Synthesis of Sulfide Solid Electrolytes through the Liquid Phase: Optimization of the Preparation Conditions

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ABSTRACT: All-solid-state lithium batteries using inorganic sulfide solid electrolytes have good safety properties and high rate capabilities as expected for a next-generation battery. Presently, conventional preparation methods such as mechanical milling and/or solid-phase synthesis need a long time to provide a small amount of the product, and they have difficulty in supplying a sufficient amount to meet the demand. Hence, liquid-phase synthesis methods have been developed for large-scale synthesis. However, the ionic conductivity of sulfide solid electrolytes prepared via liquid-phase synthesis is typically lower than that prepared via solid-phase synthesis. In this study, we have controlled three factors: (1) shaking time, (2) annealing temperature, and (3) annealing time. The factors influencing lithium ionic conductivity of Li$_3$PS$_4$ prepared via liquid-phase synthesis were quantitatively evaluated using high-energy X-ray diffraction (XRD) measurement coupled with pair distribution function (PDF) analysis. It was revealed from PDF analysis that the amount of Li$_2$S that cannot be detected by Raman spectroscopy or XRD decreased the ionic conductivity. Furthermore, it was revealed that the ionic conductivity of Li$_3$PS$_4$ is dominated by other parameters, such as remaining solvent in the sample and high crystallinity of the sample.

INTRODUCTION

Lithium-ion rechargeable batteries (LIBs) have been expected for application to electric vehicles and to play the role of peak shaving and load shifting in a grid. These power sources and power storage demand to improve energy density, rate characteristics, safety, and lifetime. However, current LIBs using organic liquid electrolytes have a safety issue, and the operating temperature is limited because of combustion hazards. During past decades, all-solid-state batteries using inorganic solid electrolytes have been developed. The inorganic solid electrolytes are nonleaking and non-volatile and have a wide potential window and operating temperature, ensuring safety and durability. Moreover, the lithium-ion transfer number of inorganic solid electrolytes is 1, leading to high-power batteries.

Solid electrolytes are of several types such as oxide and sulfide solid electrolytes; especially, sulfide solid electrolytes show high ionic conductivities. Furthermore, the sulfide solid electrolytes can easily contact the active material via mechanical pressing because of their lower elastic modulus compared to oxide solid electrolytes. Therefore, the commercial viability of the all-solid-state battery using sulfide solid electrolytes is expected as the first popularization stage.

Sulfide solid electrolytes are commonly synthesized by solid-phase methods, classified into the mechanical milling method and the method synthesizing via heating the evacuated quartz ampoule. The mechanical milling method is widely used in the synthesis of Li$_3$S–P$_2$S$_5$ sulfide glasses and glass ceramics and lithium argyrodite Li$_6$PS$_5$X (X = Cl, Br, or I). Lithium superionic conductor-like crystalline compounds including Li$_{10}$GeP$_2$S$_{12}$ have been prepared via heating of the evacuated quartz ampoule. These methods have disadvantages.
from the aspect of economical demand for large-scale synthesis and low energy because they cannot provide a large amount of the product and take a long time.\textsuperscript{16,22,25,30,31} Therefore, developing a novel manufacturing method for large-scale synthesis is desired.

Since Liu et al.\textsuperscript{17} first reported liquid-phase synthesis of sulfide solid electrolytes,\textsuperscript{17} many researchers have attempted to synthesize them via liquid-phase synthesis to solve these current issues.\textsuperscript{17,34--42} Several studies reported that the Li$_3$S–P$_2$S$_5$ solid electrolyte was synthesized via stirring Li$_2$S and P$_2$S$_5$ in polar organic solvents.\textsuperscript{17,34,38--41} In all cases, the ionic conductivity of Li$_3$PS$_4$ prepared via liquid-phase synthesis was lower than that via solid-phase synthesis.\textsuperscript{17,34,38--41} The relatively low ionic conductivity of Li$_3$PS$_4$ in the liquid phase is hypothesized to be due to two factors: the residual unreacted Li$_2$S and/or its relatively high crystallinity.\textsuperscript{39,43,44} Shin et al.\textsuperscript{42} reported that the reason for the low ionic conductivity was the unreacted starting material, Li$_2$S.\textsuperscript{39} However, the unreacted Li$_2$S was not confirmed using X-ray diffraction (XRD) and/or Raman spectroscopy in other studies.\textsuperscript{17,34,38,40--42} Crystallinity is another factor for influencing the lithium ionic conductivity. Other researchers reported that the ionic conductivity decreased with increasing crystallinity.\textsuperscript{15,44} In the case of the liquid-phase synthesis, Li$_3$PS$_4$ is highly crystallized during the annealing process for removing the solvent, resulting in the decrease of the ionic conductivity.\textsuperscript{17,34,38--41}

