Preparation of \( \text{Li}_{2-3x}\text{Al}_x\text{S} \) for All-Solid-State Li-S Battery

Nguyen Huu Huy Phuc*, Maeda Takaki, Muto Hiroyuki and Matsuda Atsunori*

Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, Toyohashi, Japan

\( \text{Li}_{2-3x}\text{Al}_x\text{S} \) (0 \( \leq \) \( x \) \( \leq \) 0.1667) was prepared via the planetary ball-milling method. Diffuse reflection UV-Vis measurements revealed that the band gap and electronic structure of \( \text{Li}_2\text{S} \) changed with the formation of defective \( \text{Li}_{2-3x}\text{Al}_x\text{S} \). Compared with \( x = 0 \), the ionic conductivity for the sample with \( x = 0.1334 \) improved by \( \sim 3 \) orders of magnitude. The lithium movement activation energy and pre-exponential factor \( A \) were found to be dependent on the \( x \) value. Compared with \( \text{Li}_2\text{S} \), a \( \sim 10 \)-fold improvement in the electronic conductivity was realized with the addition of \( \text{Al}_2\text{S}_3 \). Additionally, the all-solid-state Li-S battery cell performance also displayed an enhancement in both the initial capacity and stability for sample \( x = 0.1667 \) compared with \( x = 0 \). This study highlighted the importance of the intrinsic electronic conductivity of the active materials (but not the electrode) on the performance of the all-solid-state Li-S battery.

Keywords: lithium sulfur battery, Li-S battery, \( \text{Li}_2\text{S} \) conductivity, all-solid-state, mutivalence cation

INTRODUCTION

Lithium-sulfur (Li-S) batteries have attracted significant attention because of their high theoretical energy density (Yang et al., 2013). Research on Li-S batteries has progressed in various directions, including towards understanding the charging-discharging mechanism, irreversible capacity, and cathode composite structure. Many types of electrolytes have been employed in Li-S batteries to date, such as liquid electrolytes, liquid ionic electrolytes, sulfide solid electrolytes, oxide-based solid electrolytes, and polymer electrolytes. The use of either conventional liquid electrolytes or liquid ionic electrolytes has issues related with the formation and dissolution of polysulfides; this results in the loss of active material in the cathode and, thus, a reduced cell capacity or the migration and deposition of polysulfides on the anode, which terminates the cycling process (Li G. et al., 2018). The suppression of polysulfide dissolution and migration could be enabled via various methods, including absorption on large surface area materials, design of the cathode structure, the use of separators, and replacement of the liquid electrolyte with a solid electrolyte (Hayashi et al., 2003; Hayashi et al., 2008; Nishio et al., 2009; Pan et al., 2017; He et al., 2018; Yun et al., 2018).

In general, there are three types of Li-S batteries that employ either sulfur, lithium sulfide, or metal sulfide as the active material (Yao et al., 2016; Li M. et al., 2018). The use of either sulfur or a metal sulfide as the active material provides the benefit of facile cathode composite preparation, due to their stability in the ambient atmosphere; the anode in this case must contain lithium, such as lithium metal or a lithium alloy. However, the use of \( \text{Li}_2\text{S} \) limits the available composite preparation methods because it is unstable in an ambient atmosphere and reacts with moisture to release hydrogen sulfide. Hence, the use of common anode materials, such as graphite and silicon, is desired because they are safer than lithium.

