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# Amorphous $\text{Li}_2\text{O-LiI-MoO}_3$ solid electrolytes: mechanochemical synthesis and application to all-solid-state batteries

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All-solid-state batteries are attractive because of their high safety and energy densities. The use of oxide solid electrolytes in all-solid-state batteries can enhance safety. Crystalline oxide solid electrolytes have attracted attention owing to their high ionic conductivity. However, they require high-temperature sintering for densification, which leads to unfavorable side reactions; hence, an oxide solid electrolyte with high ionic conductivity, ductility, and stability to Li metal prepared by low-temperature synthesis is required. In this study, amorphous-type  $\text{Li}_2\text{O-LiI-MoO}_3$  solid electrolytes are prepared using a mechanochemical method. The materials are synthesized, characterized, and fabricated, and measurements were subsequently obtained under specific conditions of temperature and pressure. The  $\text{Li}_2\text{O-LiI-MoO}_3$  solid electrolytes exhibit a high ionic conductivity of  $10^{-5} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ , sufficient ductility to densify by pressing at room temperature, and stability to Li metals. In addition, full cells with  $\text{Li}_2\text{S}$  and Si as active materials and the  $\text{Li}_2\text{O-LiI-MoO}_3$  solid electrolytes work reversibly at  $25^\circ\text{C}$ . This study demonstrates the potential of amorphous solid electrolytes to enhance the performance of all-solid-state batteries, thereby prompting further research and development of oxide-based solid electrolytes.

## 1. Introduction

All-solid-state lithium-ion batteries are promising alternatives to conventional liquid-type batteries owing to their high safety and energy densities. Oxide-based solid electrolytes are attractive for application in all-solid-state batteries owing to their chemical stability; moreover, they enable the construction of batteries that are safer than conventional batteries.<sup>1</sup> To date, there have been many reports on crystalline oxide-based solid electrolytes such as garnet<sup>2</sup> and NASICON-type<sup>3</sup> solid electrolytes, which exhibit a high ionic conductivity of approximately  $10^{-4}$ – $10^{-3} \text{ S cm}^{-1}$  at room temperature. However, these crystal-type solid electrolytes usually need to be sintered at high temperatures ( $> 800^\circ\text{C}$ ) to densify and reduce grain boundaries, which causes unfavorable side reactions. Consequently, preparation methods at low temperatures have been studied extensively,<sup>4</sup> including cold-sintering<sup>5,6</sup> and sol-gel methods.<sup>7,8</sup> For application in all-solid-state lithium-ion batteries, oxide solid electrolytes must be prepared at low temperatures;

moreover, they should have high ionic conductivity and ductility and exhibit stability to Li metal.

One way to achieve the desired oxide solid electrolytes is to use glass or amorphous oxide solid electrolytes with low melting points.<sup>9,10</sup> These solid electrolytes are prepared by low-temperature sintering and mechanochemical methods and have relatively high ionic conductivities and mechanical properties.<sup>11–13</sup> We have also investigated and reported glass and glass-ceramic oxide solid electrolytes.<sup>14–18</sup> For example,  $90\text{Li}_3\text{BO}_3 \cdot 10\text{Li}_2\text{SO}_4$  glass-ceramics have an ionic conductivity of  $10^{-5} \text{ S cm}^{-1}$ , good formability and stability to Li metal, and have been applied to all-solid-state batteries.<sup>19–21</sup>

Recently, new types of  $\text{Li}_2\text{O-LiI}$  amorphous materials have been developed as solid electrolytes superior to these glass-based oxide solid electrolytes in terms of their ionic conductivity, ductility, and stability to Li metal.<sup>22,23</sup> The  $\text{Li}_2\text{O-LiI}$  solid electrolytes were prepared simply by a mechanochemical process using lithium oxide and lithium iodide as starting materials and were largely composed of amorphous structures comprising  $\text{Li}^+$ ,  $\text{O}^{2-}$ , and  $\text{I}^-$  with high ionic conductive properties. All-solid-state batteries with  $\text{Li}_2\text{O-LiI}$  solid electrolytes were also investigated and showed high capacity and stable cycling.<sup>24–27</sup> Therefore, the  $\text{Li}_2\text{O-LiI}$  solid electrolyte is a promising material for all-solid-state batteries, and it is necessary to explore new materials that are

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based on it. Two methods may be used to enhance the ionic conductivity of the  $\text{Li}_2\text{O}$ – $\text{LiI}$  solid electrolyte, namely (1) increasing the amorphous region in the  $\text{Li}_2\text{O}$ – $\text{LiI}$  solid electrolyte and (2) increasing the ionic conductivity of the amorphous component. The  $\text{Li}_2\text{O}$ – $\text{LiI}$  solid electrolyte is composed of 70–80% amorphous components and 20–30% unreacted  $\text{Li}_2\text{O}$  and  $\text{LiI}$  crystals.<sup>23</sup>  $\text{Li}_2\text{O}$  crystals are known to form ionically conductive glasses with glass-forming oxides such as  $\text{B}_2\text{O}_3$ ,<sup>28</sup>  $\text{SiO}_2$ ,<sup>29</sup> and  $\text{P}_2\text{O}_5$ .<sup>30</sup> When forming lithium-ion conductive glasses, the addition of glass-forming oxides is expected to increase the amorphous region and ionic conductivity. However, the addition of an oxide that readily reacts with  $\text{Li}_2\text{O}$  to form glass reduces the ratio of the amorphous structure with high ionic conductivity formed between  $\text{Li}_2\text{O}$  and  $\text{LiI}$ ; thus, the choice of oxide type is important. Zachariassen's law<sup>31</sup> is widely recognized for its relevance to the ease of glass formation and the vitrification conditions for oxide glasses. In the context of solid electrolytes, such as the  $\text{Li}_2\text{O}$ – $\text{LiI}$  solid electrolyte, the addition of a small amount of oxides is considered one of the most effective methods for enhancing ionic conductivity.

In this study,  $\text{Li}_2\text{O}$ – $\text{LiI}$ – $\text{MoO}_3$  solid electrolytes were investigated using  $\text{MoO}_3$ , which is an intermediate oxide that has a favorable glass-forming ability to enhance the properties of  $\text{Li}_2\text{O}$ – $\text{LiI}$ , including its ionic conductivity. The  $\text{Li}_2\text{O}$ – $\text{LiI}$ – $\text{MoO}_3$  solid electrolytes were prepared using a mechanochemical method. The structures of the obtained samples were analyzed using several techniques, and their ionic conductivities were measured. To investigate the stability of the Li metals, Li symmetric cells were assembled and charge–discharge tests were performed. Furthermore, for application to all-solid-state batteries, half cells and full cells were fabricated using  $\text{Li}_2\text{S}$  and Si as active materials, and charge–discharge tests were conducted.