These factors are influenced by synthesis and annealing conditions, which depend on the solvent properties such as solubility and boiling point. However, their contributions to the ionic conductivity have not been totally clarified because quantitative evaluation of the amount of the raw materials such as Li$_2$S and the degree of crystallinity is difficult by using conventional analytical methods such as Raman spectroscopy and XRD measurements. Pair distribution function (PDF) analysis is a method of structural analysis using total scattering data including not only Bragg but also diffuse scattering which can obtain both periodic and nonperiodic structural information. In addition, PDF analysis can quantitatively evaluate the crystallinity of the materials.\textsuperscript{43,44} Therefore, PDF analysis is expected to be a powerful technique to clarify the reason of the relatively low ionic conductivity of Li$_3$PS$_4$ prepared by liquid-phase synthesis.

In this study, we prepared Li$_3$PS$_4$ electrolytes with various mixing times and annealing conditions via liquid-phase synthesis. High-energy XRD measurement coupled to PDF analysis is performed for the Li$_3$PS$_4$ electrolytes to evaluate quantitatively the amount of the raw material and crystallinity. This study is useful to optimize the liquid-phase synthesis process for sulfide solid electrolytes.

**EXPERIMENTAL SECTION**

**Synthesis Methods of Li$_3$PS$_4$.** Liquid-phase synthesis was used for the preparation of Li$_3$PS$_4$, which was reported by Matsuda et al.\textsuperscript{37} Li$_2$S (Mitsuwa Chemical Co., Ltd.) and P$_2$S$_5$ (Merck & Co., Inc.), at a molar ratio of 3:1, were shaken with a zirconia ball for up to 360 min at 1500 rpm in ethyl propanolate (Sigma-Aldrich Co., LLC). The residual solvent was removed via centrifugation and reduced pressure drying at room temperature. Li$_3$PS$_4$ was synthesized by annealing of the precursor at 80, 100, 120, and 170 °C. In this study, the shaking time varied from 5, 10, 30, 60, 120, 240, to 360 min. In addition, another Li$_3$PS$_4$ was prepared via the mechanical milling method for a reference material. Li$_2$S (Mitsuwa chemical Co., Ltd.), P$_2$S$_5$ (Merck & Co., Inc.), and zirconia balls were added to a zirconia pot and mixed via a planetary ball mill apparatus at 370 rpm for 20 h.

**Raman Spectroscopy, Thermogravimetry, XRD Measurements, and Scanning Electron Microscopy Observation.** Raman spectroscopy was conducted using a MultiRam (Bruker Optics Co., Ltd.) equipped with a Nd-YAG laser (1064 nm) at room temperature. Raman spectra of the precursor were recorded between 3600 and 100 cm$^{-1}$. All samples were sealed in glass vessels in an argon-filled glovebox and measured without air exposure. Thermogravimetry (TG) measurement was performed for the precursor with a shaking time of 360 min. The precursor was loaded on an alumina pan in a glovebox. The alumina pan was transferred into the chamber of the TG instrument, and the chamber was purged with argon gas. The weight loss of the precursor was measured between 25 and 350 °C. XRD measurement was conducted using an X-ray diffractometer (RINIT-Ultima III, Rigaku) with Cu Kα radiation. Samples were sealed in a holder in a glovebox to prevent air exposure. Scanning electron microscopy (SEM) observation was performed using a field emission scanning electron microscope (SU8220, Hitachi High-Technologies) to observe the sample morphology.

**High-Energy XRD Measurement Coupled to PDF Analysis.** High-energy XRD measurements of all samples were carried out at the SPring-8 (Hyogo, Japan) beamline BL08W. The X-ray energy was 115 keV (0.108 Å), and the scattering X-ray was detected using a flat panel detector. The samples were sealed in a 2ϕ quartz capillary to prevent air exposure. Scattering data of each sample were corrected for background, absorption, multiple scattering, and inelastic scattering. The structure factor $S(Q)$ was obtained from the standardization of the corrected scattering data by the number of atoms and the scattering intensity from one atom. Moreover, the reduced PDF, $G(r)$, was calculated by the Fourier transform of $S(Q)$. $G(r)$ is defined by the equation $G(r) = 4\pi r \rho_0 \rho(r)/\rho_0 - 1$, where $r, \rho_0$ and $\rho(r)$ are the real space distances, average atomic number density, and local atomic number density, respectively. Therefore, the information regarding the existing probability to the real distance is obtained using high-energy XRD measurement coupled to PDF analysis.