Sulfide solid electrolytes are materials based on \( \text{Li}_2\text{S} \cdot \text{P}_2\text{S}_5 \) and have high ionic conductivities and unique mechanical properties, so have attracted significant research attention in the domain of solid-
state ionic materials (Lau et al., 2018). Li2S-P2S5 glass-ceramic solid electrolytes generally exhibit decent ionic conductivities of $\sim 10^{-2} - 10^{-3}$ Scm$^{-1}$ at room temperature (Tatsumisago and Hayashi, 2012; Seino et al., 2014). The addition of a lithium halide, generally LiI, could further increase the ionic conductivity of the Li1PS4 solid electrolyte from $10^{-4}$ to $10^{-3}$ Scm$^{-1}$ at room temperature (Han et al., 2018; Feng et al., 2019; Spannenberger et al., 2019). Li10GeP2S12 and related materials have been reported to have ionic conductivities of up to $10^{-2}$ Scm$^{-1}$ with an Li+ ion transference number of nearly 1 (Kamaya et al., 2011; Kato et al., 2016). Argyrodite-type solid electrolytes, which are derived from Li1PS6, have also been able to realize ionic conductivities of $10^{-2}$ Scm$^{-1}$ at room temperature (Adeli et al., 2019).

Li2S is partially an electric insulator and has extremely poor ionic conductivity at room temperature. Some controversy exists regarding the ionic conductivity of Li2S. Lin et al. previously reported a value lower than $10^{-13}$ Scm$^{-1}$ at room temperature (value extrapolated from their report) (Lin et al., 2013). Subsequently, Hakari et al. observed an ionic conductivity as high as $10^{-8}$ Scm$^{-1}$ at room temperature for Li2S pretreated via planetary ball milling (Hakari et al., 2017). Lorger et al. published a systematic study on the ionic conductivity of Li2S and concluded that single-crystal Li2S had a conductivity of $\sim 10^{-8}$ Scm$^{-1}$ at room temperature (Lorger et al., 2018). Because of its low intrinsic conductivity, Li2S is usually been blended with both electronic and ionic conductors to prepare electrolyte composites for application in Li-S batteries.

All-solid-state (ASS) Li-S batteries employing sulfidic solid electrolytes (SE) and Li2S have advantages in cathode composite preparation because the sulfidic SE is usually synthesized from Li2S and P2S5. Nano Li2S coated with Li1PS5 was prepared via a reaction between nano Li2S and P2S5 with a molar ratio of 9:1 in tetrahydrofuran (THF) (Lin et al., 2013). In the same manner, Li2S@Li1PS5 was prepared via either planetary ball milling or liquid-phase synthesis for application in the ASS Li-S battery (Jiang et al., 2019; Jiang et al., 2020). Nano composites of Li2S and carbonaceous materials were also generated using various methods for battery application. Typically, Li2S was dissolved in ethanol and the electronic conductor was then immersed into the solution; this was followed by solvent vaporization and subsequent heat treatment (Eom et al., 2017). Li2S embedded in a carbon matrix was also generated in situ via the reaction between CS2 and lithium at a high temperature in an autoclave (Han et al., 2016).

A solid solution of Li2S-Li1X (X = Cl, Br, I) improved the low intrinsic ionic conductivity of Li2S, but the effect on battery performance originated from an increase in redox centers due to $\Gamma^-$ incorporation (Hakari et al., 2017). Recently, Nguyen et al. showed that the conductivity of Li2PS4 was drastically improved at temperatures higher than room temperature via doping with a multivalence cation (Ca$^{2+}$, Mg$^{2+}$) (Phuc et al., 2020a). In this study, Li2-3xAlxS samples were prepared via planetary ball milling for application in an ASS Li-S battery. Argyrodite-type Li5.5PS4.5Cl1.5 was synthesized and employed as the solid electrolyte in the battery performance test. The addition of Al2S3 improved not only the ionic conductivity of Li2S but also Li2S utilization in the ASS Li-S battery.

**EXPERIMENTAL**

Li2S (99.9%, Mitsuwa), P2S5 (99%, Merck), LiCl (99.99%, Wako Fujifilm), and Al2S3 (99.9%, Kojundo Laboratory) were used as received.

Li2-3xAlxS (0 ≤ x ≤ 0.1667) was prepared via planetary ball milling. Li2S and Al2S3 were mixed for 10 min using an agate mortar, and then put into a 45-ml zirconia pot with zirconia balls (10 mm, 15 balls). The pots were rotated at 500 rpm for 12 h using a Pulverisette 7 (Fritschi). The obtained samples were recovered and used without any further heat treatment.