## 2. Experimental

### 2.1 Synthesis

A mechanochemical process was employed to prepare  $\text{Li}_2\text{O}$ – $\text{LiI}$ – $\text{MoO}_3$  samples. The starting materials  $\text{Li}_2\text{O}$  (99.9%, Furuuchi Chem.),  $\text{LiI}$  (99.999%, Sigma-Aldrich), and  $\text{MoO}_3$  (99%, FUJIFILM Wako Pure Chem. Co.) were weighed according to the following ratios:  $\text{Li}_2\text{O}:\text{LiI}:\text{MoO}_3 = 67:33:0$ ,  $66:33:1$ ,  $63:32:5$ , and  $60:30:10$  (mol%). The weighed materials were placed in a  $\text{ZrO}_2$  pot (45 mL) containing 32.5 g of  $\text{ZrO}_2$  balls (diameter = 5 mm). Ball milling was conducted at 510 rpm for 70 h using a planetary ball-milling apparatus (PULVERISETTE 7; Fritsch). The  $\text{Li}_3\text{PS}_4$  glass was synthesized using the mechanochemical process. The starting materials,  $\text{Li}_2\text{S}$  (99.9%, Mitsuwa Chemicals Co., Ltd.) and  $\text{P}_2\text{S}_5$  (99%, Sigma-Aldrich), were weighed at a molar ratio of 3 : 1 and placed in a  $\text{ZrO}_2$  pot (250 mL) with 450 g of  $\text{ZrO}_2$  balls (diameter = 4 mm). The mechanochemical technique was performed at 210 rpm for 70 h using a planetary ball-milling apparatus (PULVERISETTE 5; Fritsch). All the procedures were performed under a dry Ar atmosphere.

### 2.2 Material characterization

X-ray diffraction (XRD) measurements ( $\text{CuK}\alpha$ ) were conducted using a diffractometer (SmartLab; Rigaku Corp.). The diffraction

data were collected in increments of  $0.02^\circ$  in the  $2\theta$  range of  $10$ – $80^\circ$  at a scan rate of  $10^\circ \text{ min}^{-1}$ . XRD measurements were performed using the reference intensity ratio (RIR) technique to determine the proportion of amorphous components in the prepared samples. The prepared  $\text{Li}_2\text{O}$ – $\text{LiI}$ – $\text{MoO}_3$  samples and  $\text{Al}_2\text{O}_3$  powder (FUJIFILM Wako Pure Chem. Co.) were mixed at a weight ratio of 1 : 2 using an agate mortar. The starting materials  $\text{Li}_2\text{O}$ ,  $\text{LiI}$ , and  $\text{MoO}_3$  powders were mixed with  $\text{Al}_2\text{O}_3$  powders. XRD measurements were conducted for both mixtures, and the weight ratios of the crystalline and amorphous phases were calculated by comparing the peak intensities of both mixtures using the peaks derived from  $\text{Al}_2\text{O}_3$  in the obtained XRD as a reference. Raman spectroscopy was performed using a Raman spectrophotometer (LabRAM HR-800, HORIBA) with a 325-nm He–Cd laser. X-ray photoelectron spectroscopy (XPS) was conducted using an apparatus (K-Alpha, Thermo Fisher Scientific) with a monochromatic Al  $\text{K}\alpha$  source (1486.6 eV). The obtained peaks were aligned to the peak of C 1s at 284.7 eV on the surface for calibration. The alignment was consistent with that of another one using the Au 4f peak at 84.0 eV.  $\text{Ar}^+$  etching was performed on some samples to remove surface impurities. Samples whose electronic states were changed by etching are not discussed with respect to the depth profiles.  $^7\text{Li}$  magic-angle spinning nuclear magnetic resonance (MAS-NMR) measurements were performed using an NMR spectrometer (JEOR JNM-ECX 400). The spectra were obtained using a single pulse width of 3.5  $\mu\text{s}$  (equivalent to one-third of the  $90^\circ$  pulse width). Samples were placed in a cylindrical zirconia spinner and rotated at 12–15 kHz.  $\text{LiCl}$  (−1.19 ppm) was used as the standard material. The recycle delay was 5 s, and the accumulation count was 50. The morphologies of the prepared samples were observed by scanning electron microscopy (SEM, JSM-6610A; JEOL). Energy-dispersive X-ray (EDX) spectroscopy analysis was also performed. Transmission electron microscopy (TEM) observation was performed using a JEM-2100Plus microscope (JEOL Co., Ltd) at an accelerating voltage of 200 kV. A single-tilt vacuum-transfer TEM specimen holder (Mel-Build) was used to prevent exposure of the samples to air during the TEM experiments. A complementary metal–oxide–semiconductor (CMOS) camera (OneView, Gatan Inc.) was utilized, which can acquire 16-megapixel images and videos with high speed and high sensitivity. The microstructures were examined by obtaining electron diffraction (ED) patterns and hollow-cone dark-field (HCDF) images. All measurements were conducted under a dry Ar atmosphere. The relative densities were calculated by dividing the bulk density of the pellets pressed at 360 MPa by the apparent density of the powder. The bulk densities of the pellets were calculated from their weights and volumes. The apparent density was measured using a gas pycnometer (AccuPycII 1340, Shimadzu Corp.).

### 2.3 Electrochemical characterization

The ionic conductivities of the samples were measured using the alternating current (AC) impedance method with an impedance/gain phase analyzer (SI-1260A; Solartron). Pellets (diameter: 10 mm) were formed using a uniaxial press at 360 MPa for 5 min. Gold electrodes were formed by sputtering both surfaces of the pellets as current collectors. The AC impedance



was measured under a dry Ar atmosphere. Direct current (DC) measurements were performed to determine the electronic conductivity of the samples using ion-blocking cells (stainless steel (SS)/sample/SS). The electronic conductivity was calculated using the current density and potential after 300 s. The prepared cells were measured at 25 °C using a potentiostat/galvanostat (SI-1287; Solartron Analytical). To investigate the stability of the prepared samples to Li metals, Li symmetric cells (SS/Li/sample/Li/SS) were fabricated, and electrochemical measurements were performed at 100 °C using a charge-discharge measurement device (BTS-2005, Nagano Co. Ltd.).

## 2.4 Fabrication of all-solid-state batteries

The composite positive and negative electrodes were fabricated using the ball-milling technique. The composite electrodes were composed of  $\text{Li}_2\text{S}$  or small-sized silicon (<1  $\mu\text{m}$ ), vapor-grown carbon fiber (VGCF, Showa-Denko), and the  $\text{Li}_2\text{O}$ -LiI-MoO<sub>3</sub> samples in the weight ratio 30:10:60. The weighed materials were placed in a ZrO<sub>2</sub> pot (45 mL) containing 40 g of ZrO<sub>2</sub> balls (diameter = 5 mm). Ball-milling was conducted at 370 rpm for 8 h. The prepared composites were used as electrode layers and three types of cells were fabricated:  $\text{Li}_2\text{S}$ -half cells (Li-In/ $\text{Li}_3\text{PS}_4$  glass/ $\text{Li}_2\text{S}$ -VGCF- $\text{Li}_2\text{O}$ -LiI-MoO<sub>3</sub>), Si-half cells (Li-In/ $\text{Li}_3\text{PS}_4$  glass/Si- $\text{Li}_2\text{O}$ -LiI-MoO<sub>3</sub>-VGCF), and Si/ $\text{Li}_2\text{S}$  full cells (Si- $\text{Li}_2\text{O}$ -LiI-MoO<sub>3</sub>-VGCF/ $\text{Li}_2\text{O}$ -LiI-MoO<sub>3</sub>/ $\text{Li}_2\text{S}$ -VGCF- $\text{Li}_2\text{O}$ -LiI-MoO<sub>3</sub>).  $\text{Li}_3\text{PS}_4$  glass powders (80 mg) or  $\text{Li}_2\text{O}$ -LiI-MoO<sub>3</sub> samples (30 mg) used as separator layers were placed in a polycarbonate cylinder (diameter = 10 mm) and pressed for a few seconds at ~100 MPa. To fabricate the half-cells, composite electrodes were placed on the surface of the separator, and the composites and separator were pressed together at 720 MPa for 5 min. Li-In alloys were prepared by touching lithium foils (99.9%, 250  $\mu\text{m}$ , Furuuchi Chemical Corp.) and In foils (99.999%, 300  $\mu\text{m}$ , Furuuchi Chem. Corp.). The Li-In alloy was placed on another surface of the separator and pressed together at 36 MPa for 2 min. For the Si/ $\text{Li}_2\text{S}$  full cells, the  $\text{Li}_2\text{S}$  composite electrode was placed on the surface of the separator and pressed at 180 MPa for 2 min. A Si-composite electrode was placed on the other side of the separator, and they were pressed together at 720 MPa for 5 min. Stainless steel stamps were used as current collectors. All the cells were tightly constrained (>100 MPa).  $\text{Li}_2\text{S}$ - and Si-loadings were ca. 3.8 mg  $\text{cm}^{-2}$  and ca. 2 mg  $\text{cm}^{-2}$ , respectively. Charge-discharge tests were performed at 25 °C at 0.1 mA using a charge-discharge measurement device (BTS-2004, Nagano Co. Ltd.).