**Ionic Conductivity.** The ionic conductivity of the solid electrolytes was obtained by alternating current impedance measurements. The measurements were conducted at 25 °C within a frequency range from 1 MHz to 1 Hz with an amplitude of 100 mV using an impedance analyzer (ModuLab XM ECS, Solartron Analytical). Pellets of samples, approximately 0.7 mm in thickness and 10.0 mm in diameter, were prepared via uniaxial pressing of a powdery sample at a pressure of 360 MPa in a cell. The pellets were held by two stainless-steel rods. These operations were conducted in a dry argon gas atmosphere.

**RESULTS AND DISCUSSION**

Raman spectra for the precursors with different shaking times are shown in Figure S1. Li$_3$PS$_4$ of solid-phase synthesis and Li$_2$S as the raw material are listed for comparison. Peaks at 372, 422, and 407 cm$^{-1}$ were observed in the sample after shaking for 5 min. These peaks were attributed to the vibration of the sublattice of Li$_2$S, the P$_2$S$_7^{4–}$ anion, and the P$_2$S$_6^{4–}$ anion, respectively.\textsuperscript{45} The peak intensities of Li$_2$S and the P$_2$S$_7^{4–}$ anion decreased with the increase of the shaking time and...
completely disappeared after 30 min. In contrast, the peak intensity of the PS4⁻ anion increased with the increase of the shaking time.

Figure S2a shows the TG curve for the precursor prepared after a shaking time of 360 min. The TG curve showed a dramatic weight loss from 50 to 130 °C. The dramatic weight loss in our synthesis may be related to ethyl propionate volatilization. Liang et al. reported a similar result using the tetrahydrofuran solvent during liquid-phase synthesis and mentioned that the weight loss was derived from solvent volatilization.¹⁷ According to the TG data, we fixed the annealing temperature at 170 °C for 2 h.

The XRD pattern of the precursor is shown in Figure S2b. The peaks from raw materials were not observed, and the observed Bragg peaks could not be assigned to any known structure. Similar results have been reported.¹⁷,³⁶,³⁷

Figure S3 shows the XRD patterns of the precursor with different shaking times after annealing at 170 °C for 2 h. Strong diffraction peaks of Li2S were observed at 27.0 and 31.3°, and weak diffraction peaks of β-Li3PS4 were also observed at 27.4, 29.1, and 29.8° for a sample prepared by shaking for 5 min. The peak intensity of Li2S decreased with the increase of shaking time and disappeared after 60 min, while the peak intensity for β-Li3PS4 increased with the increase of shaking time. These results indicate β-Li3PS4 formation, which is consistent with the result of Raman spectroscopy. XRD and Raman spectroscopy measurements showed the formation of β-Li3PS4; however, Li2S can be detected within 30 min via Raman measurement and within 60 min via XRD measurement. In the previous report, Li3PS4 formed from the surface of Li2S via the conversion reaction of Li2S and dissolved species.³³ Raman spectroscopy is sensitive to the information of the surface structure, whereas XRD measurement can obtain information of the bulk structure. Therefore, Raman measurement may not detect the peak derived from Li2S after Li3PS4 formation at the surface, which caused the different disappearance times between the XRD and Raman measurements.

Figure 1 shows the ionic conductivities for the sample prepared with different shaking times after annealing at 170 °C for 2 h. The lithium ionic conductivity logarithmically increased with the increase of the shaking time. It was observed that the particle size of the sample was a few micrometers from 5 to 60 min with shaking time and decreased to sub-micrometer from 60 to 360 min with shaking time by SEM (Figure S4). This particle size tendency cannot explain the tendency of the ionic conductivity change with shaking time. Although the XRD result shown in Figure S3 suggests that Li2S disappeared after 60 min shaking time, the lithium ionic conductivity increased above 60 min shaking time. The reason for the low ionic conductivity at the short shaking time is the remaining Li5S3; our XRD results did not seem to agree well with the ionic conductivity result. In addition, the ionic conductivity of the liquid-phase synthesis was lower than that of the mechanical milling preparation. To clarify the reason, XRD measurement is not a sufficiently powerful tool because of the trace amount of the raw material and the low crystallinity of products. We attempted to confirm the reason for the low ionic conductivity using PDF analysis.

