bare Mo<sub>6</sub>S<sub>8</sub> (Figure S8 and S9).

Long-term cycling stabilities of  $Mo_6S_8$  and SE-coated  $Mo_6S_8$ were also evaluated in ASIBs at a high current density of 60 mA g<sup>-1</sup> at 60 °C. As shown in Figure 6, the SE-coated  $Mo_6S_8$ exhibits a much better cycling performance than bare  $Mo_6S_8$ . Moreover, the coulombic efficiency of the SE-coated  $Mo_6S_8$ 



Figure 6. Cycling performances and Coulombic efficiencies of the  $Mo_6S_8$  and SE-coated  $Mo_6S_8$  cathodes in ASIBs at 60 mA g<sup>-1</sup> at 60 °C. Both cells were tested within a voltage range of 0.9–1.9 V.

electrode is also higher than that of the bare  $Mo_6S_8$  electrode especially at first few cycles. The capacity of the bare  $Mo_6S_8$ electrode drops to 20 mA h g<sup>-1</sup> after 100 cycles, whereas the capacity of SE-coated  $Mo_6S_8$  still maintains 52 mA h g<sup>-1</sup> after 500 cycles, representing the best cycling performance in all sulfide electrolyte-based ASIBs reported so far. Such a cycling performance of SE coated  $Mo_6S_8$  at 60 °C is even much better than that of  $Mo_6S_8$  in the liquid-electrolyte batteries, as shown in Figures S10 and S11.<sup>35</sup> Even the ionic conductivity of the  $Na_3PS_4$  electrolyte at 60 °C is still lower than that of the liquid electrolyte at 25 °C. The result also demonstrates the great advantage of using inorganic sulfide as the electrolyte to mitigate the capacity loss during long-term charge/discharge cycles.

All aforementioned results indicate that the electrochemical performance of  $Mo_6S_8$  as a cathode in ASIBs can be largely improved by coating a thin layer of SE. Although the energy density of the ASIBs using the SE-coated  $Mo_6S_8$  cathode is still low, the key point of this work is to validate the design principles for a cathode composite for a long-cycle life ASIB, that is a cycling-stable ASIB can be achieved only if the designed cathode could address the insufficient interfacial contact, electrochemical and chemical instability, and strain/stress during operation simultaneously. The design principles could also be applied to other electrode materials with a higher capacity and/or voltage.

# CONCLUSIONS

An ideal cathode composite should be able to simultaneously address the insufficient interfacial contact, electrochemical and chemical instability, and strain/stress during operation, rather than only addressing one or part of these challenges. Because  $Mo_6S_8$  has inherent high electronic conductivity and small volume change during Na<sup>+</sup> intercalation/deintercalation and is electrochemically and chemically stable with the Na<sub>3</sub>PS<sub>4</sub> sulfide

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electrolyte, the only challenge of using  $Mo_6S_8$  as the cathode for ASIBs would be the insufficient contact between solid  $Mo_6S_8$  and the SE. A solution method was used to coat a thin layer of the SE on the surface of  $Mo_6S_8$  to improve the interfacial contact between  $Mo_6S_8$  and the  $Na_3PS_4$  electrolyte. As expected, the SE-coated  $Mo_6S_8$  cathode enabled an ASIB to be stably cycled for 500 times at 60 °C, representing the best cycling performance for ASIBs reported so far. The cycle performance of such an ASIB is even much higher than that of the liquid-electrolyte sodium batteries with the  $Mo_6S_8$  cathode. This paper provides valuable design principles for a highperformance cathode composite with the aim to improve the cycle life of ASIBs.

## ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b12610.

Characterization of  $Na_3PS_{44}$ , elemental mappings of the cathode, impedance profile of  $Pt/Na_3PS_4/Pt$ , XRD pattern of the anode, equivalent circuit for fitting, TEM images, electrochemical properties in all-solid-state batteries at room temperature, electrochemical properties in liquid batteries, Ragone plot (PDF)

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Author Contributions

J.Y. and X.Z. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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