## 3. Results and discussion

### 3.1 Material characteristics

The XRD patterns (Fig. 1) show peaks derived from  $\text{Li}_2\text{O}$  and LiI, which are supposed to be non-reactive. The starting materials MoO<sub>3</sub> and its related compounds, such as  $\text{Li}_2\text{MoO}_4$  (ref. 32 and 33) and  $\text{Li}_4\text{MoO}_5$  (ref. 34), were not observed in the XRD patterns. In addition, MoO<sub>3</sub> is an intermediate oxide and this experiment demonstrated that MoO<sub>3</sub> alone cannot achieve an amorphous phase by ball-milling. This indicates that MoO<sub>3</sub>

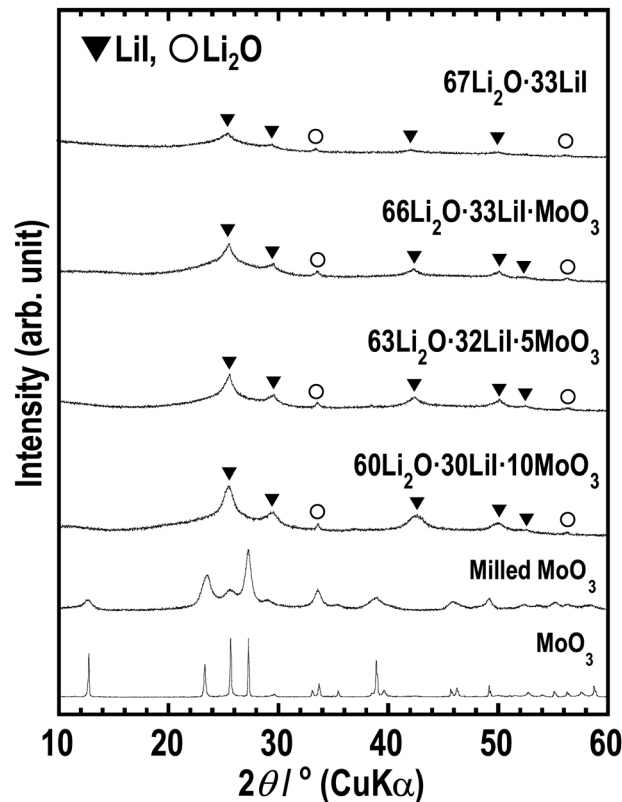


Fig. 1 XRD patterns of 67 $\text{Li}_2\text{O}$ ·33LiI, 66 $\text{Li}_2\text{O}$ ·33LiI·MoO<sub>3</sub>, 63 $\text{Li}_2\text{O}$ ·32LiI·5MoO<sub>3</sub>, 60 $\text{Li}_2\text{O}$ ·30LiI·10MoO<sub>3</sub>, milled MoO<sub>3</sub>, and MoO<sub>3</sub>.

formed amorphous phases with  $\text{Li}_2\text{O}$  and LiI. The prepared samples have mainly amorphous components such as  $\text{Li}_2\text{O}$ -LiI solid electrolytes, which have large amounts of amorphous components, i.e., approximately 70 to 80%.<sup>23</sup> As the amount of MoO<sub>3</sub> increased, the peak intensity of LiI increased. This indicates that the formation of an amorphous structure between  $\text{Li}_2\text{O}$  and MoO<sub>3</sub> was more dominant than that between  $\text{Li}_2\text{O}$  and LiI. Fig. 2(a) shows SEM-EDX images of the 63 $\text{Li}_2\text{O}$ ·32LiI·5MoO<sub>3</sub> sample powders. No aggregation of the starting materials was observed at the micrometer scale. Fig. 2(b) shows the ED pattern and the HCD image of the 63 $\text{Li}_2\text{O}$ ·32LiI·5MoO<sub>3</sub> sample. The ED pattern exhibits the Debye-Scherrer rings of LiI, along with several discrete diffraction spots of  $\text{Li}_2\text{O}$ , which is consistent with the XRD patterns. Nanocrystalline MoO<sub>3</sub> and related compounds were not observed, confirming that MoO<sub>3</sub> forms an amorphous structure with  $\text{Li}_2\text{O}$  and LiI. The HCD image was derived from the 022 diffraction ring of LiI, revealing the precipitation of LiI nanocrystals with sizes ranging from approximately 2 to 12 nm.

Raman spectroscopy is an important method for investigating amorphous structures. Fig. 3 shows the Raman spectra of the samples. The samples with MoO<sub>3</sub> showed peaks that were different from the peaks obtained for the 67 $\text{Li}_2\text{O}$ ·33LiI sample. The peak at approximately 900  $\text{cm}^{-1}$  is attributed to  $\text{MoO}_4^{2-}$ ,<sup>33,35,36</sup> indicating that MoO<sub>3</sub> reacted with  $\text{Li}_2\text{O}$ . The other peaks were not completely assigned to any other previously reported material; this may be because of the disordered