Figure S5 shows the results of the PDF analysis for Li3PS4 prepared via liquid-phase synthesis with various shaking times and starting materials. After shaking for 360 min, the sample did not include starting materials and was nearly all Li3PS4. Li3PS4 had peaks at approximately 2.0, 3.3, and 4.1 Å and a broad peak around 7.0 Å corresponding to the P=– bond in the PS4³⁻ tetrahedral anion, S–S correlation in the PS4³⁻ tetrahedral anion, S–S correlation between the PS4³⁻ tetrahedral anions, and P–P correlation between the PS4³⁻ tetrahedral anions, respectively. Li2S had characteristic peaks at approximately 2.5, 4.0, and 7.0 Å, as shown by the brown line in Figure S5. The peaks of Li2S were observed in the samples prepared by shaking from 5 to 10 min. Then, the peak intensity of Li2S decreased with the increase of the shaking time, whereas the peak intensity of Li3PS4 increased. It was reported in a previous study that differential PDF analysis can be used as a method for evaluating the ratio of glassy and crystalline phases.⁴³ We applied this method for estimating the ratio of the unreacted substance Li2S and the product substance Li3PS4. We describe the details of the analytical method in the Supporting Information. The ratio of Li2S to Li3PS4 estimated using the method is shown in Figure 2a. The ratio of Li2S decreased, while the ratio of Li3PS4 increased with the increase of the shaking time.
of the shaking time. Intriguingly, it was shown using this analysis method that Li$_2$S, which was not detected in the Raman spectroscopy and XRD measurements, remained at several percentage points in the samples prepared by shaking up to 120 min. The sample prepared by shaking for 360 min did not have the unreacted material Li$_2$S. The correlation between the volume ratio of Li$_2$S and the ionic conductivity is shown in Figure 2b. The ionic conductivity increased with a decreasing amount of Li$_2$S with the increase of shaking time. However, Li$_3$PS$_4$ prepared via liquid-phase synthesis showed a lower ionic conductivity than that of the mechanical milling method despite not including Li$_2$S. These results clearly indicate that high-energy XRD coupled to PDF analysis is a powerful tool to detect trace amounts of compounds which cannot be detected by XRD.

High-energy XRD coupled to PDF analysis showed that the starting materials were completely removed in the sample obtained with a 360 min shaking time. Therefore, we compared the structure of Li$_3$PS$_4$ prepared by the mechanical milling method and liquid-phase synthesis after annealing. The XRD patterns of Li$_3$PS$_4$ prepared by annealing the precursor synthesized via liquid-phase synthesis and the mechanical milling method are shown in Figure S8. The XRD pattern of Li$_3$PS$_4$ prepared by liquid-phase synthesis was assigned to β-Li$_3$PS$_4$ (Figure S8a). In contrast, the XRD pattern of Li$_3$PS$_4$ prepared by mechanical milling showed broad peaks that were difficult to assign (Figure S8b). Therefore, samples prepared via liquid-phase and solid-phase synthesis were compared using high-energy XRD measurement coupled to PDF analysis, which can analyze both crystalline and amorphous structures to examine the local structure. The results of PDF analysis using the data are shown in Figure 3. Both the samples prepared via mechanical milling and liquid-phase synthesis after annealing showed the characteristic peaks of Li$_3$PS$_4$ at approximately 2, 3.3, and 4.1 Å and a broad peak around 7.0 Å, which were related to the P−S correlation, S−S correlation in the PS$_4^{3-}$ anions, S−S correlation between the PS$_4^{3-}$ anions, and P−P correlation between the PS$_4^{3-}$ anions, respectively. The previous study reported that increasing the peak intensity of the S−S correlation and P−P correlation between the PS$_4^{3-}$ anions was in accordance with increasing crystallinity. These peaks of the sample prepared via liquid-phase synthesis were higher than those via solid-phase synthesis. This result implies that the annealing sample prepared via liquid-phase synthesis had higher crystallinity than the sample prepared by the mechanical milling method. This is the reason for the lower ionic conductivity of the solid electrolyte prepared via liquid-phase synthesis than that of the solid electrolyte prepared by solid-phase synthesis because the ionic conductivity of Li$_3$PS$_4$ decreased with increasing crystallinity.

Therefore, we annealed the precursor not including raw materials, which was confirmed by PDF analysis, at low temperature for the suppression of crystallization and optimized the annealing time. Figure 4 shows the lithium ionic conductivity of samples annealed at 80, 100, and 120 °C for different times under an Ar atmosphere. In the case of the sample annealed at 80 °C, the lithium ionic conductivity increased with the increase of the annealing time and reached a maximum value (0.109 mS cm$^{-1}$) at 12 h. Subsequently, it decreased with the increase of the annealing time. In the case of the sample annealed at 100 °C, the lithium ionic conductivity showed the same tendency as the samples annealed at 80 °C. In addition, it showed a higher ionic conductivity (0.167 mS cm$^{-1}$) than that of 80 °C. The ionic conductivity of the samples annealed at 120 °C decreased with the increase of the annealing time, the tendency of which was different from the others. The lithium ionic conductivity of all samples prepared via liquid-phase synthesis was lower than the ionic conductivity of the mechanical milling method. We focused on the samples annealed at 100 °C and examined the relationship between the structure and the ionic conductivity. The XRD patterns of the samples annealed at 100 °C in each annealing time are shown in Figure S9. The Bragg peaks at 27.4, 29.1, and 29.8° attributed to Li$_3$PS$_4$ (space group: Pnma) were observed from all samples. The Bragg peaks were obtained from all annealing samples, and the peaks increased with annealing time and temperature. It is reported that Li$_3$PS$_4$ with an amorphous structure shows higher lithium ionic conductivity than Li$_3$PS$_4$ with a crystal structure. This result can explain the reason why the lithium ionic conductivity was decreased by annealing over 12 h but cannot explain the reason why the lithium ionic conductivity increased with annealing time and reached a maximum value at 12 h.