Then, 1 g of Li2S, P2S5, and LiCl with the molar ratio required to form Li5.5PS4.5Cl1.5 was mixed in an agate mortar. The obtained mixture was then ball milled at 600 rpm for 24 h. The as-obtained sample was further heat treated at 440°C for 2 h to obtain the Li5.5PS4.5Cl1.5 argyrodite-type SE with an ionic conductivity of $2.8 \times 10^{-4}$ Scm$^{-1}$ at room temperature.

A composite cathode composed of Li2-3xAlxS, Li5.5PS4.5Cl1.5, and Ketjen Black (KB) with a weight ratio of 50:40:10 was prepared via planetary ball milling. Zirconia balls (160 ball, 4 mm) and a 300-mg of mixture of (100-x) Li2S–xAl2S3 and Li5.5PS4.5Cl1.5 KB were placed into a 45-ml zirconia pot, and the two pots were then rotated at 510 rpm for 10 h. Composites containing Li2-3xAlxS and KB (without Li5.5PS4.5Cl1.5) were also prepared and their cycling performance in an ASS Li-S battery was investigated.

The structure of the prepared Li2-3xAlxS powders was characterized via X-ray diffraction (XRD; Ultima IV, Rigaku), Raman spectroscopy (NRS-3100, Jasco), and diffuse reflection UV-Vis spectroscopy (V-670, Jasco). For analysis, the samples were sealed in special holders in an Ar-filled glove box to avoid exposure to humidity.

The temperature dependence of the ionic conductivity of the prepared samples was investigated using a previously reported procedure (Phuc et al., 2017). The conductivity at room temperature was measured via the direct current polarization method. Prior to the measurements, the samples were pressed into pellets of ~10 mm in diameter at a pressure of 550 MPa at room temperature. The pellets were then placed in a PEEK holder with two stainless steel rods as blocking electrodes. Voltages of 0.2, 0.5, and 1.0 V (DC) were then applied to the prepared cells for 60 min and the current was measured. The experiments were carried out using potentiostat SI 1287 (Solartron). ASS Li-S cells were fabricated with a structure resembling one reported elsewhere (Phuc et al., 2020c). All the experiments were conducted in an Ar-filled glove box (water <0.1 ppm) or an airtight sample holder to avoid the direct exposure of the samples to ambient humidity.

**RESULTS AND DISCUSSION**

Figure 1 shows the structural characteristics of Li2-3xAlxS (0 ≤ x ≤ 0.1667) investigated via powder XRD, Raman spectroscopy, and diffuse reflection UV-Vis spectroscopy. The XRD patterns (Figure 1A) displayed only the peaks of Li2S without any features of the Al2S3 structure. This indicated that either Al2S3...
formed a solid solution with Li$_2$S or that Al$_2$S$_3$ was present in the amorphous form together with the Li$_2$S crystal. The Raman spectrum of Li$_2$S showed one sharp peak located at 372 cm$^{-1}$ (Figure 1B). Al$_2$S$_3$ exhibited many small peaks in the range of 200–300 cm$^{-1}$ with one peak at 240 cm$^{-1}$ that had a slightly higher intensity than the others. The Al$_2$S$_3$ spectrum resembled previously reported results for $\alpha$-Al$_2$S$_3$ (Haeuseler et al., 1981). The sample Li$_{2-3x}$Al$_x$S had nearly no special features in the measured range of 200–1,000 cm$^{-1}$ except for a shoulder between 200 and 400 cm$^{-1}$. The peak for Li$_2$S was absent in the spectra and the peaks for Al$_2$S$_3$ were extremely weak, and hence, hard to detect. It was observed that the Raman peaks of graphene and the carbon nanotube were drastically altered or even disappeared because of the disorder in the local structure, which resulted from defect introduction (Eckmann et al., 2013).