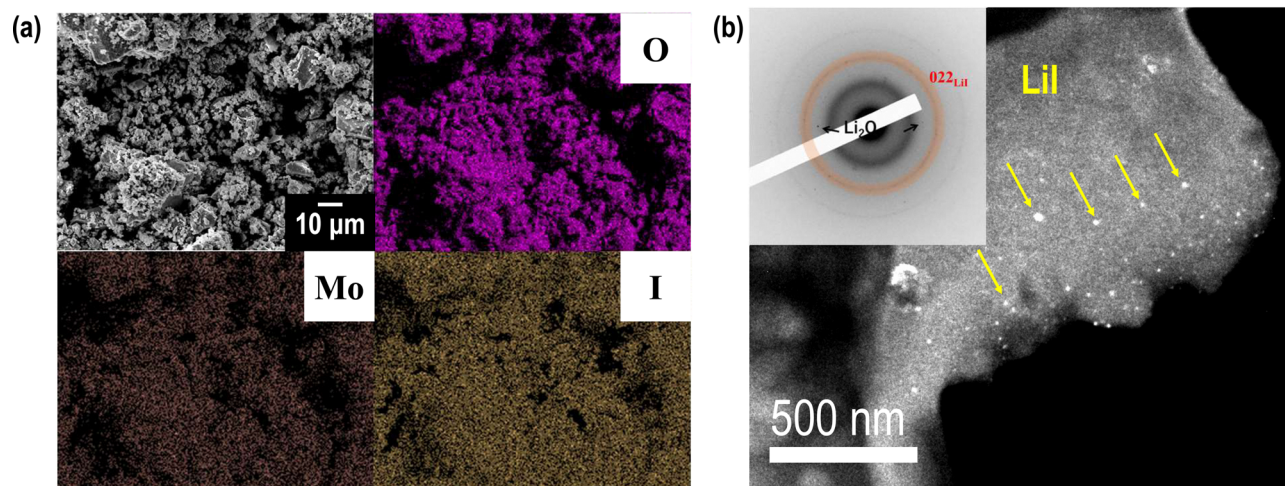


Fig. 2 (a) SEM-EDS images and (b) HCDF image and ED pattern of  $63\text{Li}_2\text{O} \cdot 32\text{LiI} \cdot 5\text{MoO}_3$ . In (b), bright-contrast regions indicated by arrows in yellow correspond to the LiI nanocrystals.

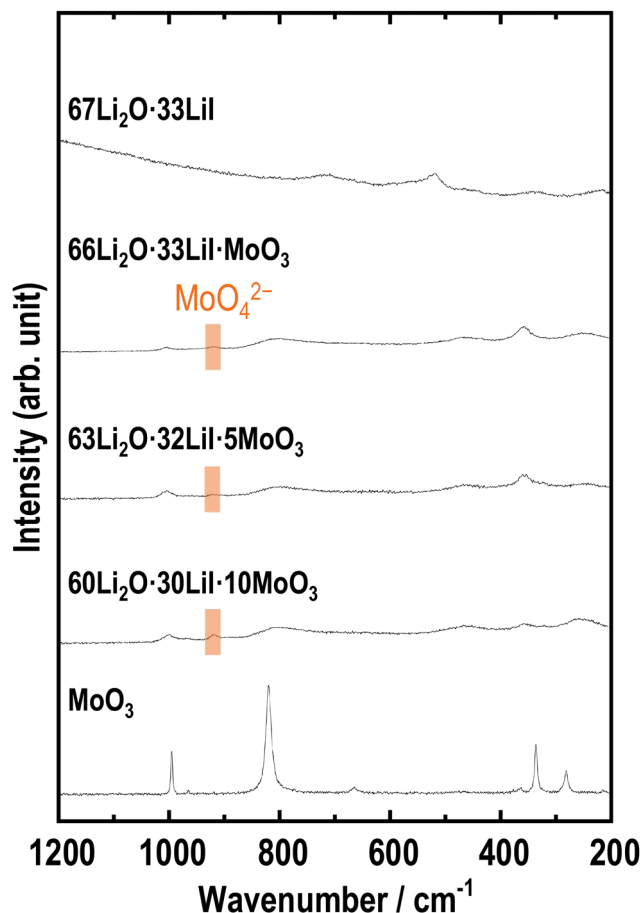


Fig. 3 Raman spectra of  $67\text{Li}_2\text{O} \cdot 33\text{LiI}$ ,  $66\text{Li}_2\text{O} \cdot 33\text{LiI} \cdot \text{MoO}_3$ ,  $63\text{Li}_2\text{O} \cdot 32\text{LiI} \cdot 5\text{MoO}_3$ ,  $60\text{Li}_2\text{O} \cdot 30\text{LiI} \cdot 10\text{MoO}_3$ , and  $\text{MoO}_3$ .

amorphous-like structure prepared by ball milling. If these peaks are estimated, peaks at *ca.* 250, 350, 800, and  $1000\text{ cm}^{-1}$  appear to be shifted  $\text{MoO}_3$  peaks, and peaks at around  $500\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$  are attributed to  $\text{Li}_2\text{MoO}_3$  (ref. 37) and  $\text{Li}_2\text{MoO}_4$ ,<sup>32,33</sup> respectively.

To examine the effects of incorporating  $\text{MoO}_3$  into the amorphous structure on the local mobility and environment around the Li ions,  $^7\text{Li}$  MAS-NMR measurements were conducted on the prepared samples. Fig. 4 shows the  $^7\text{Li}$  MAS NMR spectra of the prepared samples. We previously reported that the  $67\text{Li}_2\text{O} \cdot 33\text{LiI}$  sample showed three kinds of peaks of  $\text{Li}_2\text{O}$ , LiI, and amorphous components.<sup>23</sup> The samples containing  $\text{MoO}_3$  also exhibit three types of peaks, indicating the presence of amorphous components. In addition, the peak derived from the amorphous phase at approximately 0 ppm shifted to lower chemical shifts with increasing  $\text{MoO}_3$  content.  $^7\text{Li}$  MAS-NMR of  $\text{Li}_2\text{MoO}_4$  has already been reported, and a sharp peak appears below 0 ppm.<sup>38</sup> The peak shift may indicate a change in the environment of Li in amorphous components by forming  $\text{MoO}_4^{2-}$ .

XPS measurements were performed to investigate the electronic states of the prepared samples. If  $\text{MoO}_3$  was reduced and formed reduction products such as  $\text{MoO}_3^{2-}$  by high energy ball-milling, the valence of Mo should be reduced from  $\text{Mo}^{6+}$  to  $\text{Mo}^{4+}$ . Fig. 5 shows the (a) Mo 3d and (b) I 3d XPS spectra of all the samples and their starting materials. The Mo 3d and I 3d spectra were separated into  $3d_{5/2}$  and  $3d_{3/2}$  peaks, and only the binding energies of the  $3d_{5/2}$  peaks were discussed. The Mo 3d spectra of the prepared samples exhibited binding energies that were comparable to those of the starting material  $\text{MoO}_3$ , indicating that the electronic state of Mo is  $\text{Mo}^{6+}$ . This indicates that Mo did not undergo reduction during the mechanochemical process. In addition, the I 3d spectra showed only one peak attributed to  $\text{I}^-$  in all samples, indicating that  $\text{I}^-$  is present in LiI or the amorphous components whose electronic states were almost the same.<sup>23</sup> The XPS measurements show that the valence of Mo remained  $\text{Mo}^{6+}$ , and  $\text{MoO}_3$  reacted with  $\text{Li}_2\text{O}$ , leading to the formation of  $\text{MoO}_4^{2-}$  amongst a group of compounds consisting of Li, O, and Mo elements.