Therefore, high-energy XRD measurement coupled to PDF analysis was applied to compare the local structure of each sample for revealing the reason. The result of PDF analysis of samples annealed at 100 °C is shown in Figure S10. The samples prepared via liquid-phase synthesis and the mechanical milling method showed peaks of Li$_3$PS$_4$ around 2.0, 3.3, and 4.1 Å and a broad peak around 7.0 Å. In addition, the peak corresponding to S−S correlation between the PS$_4^{3-}$ tetrahedral anions increased with the increase of annealing.

![Figure 3. Reduced PDFs of Li$_3$PS$_4$ prepared via (a) liquid-phase synthesis after annealing at 170 °C for 2 h (black line) or (b) solid-phase synthesis (red line).](image-url)

![Figure 4. Lithium ionic conductivity of samples prepared by liquid-phase synthesis after annealing at 80 °C (black plots), 100 °C (red plots), and 120 °C (green plots) for each time.](image-url)
time. It is reported that the peak intensity of S–S correlation between PS$_4^{3−}$ units increased with the increase of crystallinity and the crystallinity can be quantitatively evaluated by reproducing the experimental PDF with amorphous Li$_3$PS$_4$ and crystalline Li$_3$PS$_4$ by the following equation.\(^{43}\) We quantitatively evaluated the crystallinity of the samples by using same technique.

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G(r)_{\text{experimental data}} = (1-x)G(r)_{\text{amorphous}} + xG(r)_{\text{crystal}}
\]

where $G(r)_{\text{experimental data}}$, $G(r)_{\text{amorphous}}$, and $G(r)_{\text{crystal}}$ are the reduced PDF of the sample prepared by liquid-phase synthesis after annealing at 100 °C, reduced PDF of Li$_3$PS$_4$ prepared by mechanical milling, reduced PDF of Li$_3$PS$_4$ prepared by mechanical milling after annealing at 270 °C, and crystallinity, respectively. Figure 5a shows the annealing time dependence of the crystallinity. The crystallinity of the samples annealed at 100 °C increased with the increase of the annealing time. These results indicated that the crystallinity of Li$_3$PS$_4$ prepared via liquid-phase synthesis increased as annealing time increased. The correlation between the crystallinity and the ionic conductivity of the samples annealed at 100 °C is shown in Figure 5b. The lithium ionic conductivity decreased as the annealing time increased. Therefore, the lithium ionic conductivity was increased by decreasing intermediate with annealing time between 6 and 12 h. These results showed that the increase of the intermediate and the increase of the crystallinity occurred simultaneously as annealing time increased, indicating that ionic conductivity shows a volcano behavior.

**CONCLUSIONS**

In this study, the factors determining lithium ionic conductivity in Li$_3$PS$_4$ prepared via liquid-phase synthesis were studied. High-energy XRD coupled to PDF analysis can detect trace amounts of the Li$_3$S starting material, which were difficult to detect using Raman spectroscopy and XRD measurements (Figure 7a). It takes a longer sample shaking time than 360 min to completely remove the starting material. In addition, it was shown that the Li$_3$PS$_4$ prepared via liquid-phase synthesis after a long shaking time and annealed at 170 °C had higher crystallinity than that prepared via solid-phase synthesis.

Therefore, we optimized the annealing process in the liquid-phase synthesis of Li$_3$PS$_4$ for the suppression of crystallization. The sample annealed at 100 °C showed the highest ionic conductivity (0.167 mS cm$^{-1}$) at 12 h for the annealing time, whose ionic conductivity was higher than the ionic conductivity of the sample annealed at 170 °C. However, the sample prepared by annealing at 100 °C shows lower ionic conductivity than that prepared by the mechanical milling method. The high-energy XRD measurement coupled to PDF analysis indicates that the residual amount of the intermediate...
in the sample decreased with the increase of the annealing time, while the crystallinity of Li₃PS₄ increased. This trade-off relationship between the crystallinity and the residual amount of the solvent in the sample determines the lithium ionic conductivity as shown in Figure 7b.