For the UV-Vis absorption measurements, Li$_2$S exhibited one small shoulder centered at 270 nm and a large shoulder in the range of 200–300 nm (Figure 1C). Al$_2$S$_3$ showed a large absorption shoulder ranging from ~400 to 190 nm. The addition of a small amount of Al$_2$S$_3$ into Li$_2$S ($x = 0.034$) led to the formation of Li$_{1.9}$Al$_{0.034}$S and resulted in a drastic change in the electronic structure of the material when compared with its constituent raw materials, Li$_2$S and Al$_2$S$_3$. The adsorption shoulder of Li$_2$S centered at 270 nm and the large adsorption shoulder of Al$_2$S$_3$ disappeared along with the appearance of a new absorption band centered at 355 nm. This special absorption band was also observed in other samples. The absorption feature of Al$_2$S$_3$ was detected in the sample with $x \geq 0.066$, but the shoulder of Li$_2$S located at 270 nm completely disappeared. It should be noted that the milled Li$_2$S showed no absorption in the visible range (400–800 nm), but the absorption shoulder of the Li$_{2-3x}$Al$_x$S ($0 \leq x \leq 0.1667$) samples could be tailored from the UV to the visible spectral range; in particular, the sample $x = 0.1667$ exhibited a drastic adsorption enhancement in the visible range compared with Li$_2$S and the other samples. The diffuse reflection UV-Vis measurements revealed that the band gap and electronic structure of Li$_2$S changed with the formation of Li$_{2-3x}$Al$_x$S, even though the XRD measurements showed no change in the Li$_2$S crystal structure. Thus, it can be concluded that defect-rich Li$_{2-3x}$Al$_x$S was formed by doping of Al$_2$S$_3$ to Li$_2$S via the planetary ball-milling method.

Figure 2 shows the temperature dependence of the ionic conductivity, the ionic conductivity at 50°C, the activation energy, the pre-exponential factor $A$, electronic conductivity, and their I-V correlation as a function of $x$ in the Li$_{2-3x}$Al$_x$S ($0 \leq x \leq 0.1667$) samples. The ionic conductivity of bare Li$_2$S (after planetary ball milling) was $\sim 10^{-10}$ Scm$^{-1}$ at room temperature. This value was extrapolated from the temperature dependence of the ionic conductivity because the resistivity was too large to measure. The value of $10^{-8}$ Scm$^{-1}$ displayed in Figure 2B was
obtained from references (Hakari et al., 2017; Lorger et al., 2018). Compared with $x = 0$, the ionic conductivity drastically improved with the addition of Al$_2$S$_3$. For example, the conductivity at 150 °C increased by three orders of magnitude for sample $x = 0.1334$. The activation energy of bare Li$_2$S was $\sim 86$ kJ mol$^{-1}$ and the addition of a small amount of Al$_2$S$_3$ into Li$_2$S led to a decrease in the activation energy to 44 kJ mol$^{-1}$ ($x = 0.0334$). Further addition of Al$_2$S$_3$ only resulted in a slight improvement to 38 kJ mol$^{-1}$ ($x = 0.1667$). The ionic conductivity at 50°C had the opposite trend as the activation energy. The addition of Al$^{3+}$ into Li$_2$S enhanced the ionic conductivity and reached a peak at $x = 0.1334$. Further Al$^{3+}$ addition resulted in a slight decrease in the ionic conductivity. The pre-exponential factor $A$ was also calculated, as illustrated in Figure 2B. The value had the same trend as the ionic conductivity and reached a maximum value at $x = 0.1334$, and then drastically decreased with the further increase of $x$. These results suggest that the addition of Al$^{3+}$ into Li$_2$S led to an improvement of both the ionic conductivity and the activation energy because of defect formation. The results obtained in this study also differed from those obtained for the ionic conductivity. In a reported theoretical study, density function theory (DFT) was employed to investigate the effect of transition metal (Fe, Cu, Co, Ni) doping on the Li redox properties and electrode potential of Li$_2$S (Luo et al., 2012). It was found that Fe doping could lower the band gap of Li$_2$S because Fe-S (Fe 3d and S 3p orbitals) gap state appeared between the S 3p valence band and the empty Li 2s states. Hence, the electronic structure of Fe doped Li$_2$S was altered from insulating to the conducting regimen. Therefore, improvement in the electronic conductivity of Al$_2$S$_3$-doped Li$_2$S was expected to originate from the electronic structure of the Al-S bonding, which filled the large gap between Li 2s and S 3d in intrinsic Li$_2$S. The electronic conductivity of Li$_{2-3x}$Al$_x$S ($0 \leq x \leq 0.1667$) was independent of the Al content, but the polarization current values varied linearly with the applied voltage and Al content (Figure 2D). These results confirmed that the overlap of the Al-S and Li-S gap states could accommodate electron movement during Li insertion/extraction.