Furthermore, RIR measurements were conducted on the sample to investigate the ratio of amorphous components in the sample. Fig. 6(a) shows the XRD pattern of a mixture of  $63\text{Li}_2\text{O} \cdot 32\text{LiI} \cdot 5\text{MoO}_3$  and  $\text{Al}_2\text{O}_3$ ; Fig. 6(b) shows the weight ratio of  $\text{Li}_2\text{O}$  crystal, LiI crystal, and amorphous components. The



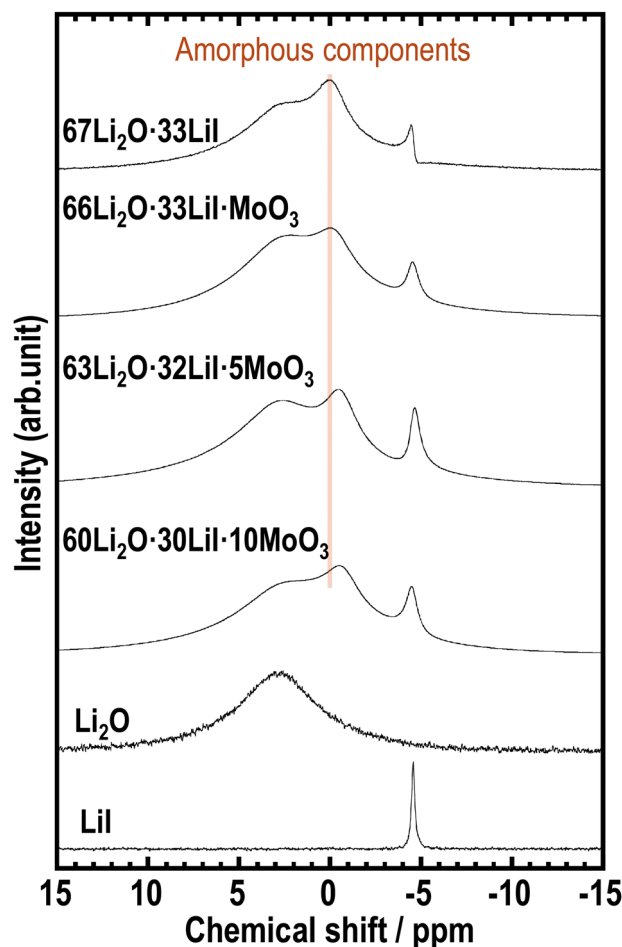


Fig. 4  ${}^7\text{Li}$  MAS-NMR spectra of  $67\text{Li}_2\text{O}\cdot 33\text{LiI}$ ,  $66\text{Li}_2\text{O}\cdot 33\text{LiI}\cdot \text{MoO}_3$ ,  $63\text{Li}_2\text{O}\cdot 32\text{LiI}\cdot 5\text{MoO}_3$ ,  $60\text{Li}_2\text{O}\cdot 30\text{LiI}\cdot 10\text{MoO}_3$ ,  $\text{Li}_2\text{O}$ , and  $\text{LiI}$ .

peaks of  $\text{MoO}_3$  were not observed, and the ratio of the three components was therefore calculated. Based on the results obtained, the ratio was 20.8:73:6.2 among  $\text{Li}_2\text{O}$  crystals, amorphous components, and  $\text{LiI}$  crystals. Previously, the same experiments were conducted on the  $\text{Li}_2\text{O}$ – $\text{LiI}$  samples, and the corresponding ratio was 20.3:77.8:1.8.<sup>23</sup> To add  $\text{MoO}_3$  into the  $\text{Li}_2\text{O}$ – $\text{LiI}$  sample, the ratio of  $\text{Li}_2\text{O}$  crystals was slightly increased whereas that of amorphous components was decreased and that of  $\text{LiI}$  crystals was increased. This result correlates well with the augmented intensity of the  $\text{LiI}$  peak in the XRD pattern shown in Fig. 1. It is speculated that the addition of  $\text{MoO}_3$  favors the reaction between  $\text{Li}_2\text{O}$  and  $\text{MoO}_3$ , inhibiting the formation of  $\text{Li}_2\text{O}$ – $\text{LiI}$  amorphous. The decrease in  $\text{Li}_2\text{O}$ – $\text{LiI}$  amorphous was larger than the increase in  $\text{Li}_2\text{O}$ – $\text{MoO}_3$  amorphous, and thus the amorphous region decreased. Although the amorphous region was not expanded in this study, the samples still consisted predominantly of amorphous components, which is expected to lead to high ionic conductivity.

In this study, the structural analyses performed so far have shown that the  $\text{Li}_2\text{O}$ – $\text{LiI}$ – $\text{MoO}_3$  sample is an amorphous material with  $\text{MoO}_3$  incorporated into the original  $\text{Li}_2\text{O}$ – $\text{LiI}$  system, and  $\text{MoO}_4^{2-}$  was partially formed although unreacted  $\text{LiI}$  was

observed. There have been previous reports on  $\text{Ag}_2\text{O}$ – $\text{AgI}$ – $\text{MoO}_3$  electrolytes, which are silver ionic conductors composed of elements similar to the elements treated in this study.<sup>39–47</sup> However, most studies reported compositions rich in  $\text{AgI}$  or  $\text{MoO}_3$  and low in  $\text{Ag}_2\text{O}$ , which are different from the compositions of samples prepared in this study, including a large molar ratio of  $\text{Li}_2\text{O}$ . The amorphous structure would also differ from that of well-known Ag ionic conductors because the Raman spectroscopy results of the prepared samples in this study were not in perfect agreement with those of the reported Ag ionic conductors. Indeed, locally formed  $\text{MoO}_4^{2-}$  itself showed lithium ionic conduction,<sup>48,49</sup> and it may thus have a positive effect on ionic conductivity. More advanced and detailed analyses, such as pair distribution function analysis, are required to identify the amorphous structures.

### 3.2 Conductivity

AC impedance measurements were conducted on the prepared samples. Fig. 7(a) displays a cross-sectional SEM image of a pellet of  $63\text{Li}_2\text{O}\cdot 32\text{LiI}\cdot 5\text{MoO}_3$  pressed at 360 MPa at ca. 25 °C. The sample was densified by pressing; the relative density was 84%. The relative densities of the other samples are listed in Table 1; they are observed to be almost the same. Fig. 7(b) shows Nyquist plots of the prepared sample at 25 °C. A semicircle and spike were observed. The semicircle is attributed to the contributions of the bulk and grain boundary resistances in the samples, which are not distinctly separated. The ionic conductivities were determined using the resistance at the cross-point of the semicircle and spike, as summarized in Table 1. Ionic conductivity increased with the addition of  $\text{MoO}_3$ . In particular, the  $63\text{Li}_2\text{O}\cdot 32\text{LiI}\cdot 5\text{MoO}_3$  sample showed the highest conductivity at 25 °C. The ionic conductivity of  $\text{Li}_2\text{O}$ – $\text{LiI}$ – $\text{MoO}_3$  solid electrolytes is higher than those of other amorphous oxide solid electrolytes.<sup>11,14,17,18</sup> Fig. 7(c) shows the temperature dependence of the ionic conductivity of each sample. The plots of all the samples followed Arrhenius' law. The activation energy ( $E_a$ ) was calculated from the temperature dependence and is listed in Table 1.  $E_a$  decreased slightly in the sample with  $\text{MoO}_3$ . This enhancement in ionic conductivity and decrease in  $E_a$  may be due to the structural changes in the amorphous component. The electronic conductivities of the prepared samples were investigated using DC measurements. Fig. 7(d) shows the DC curve; the electronic conductivities are summarized in Table 1. Although the electronic conductivity was enhanced with an increase in the amount of  $\text{MoO}_3$ , the electronic conductivity was considerably lower than the ionic conductivity, which explains why electronic conduction is negligible to ionic conduction. In addition, the relative densities were calculated for all samples and are also summarized in Table 1. The relative densities were not significantly changed by the addition of  $\text{MoO}_3$ , indicating that the ductility of the samples was almost the same. Considering all the conductivity measurements, the ionic conductivity should be enhanced by adding  $\text{MoO}_3$  owing to the decreasing bulk resistance. To enhance the ionic conductivity of the  $\text{Li}_2\text{O}$ – $\text{LiI}$  solid electrolytes by adding  $\text{MoO}_3$ , it is necessary to either increase the amorphous region or increase