**Figure 6.** (a) Reduced PDF \( G(r) \) of samples annealed at 100 °C for 6 h (red line) and 12 h (blue line) and Li₃PS₄ prepared by the mechanical milling method (black line). (b) Enlarged view of the reduced PDF from 3.0 to 5.0 Å.

**Figure 7.** (a) Scheme of detection limits of Li₂S in the case of Raman and XRD measurements and high-energy XRD coupled to PDF analysis. (b) Scheme of the effect of annealing conditions on ionic conductivity of Li₃PS₄ prepared by the liquid-phase synthesis.

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**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04307.

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Raman spectra of raw materials and precursors at different shaking times; TG curves of Li₃PS₄ and the precursor prepared by shaking for 360 min; XRD patterns of samples prepared at different shaking times after annealing at 170 °C for 2 h; SEM images of Li₃PS₄ prepared by shaking for each time; reduced PDF, \( G(r) \), of Li₃PS₄ prepared by heating precursors with different shaking times at 170 °C for 2 h; details of the differential PDF analysis method; XRD patterns of Li₃PS₄ prepared via liquid-phase synthesis and solid-phase synthesis; XRD patterns of samples annealed at 100 °C; reduced PDF of Li₃PS₄ prepared by the mechanical milling method and the precursor and the samples annealed at 100 °C for each time; and TG–DTA curve of the precursor and Raman spectra of the samples annealed at 100 °C with different annealing times (PDF).
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Author Contributions
K.Y., A.H., M.T., H.M., A.M., and Y.U. conceived and directed the project. K.Y., M.T., N.H.H.P., and A.S. synthesized the sulﬁde solid electrolyte and measured the electrochemical properties. M.T., K.O., T.W., and T.U. performed high-energy XRD. M.T. and K.O. analyzed the local structure of the solid electrolyte by PDF analysis.

Notes
The authors declare no competing ﬁnancial interest.