![FIGURE 2](image-url)
FIGURE 3 | Charge-discharge curves of the all-solid-state cells employing Li$_{2-3x}$Al$_x$S ($0 \leq x \leq 0.1667$) cycled at room temperature. (A) $x = 0$ ($\text{Li}_2\text{S}$); (B) $x = 0.667$ ($\text{Al}_2\text{S}_3$); (C) $x = 0.1$; and (D) $x = 0.1667$.

FIGURE 4 | Charge-discharge curves and cycling performance of the prepared all-solid-state cell. (A) charge-discharge curves of $x = 0.1324$; (B) $x = 0.1667$; and (C) cycling performance of $x = 0.1324$ and $0.1667$ over 50 cycles at 30°C.
The charge-discharge curves of the ASA cells employing composite cathodes containing Li_{2-3x}AlxS are shown in Figures 3A–D. The cut off voltage was 3.0–0.1 V vs. Li-In and the prepared Li_{3.5}PS_{4.5}Cl_{1.5} pellet served as a separator. The capacity of the sample with \( x = 0 \) (LiS) was demonstrated to be \( \sim 200 \) mAh g\(^{-1}\) (Figure 3A). The cell containing only AlxS\(_3\) showed nearly no reversible reaction between AlxS\(_3\) and Li\(^+\) and e\(^-\) (Figure 3B). A first charge capacity of 450 and discharge capacity of 1,000 mAh g\(^{-1}\) were obtained with sample \( x = 0.1 \) (Figure 3C). Sample \( x = 0.1667 \) delivered capacities of 600 and 1,000 mAh g\(^{-1}\) in the first charge-discharge cycle (Figure 3D). The discharge capacity of sample \( x = 0.1667 \) was maintained at \( \sim 1,000 \) mAh g\(^{-1}\) over 15 cycles while the capacity of \( x = 0.1 \) rapidly decreased from 1,000 to 600 mAh g\(^{-1}\) over 19 cycles. The addition of MgS into LiS also resulted in improvement of not only the ionic conductivity but also the all-solid-state cell capacity and cycling performance, as reported elsewhere (Phuc et al., 2020b). Discharge curves for the two samples displayed two distinct plateaus at \( \sim 1.5 \) and 0.5 V vs. Li-In. ASS Li-S batteries employing LiS as the active material had only one plateau in the discharge curve, hence the appearance of the second plateau at 0.5 V vs. Li-In (1.1 V vs. Li/Li\(^+\)) should originate from AlxS\(_3\) and the solid electrolyte (Nagao et al., 2015; Hakari et al., 2017; Tan et al., 2019). ASS Li-S batteries that employ a metal sulfide as the active material, e.g., CuS and NiS, exhibited two distinct plateaus in the discharge curves (Hayashi et al., 2003; Hayashi et al., 2008). The capacity of the second plateau in the reported batteries was stable during cell cycling, which indicated a reversible reaction between the metal sulfides and Li\(^+\)-e\(^-\). Argyrodite-type solid electrolytes were also reported to be reduced in this voltage region, which was a reversible reaction (Tan et al., 2019). Therefore, the large capacity of \( \sim 500 \) mAh g\(^{-1}\) observed in the first discharge could be attributed to the reaction of both AlxS\(_3\) and the solid electrolyte. However, the second plateau observed in this study gradually disappeared when the cells were cycled. Thus, the differences in the discharge and charge capacity should originate from a reduction of AlxS\(_3\) in the electrode to form LiS and argyrodite to form Li\(_3\)PS\(_4\)_x, LiCl, LiS, and LiP. The stabilization of the electrode at \( x = 0.1667 \) was considered to be related to the formation of an unknown intermediate generated from AlxS\(_3\); this is because the capacity of the second plateau gradually reduced after the first cycle.