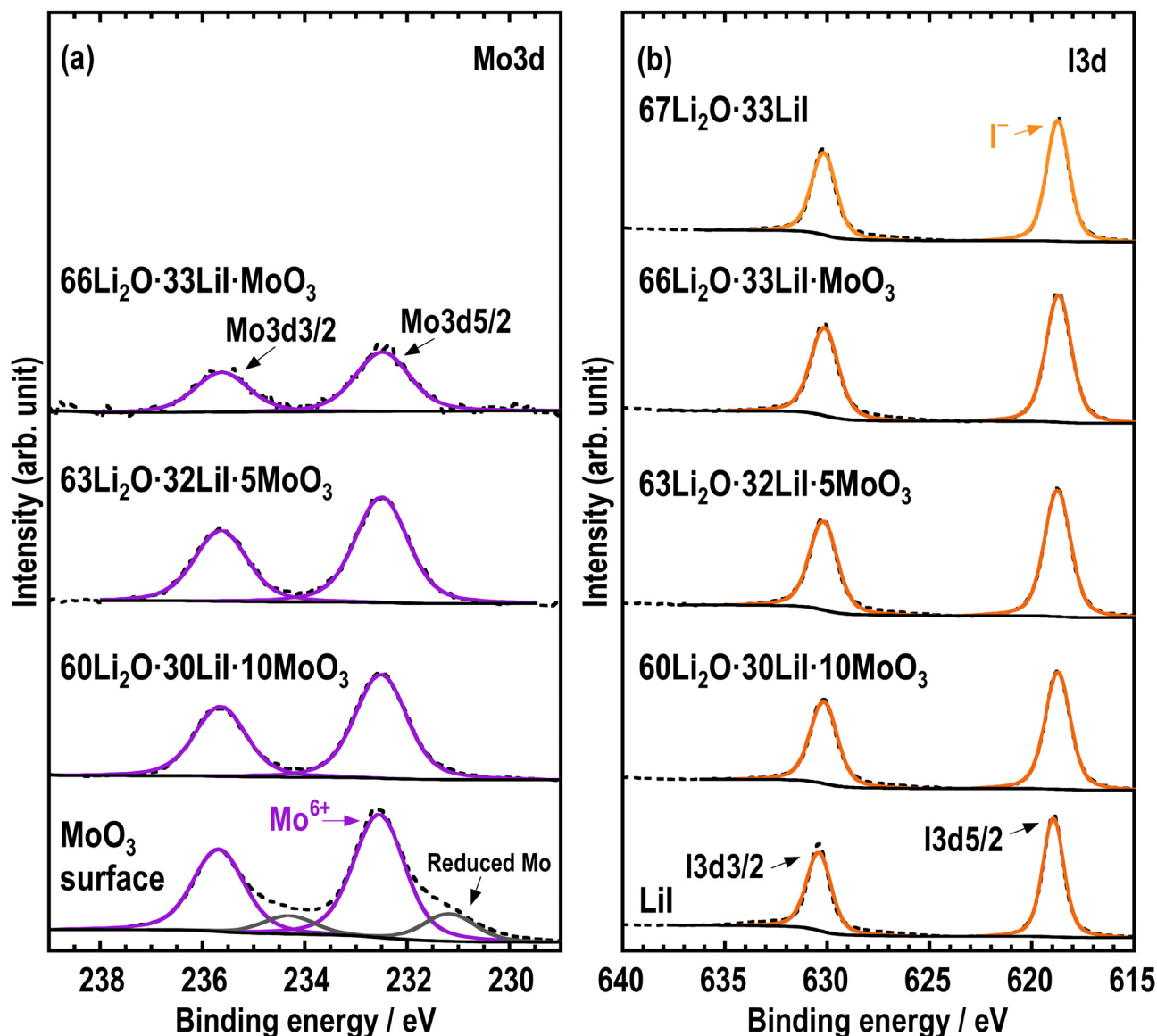


Fig. 5 (a) Mo 3d and (b) I 3d XPS spectra of  $67\text{Li}_2\text{O}\cdot 33\text{LiI}$ ,  $66\text{Li}_2\text{O}\cdot 33\text{LiI}\cdot \text{MoO}_3$ ,  $63\text{Li}_2\text{O}\cdot 32\text{LiI}\cdot 5\text{MoO}_3$ ,  $60\text{Li}_2\text{O}\cdot 30\text{LiI}\cdot 10\text{MoO}_3$ ,  $\text{MoO}_3$ , and  $\text{LiI}$ .

the conductivity of the amorphous components. The ionic conductivity should therefore be enhanced for the latter reason because the RIR measurement showed a decrease in the amorphous region. Typically, lithium ions are conducted through the large free volume in lithium-ion conductive glass solid electrolytes. Therefore, the free volume is considered to be partially expanded by adding  $\text{MoO}_3$  into  $\text{Li}_2\text{O}\text{--LiI}$ . The increase in the ionic conductivity of the amorphous component is believed to be due to a structural change in the amorphous component, as shown in the previous structural analysis. A slight increase in the electronic conductivity may contribute to an increase in ionic conduction; however, the causal relationship and mechanism were not fully examined in this study.

### 3.3 Battery performance

To investigate the stability of the  $\text{Li}_2\text{O}\text{--LiI}\text{--MoO}_3$  solid electrolytes to Li metal, Li symmetric cells were fabricated using  $63\text{Li}_2\text{O}\cdot 32\text{LiI}\cdot 5\text{MoO}_3$ , and galvanostatic cycle tests were

performed. Fig. 8 shows the long-term galvanostatic cycling tests of the cells at  $100^\circ\text{C}$ . The cell with the  $\text{Li}_2\text{O}\text{--LiI}\text{--MoO}_3$  solid electrolytes was cycled stably over 100 h, indicating that  $\text{Li}_2\text{O}\text{--LiI}\text{--MoO}_3$  solid electrolytes were stable to Li metals. Although  $\text{MoO}_3$  is not thermodynamically stable against the Li metal, a small amount of  $\text{MoO}_3$  did not decrease the stability of the entire  $\text{Li}_2\text{O}\text{--LiI}\text{--MoO}_3$  solid electrolyte against the Li metal. In addition, the overvoltage of the cell with the  $\text{Li}_2\text{O}\text{--LiI}\text{--MoO}_3$  solid electrolyte was lower than that with the  $\text{Li}_2\text{O}\text{--LiI}$  solid electrolyte. This is because the ionic conductivity of the  $\text{Li}_2\text{O}\text{--LiI}\text{--MoO}_3$  solid electrolytes was higher than that of the  $\text{Li}_2\text{O}\text{--LiI}$  solid electrolytes.