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REFERENCES
(1) Dunn, B.; Kamath, H.; Tarascon, J.-M. Electrical Energy Storage for the Grid: A Battery of Choices. Science 2011, 334, 928–935.
(2) Zubi, G.; Dufo-Lopez, R.; Carvalho, M.; Pasaoglu, G. The Lithium-Ion Battery: State of the Art and Future Perspectives. Renew. Sustain. Energy Rev. 2018, 89, 292–308.
(3) Wu, H.; Cui, Y. Designing Nanostructured Si Anodes for High Energy Lithium Ion Batteries. Nano Today 2012, 7, 414–429.
(4) Islam, M. S.; Fisher, C. A. J. Lithium and Sodium Battery Cathode Materials: Computational Insights into Voltage, Diffusion and Nanostructural Properties. Chem. Soc. Rev. 2014, 43, 185–204.
(5) Seh, Z. W.; Sun, Y.; Zhang, Q.; Cui, Y. Designing High-Energy Lithium–Sulfur Batteries. Chem. Soc. Rev. 2016, 45, 5605–5634.
(6) Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. Chem. Mater. 2010, 22, 587–603.
(7) Goodenough, J. B.; Park, K.-S. The Li-Ion Rechargeable Battery: A Perspective. J. Am. Chem. Soc. 2013, 135, 1167–1176.
(8) Whittingham, M. S. Lithium Batteries and Cathode Materials. Chem. Rev. 2004, 104, 4271–4302.
(9) Simon, P.; Gogotsi, Y. Materials for Electrochemical Capacitors. Nat. Mater. 2008, 7, 845–854.
(10) Winter, M.; Brodd, R. J. What Are Batteries, Fuel Cells, and Supercapacitors? Chem. Rev. 2010, 104, 4245–4270.
(11) Goodenough, J. B. Rechargeable Batteries: Challenges Old and New. J. Solid State Electrochem. 2012, 16, 2019–2039.
(12) Tatsumisago, M.; Nagao, M.; Hayashi, A. Recent Development of Sulﬁde Solid Electrolytes and Interfacial Modiﬁcation for All-Solid-State Rechargeable Lithium Batteries. J. Asian Ceram. Soc. 2013, 1, 17–25.
(13) Hayashi, A.; Sakuda, A.; Tatsumisago, M. Development of Sulﬁde Solid Electrolytes and Interface Formation Processes for Bulk-Type All-Solid-State Li and Na Batteries. Front. Energy Res. 2016, 4, 25.
(14) Inaguma, Y.; Liqian, C.; Itoh, M.; Nakamura, T.; Uchida, T.; Ikuta, H.; Wakihara, M. High Ionic Conductivity in Lithium Lanthanum Titanate. Solid State Commun. 1993, 86, 689–693.
(15) Murugan, R.; Thangadurai, V.; Weppner, W. Fast Lithium Ion Conduction in Garnet-Type Li-La2Zr2O7. Angew. Chem., Int. Ed. 2007, 46, 7778–7781.
(16) Kamaya, N.; Homma, K.; Yamakawa, Y.; Hirayama, M.; Kanno, R.; Yonemura, M.; Kamiyama, T.; Kato, Y.; Hama, S.; Kawamoto, K.; Mitsui, A. A Lithium Superionic Conductor. Nat. Mater. 2011, 10, 682–686.
(17) Liu, Z.; Fu, W.; Payzant, A. E.; Yu, X.; Wu, Z.; Dudney, N. J.; Kiggans, J.; Hong, K.; Rondinone, A. J.; Liang, C. Anomalous High Ionic Conductivity of Nanoporous β-Li2PS4. J. Am. Chem. Soc. 2013, 135, 975–978.
(18) Rangasamy, E.; Liu, Z.; Gobet, M.; Pillar, K.; Sahu, G.; Zhou, W.; Wu, H.; Greenbaum, S.; Liang, C. An Iodide-Based Li2PS4I Superionic Conductor. J. Am. Chem. Soc. 2015, 137, 1384–1387.
(19) Nagao, M.; Kitaura, H.; Hayashi, A.; Tatsumisago, M. High Rate Performance, Wide Temperature Operation and Long Cyclability of All-Solid-State Rechargeable Lithium Batteries Using Mo-S Chevrel-Phase Compound. J. Electrochem. Soc. 2013, 160, A819–A823.
(20) Miura, A.; Rosero-Navarro, N. C.; Sakuda, A.; Tadanaga, K.; Phuc, N. H. H.; Matsuda, A.; Machida, N.; Hayashi, A.; Tatsumisago, M. Liquid-Phase Syntheses of Sulﬁde Electrolytes for All-Solid-State Lithium Battery. Nat. Rev. Chem. 2019, 3, 189–198.
(21) Kato, Y.; Hori, S.; Saito, T.; Suzuki, K.; Hirayama, M.; Mitsui, A.; Yonemura, M.; Iba, H.; Kanno, R. High-Power All-Solid-State Batteries Using Sulﬁde Superionic Conductors. Nat. Energy 2016, 1, 16030.
(22) Hayashi, A.; Hama, S.; Morimoto, H.; Tatsumisago, M.; Minami, T. Preparation of Li2P2S4X Superionic Electrolytes by Mechanical Milling. J. Am. Ceram. Soc. 2004, 84, 477–479.
(23) Minami, T.; Hayashi, A.; Tatsumisago, M. Preparation and Characterization of Superionic Conducting Li2P2S4 Crystal from Glassy Liquids. J. Ceram. Soc. Jpn. 2010, 118, 305–308.
(24) Deiseroth, H.-J.; Kong, S.-T.; Eckert, H.; Vannahme, J.; Reiner, C.; Zaiß, T.; Schlosser, M. Li2PS4X: A Class of Crystalline Li-Rich Solids With an Unusually High Li+ Mobility. Angew. Chem. 2008, 120, 767–770.
(25) Boulneau, S.; Courty, M.; Tarascon, J.-M.; Vialet, V. MechanochemoSynthesis of Li-Arygroside Li2P2S4X (X=Cl, Br, I) as Sulfur-Based Solid Electrolytes for All Solid State Batteries Application. Solid State Ionics 2012, 221, 1–5.
(26) Sakuda, A.; Hayashi, A.; Tatsumisago, M. Sulﬁde Solid Electrolyte with Favorable Mechanical Property for All-Solid-State Lithium Battery. Sci. Rep. 2013, 3, 2261.
(27) Nam, Y. J.; Cho, S.-J.; Oh, D. Y.; Lim, J.-M.; Kim, S. Y.; Song, J. H.; Lee, Y.-G.; Lee, S.-Y.; Jung, Y. S. Bendable and Thin Sulﬁde Solid Electrolyte Film: A New Electrolyte Opportunity for Free-Standing and Stackable High-Energy All-Solid-State Lithium-Ion Batteries. Nano Lett. 2015, 15, 3317–3323.
(28) El-Shinawi, H.; Paterson, G. W.; MacLaren, D. A.; Cussen, E. J.; Corr, S. A. Low-Temperature Densification of Al-Doped Li-La-Zr-O : A Reliable and Controllable Synthesis of Fast-Ion Conducting Garnets. *J. Mater. Chem. A* 2017, 5, 319–329.

(29) Ohta, S.; Seki, J.; Yagi, Y.; Kihira, Y.; Tani, T.; Asaoka, T. Co-Sinterable Lithium Garnet-Type Oxide Electrolite with Cathode for All-Solid-State Lithium Ion Battery. *J. Power Sources* 2014, 265, 40–44.