To investigate the effect of Al\(^{3+}\) doping on the cell performance without the contribution of a reaction at 0.5 V vs. Li-In, two cells composed of samples with \( x = 0.1324 \) and 0.1667 were cycled within a cut off voltage range of 3.0–0.6 V vs. Li-In. The results are shown in Figures 4A–C. Both cells exhibited a first charge-discharge capacity of \( \sim 600 \) mAh g\(^{-1}\) (Figures 4A, B). These capacities differed from those observed when the cut off voltage was between 3.0 and 0.1 V. The discharge curves in this experiment also consisted of only one plateau. These results proved that the reduction reaction of AlxS\(_3\) was effectively suppressed by increasing the cut off voltage. The capacity of sample \( x = 0.1324 \) slightly increased from 600 to 700 mAh g\(^{-1}\) in the first 10 cycles, and then reduced to \( \sim 400 \) mAh g\(^{-1}\) after 50 cycles. In contrast, the cell with \( x = 0.1667 \) had its capacity increase from 600 mAh g\(^{-1}\) to more than 800 mAh g\(^{-1}\) in the first 10 cycles. Then, the capacity remained nearly stable and was maintained at a value of \( \sim 800 \) mAh g\(^{-1}\) after 50 cycles (Figure 4C). These cyclic performances suggest that the higher ionic conductivity of \( x = 0.1324 \) compared with \( x = 0.1667 \) had a limited contribution to the cycling performance of the ASS cells. In addition, the electronic conductivity and polarizability on voltage application seemed to be the main reasons for the superior performance of \( x = 0.1667 \) compared with those of \( x = 0 \) and 0.1324.

CONCLUSION

AlxS\(_3\) was successfully incorporated into LiS to form a solid solution of Li_{2-3x}AlxS (0 \( \leq x \) \( \leq 0.1667 \)) via planetary ball milling. It was found that the addition of Al\(^{3+}\) resulted in the formation of defects in the LiS structure, and thus improved the electronic conductivity, ionic conductivity, and activation energy. ASS Li-S cells employing Li_{2-3x}AlxS (0 < \( x \) \( \leq 0.1667 \)) had a higher capacity than those employing bare LiS. The addition of Al\(^{3+}\) (\( x = 0.1667 \)) contributed to not only improving the initial capacity but also capacity retention because of a reduction in the activation energy for the sulfur, lithium ion, and electron combination reaction. The results from this study highlighted the importance of the intrinsic electronic conductivity of the active materials (but not the electrode) on the performance of all-solid-state Li-S batteries.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

MA and MH: supervision of this project, funding acquisition, manuscript revision. NP: experimental design, supervision, manuscript preparation. TM: data acquisition.

FUNDING

This study was supported by the Advanced Low Carbon Technology Specially Promoted Research for Innovative Next Generation Batteries program of the Japan Science and Technology Agency (JST-ALCA-SPRING, Grant No. JPMJAL1301).

ACKNOWLEDGMENTS

We thank Arun Paracattil, PhD, from Edanz Group (https://en-author-services.edanzgroup.com/ac) for editing a draft of this manuscript.