To enable the application of the  $\text{Li}_2\text{O}\text{--LiI}\text{--MoO}_3$  solid electrolytes for all-solid-state batteries, all-solid-state cells were fabricated using composite electrodes, including the  $\text{Li}_2\text{O}\text{--LiI}\text{--MoO}_3$  solid electrolyte. Lithium sulfide and silicon were used as active materials in the composite positive and negative



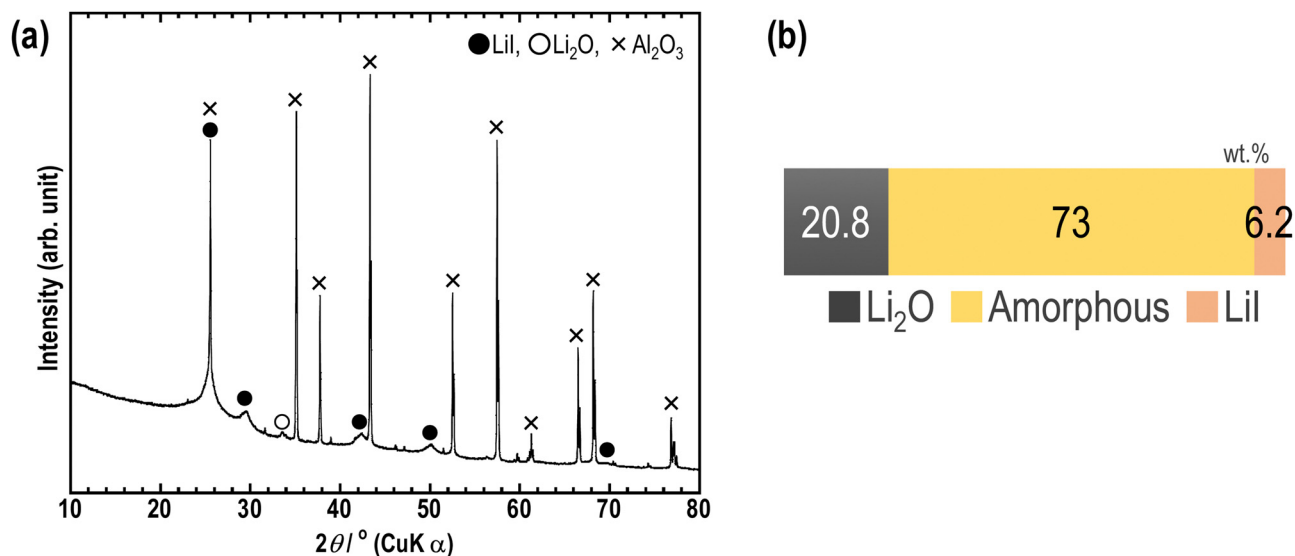


Fig. 6 (a) XRD patterns of the  $63\text{Li}_2\text{O}\cdot 32\text{LiLil}\cdot 5\text{MoO}_3\text{-Al}_2\text{O}_3$  mixture. The  $63\text{Li}_2\text{O}\cdot 32\text{LiLil}\cdot 5\text{MoO}_3$  sample was prepared using the mechanochemical method and the  $63\text{Li}_2\text{O}\cdot 32\text{LiLil}\cdot 5\text{MoO}_3\text{-Al}_2\text{O}_3$  mixture was prepared by mixing using an agate mortar. The weight ratio is 1 : 2 for  $63\text{Li}_2\text{O}\cdot 32\text{LiLil}\cdot 5\text{MoO}_3\text{-Al}_2\text{O}_3$ . (b) The weight ratios of  $\text{Li}_2\text{O}$ , amorphous, and Lil were calculated using the RIR method.

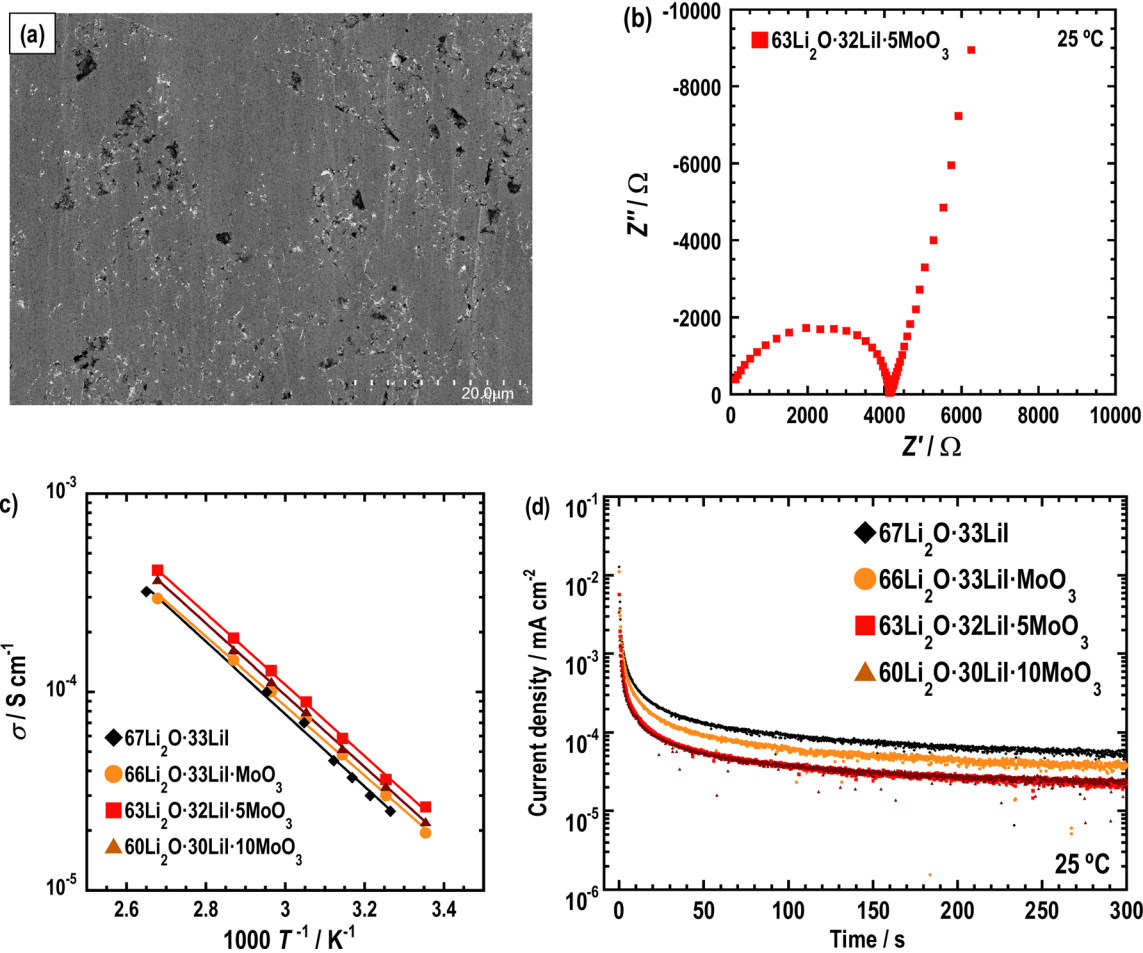
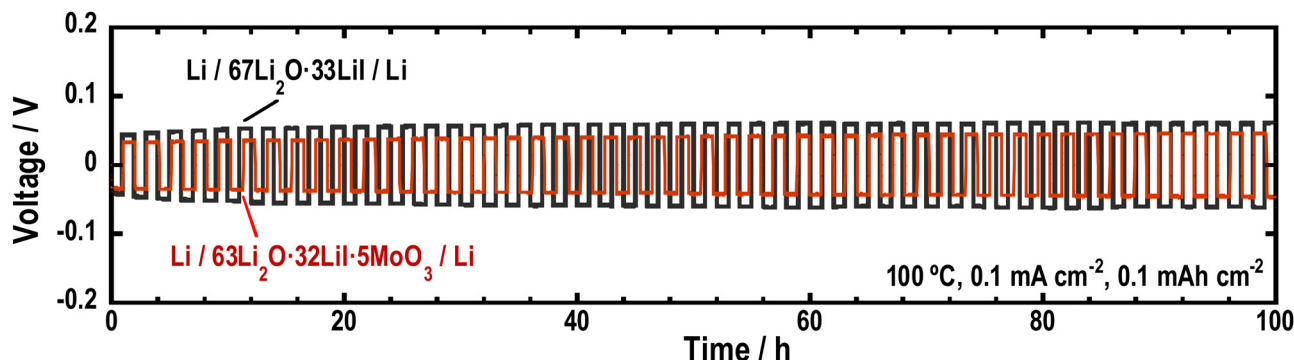