(30) Muramatsu, H.; Hayashi, A.; Ohtomo, T.; Hama, S.; Tatsumisago, M. Structural Change of Li2S−P2S5 Sulfide Solid Electrolytes in the Atmosphere. *Solid State Ionics* 2011, 182, 116–119.

(31) Auvergniet, J.; Cassel, A.; Ledeuil, J.-B.; Viallet, V.; Seznec, V.; Dedryvere, R. Interface Stability of Argyrodite Li6PS5Cl toward LiCoO2, LiNi1/3Co1/3Mn1/3O2, and LiMn2O4 in Bulk All-Solid-State Batteries. *Chem. Mater.* 2017, 29, 3883–3890.

(32) Tachez, M.; Malugani, J.; Mercier, R.; Robert, G. Ionic Conductivity of and Phase Transition in Lithium Thiophosphate Li3PS4. *Solid State Ionics* 1984, 14, 181–185.

(33) Murayama, M.; Kanno, R. Synthesis of New Lithium Ionic Conductor Thio-LISICON—Lithium Silicon Sulfides System. *J. Solid State Chem.* 2002, 168, 140–148.

(34) Teragawa, S.; Aso, K.; Tadanaga, K.; Hayashi, A.; Tatsumisago, M. Liquid-Phase Synthesis of a Li3PS4 Solid Electrolyte Using N-Methylformamide for All-Solid-State Lithium Batteries. *J. Mater. Chem. A* 2014, 2, 5095.

(35) Phuc, N. H. H.; Morikawa, K.; Totani, M.; Muto, H.; Matsuda, A. Preparation of Li3PS4 Solid Electrolyte by Liquid-Phase Shaking Using Organic Solvents with Carbonyl Group as Complex Forming Medium. *J. Jpn. Soc. Powder Powder Metall.* 2016, 63, 976–980.

(36) Phuc, N. H. H.; Morikawa, K.; Mitsuhiro, T.; Muto, H.; Matsuda, A. Synthesis of Plate-like Li3PS4 Solid Electrolyte via Liquid-Phase Shaking for All-Solid-State Lithium Batteries. *Ionics* 2017, 23, 2061–2067.

(37) Lim, H.-D.; Yue, X.; Xing, X.; Petrova, V.; Gonzalez, M.; Liu, H.; Liu, P. Designing Solution Chemistries for the Low-Temperature Synthesis of Sulfide-Based Solid Electrolytes. *J. Mater. Chem. A* 2018, 6, 7370–7374.

(38) Choi, S.; Lee, S.; Park, J.; Nichols, W. T.; Shin, D. Facile Synthesis of Li2S−P2S5 Glass-Ceramics Electrolyte with Micron Range Particles for All-Solid-State Batteries via a Low-Temperature Solution Technique (LTST). *Appl. Surf. Sci.* 2018, 444, 10–14.

(39) Wang, H.; Hood, Z. D.; Xia, Y.; Liang, C. Fabrication of Ultrathin Solid Electrolyte Membranes of Li2S−P2S5 Nanoflakes by Evaporation-Induced Self-Assembly for All-Solid-State Batteries. *J. Mater. Chem. A* 2016, 4, 8091–8096.

(40) Wang, Y.; Lu, D.; Bowden, M.; El Khoury, P. Z.; Han, K. S.; Deng, Z. D.; Xiao, J.; Zhang, J.-G.; Liu, J. Mechanism of Formation of Li2S−P2S5 Solid Electrolytes through Liquid Phase Synthesis. *Chem. Mater.* 2018, 30, 990–997.

(41) Suto, K.; Bonnick, P.; Nagai, E.; Niitani, K.; Arthur, T. S.; Muldoon, J. Microwave-Aided Synthesis of Lithium Thiophosphate Solid Electrolyte. *J. Mater. Chem. A* 2018, 6, 21261–21265.

(42) Shiotani, S.; Ohara, K.; Tsukasaki, H.; Mori, S.; Kanno, R. Pair Distribution Function Analysis of Sulfide Glassy Electrolytes for All-Solid-State Batteries: Understanding the Improvement of Ionic Conductivity under Annealing Condition. *Sci. Rep.* 2017, 7, 6972.

(43) Tsukasaki, H.; Mori, S.; Shiotani, S.; Yamamura, H. Ionic Conductivity and Crystallization Process in the Li2S−P2S5 Glass Electrolyte. *Solid State Ionics* 2018, 317, 122–126.

(44) Ghidiu, M.; Ruhl, J.; Culver, S. P.; Zeier, W. G. Solution-Based Synthesis of Lithium Thiophosphate Superionic Conductors for Solid-State Batteries: A Chemistry Perspective. *J. Mater. Chem. A* 2019, 7, 17735–17753.