Fig. 7 (a) Cross-sectional SEM image of pellets of  $63\text{Li}_2\text{O}\cdot 32\text{LiLil}\cdot 5\text{MoO}_3$ . (b) Nyquist plots, (c) temperature dependence and (d)  $I$ - $V$  curves of  $67\text{Li}_2\text{O}\cdot 33\text{LiLil}$ ,  $66\text{Li}_2\text{O}\cdot 33\text{LiLil}\cdot \text{MoO}_3$ ,  $63\text{Li}_2\text{O}\cdot 32\text{LiLil}\cdot 5\text{MoO}_3$ , and  $60\text{Li}_2\text{O}\cdot 30\text{LiLil}\cdot 10\text{MoO}_3$ .



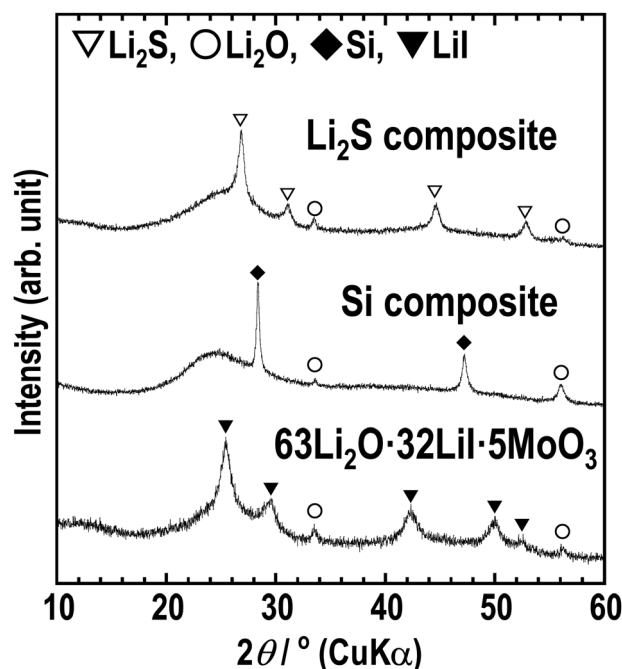
**Table 1** Ionic conductivity at 25 °C, activation energy ( $E_a$ ), electronic conductivity at 25 °C, relative density of 67Li<sub>2</sub>O·33LiI, 66Li<sub>2</sub>O·33LiI·MoO<sub>3</sub>, 63Li<sub>2</sub>O·32LiI·5MoO<sub>3</sub>, and 60Li<sub>2</sub>O·30LiI·10MoO<sub>3</sub>

	Ionic conductivity (S cm <sup>-1</sup> )	$E_a$ (kJ mol <sup>-1</sup> )	Electronic conductivity (S cm <sup>-1</sup> )	Relative density (%)
67Li <sub>2</sub> O·33LiI	$1.7 \times 10^{-5}$	35	$3.9 \times 10^{-11}$	85
66Li <sub>2</sub> O·33LiI·MoO <sub>3</sub>	$1.9 \times 10^{-5}$	34	$6.0 \times 10^{-11}$	84
63Li <sub>2</sub> O·32LiI·5MoO <sub>3</sub>	$2.6 \times 10^{-5}$	34	$1.0 \times 10^{-10}$	84
60Li <sub>2</sub> O·30LiI·10MoO <sub>3</sub>	$2.2 \times 10^{-5}$	35	$1.2 \times 10^{-10}$	83



**Fig. 8** Galvanostatic cycling tests of the symmetric cells (Li/67Li<sub>2</sub>O·33LiI/Li) and (Li/63Li<sub>2</sub>O·32LiI·5MoO<sub>3</sub>/Li).

electrodes, respectively. Fig. 9 shows the XRD patterns of the composite electrodes prepared *via* ball-milling. Sharp peaks of Li<sub>2</sub>S and Si and halo patterns were observed, indicating that the composites consisted of crystalline active materials distributed in an amorphous matrix. The peaks derived from LiI disappeared because LiI formed a solid solution with Li<sub>2</sub>S, or Si or SiO<sub>x</sub> on the surface of Si. Fig. 10(a) and (b) show half-cells with



**Fig. 9** XRD patterns of the Li<sub>2</sub>S-VGCF–63Li<sub>2</sub>O·32LiI·5MoO<sub>3</sub> composite (Li<sub>2</sub>S composite), Si-VGCF–63Li<sub>2</sub>O·32LiI·5MoO<sub>3</sub> composite (Si composite), and 63Li<sub>2</sub>O·32LiI·5MoO<sub>3</sub>.

Li<sub>2</sub>S and Si, respectively. The Li<sub>2</sub>O–LiI–MoO<sub>3</sub> electrolytes were used in the composite to evaluate suitability to the active materials. The half-cell with Li<sub>2</sub>S exhibited an irreversible capacity during the initial cycle. This is because the Li<sub>2</sub>O–LiI–MoO<sub>3</sub> solid electrolyte may be oxidized at *ca.* 2.2 V *vs.* Li–In. The oxidation voltage of the Li<sub>2</sub>O–LiI solid electrolyte was *ca.* 2.1 V *vs.* Li–In.<sup>24</sup> In addition, the Li<sub>2</sub>O–LiI–MoO<sub>3</sub> solid electrolytes include Li<sub>2</sub>O–LiI components and should have the same oxidation voltage. After the first cycle, the cell with Li<sub>2</sub>S operated reversibly, indicating that the initial irreversible capacity did not adversely affect subsequent cycles. The half-cell using Si exhibited almost 2000 mA h g<sup>-1</sup> over 20 cycles. These results showed that the Li<sub>2</sub>O–LiI–MoO<sub>3</sub> solid electrolytes can be used for both positive and negative electrodes.

Finally, all-solid-state Si/Li<sub>2</sub>S full cells were fabricated, and charge–discharge tests were performed at 25 °C. The Li<sub>2</sub>O–LiI–MoO<sub>3</sub> sample was contained in both the composite electrodes and the separator layer. Fig. 10(c) shows the charge–discharge curves of the full cell. Although an irreversible capacity was observed (for the same reason as for the Li<sub>2</sub>S-half cell), the cell worked reversibly at 25 °C over 20 cycles. Therefore, Li<sub>2</sub>O–LiI–MoO<sub>3</sub> solid electrolytes can be used in all-solid-state batteries.

## 4. Conclusions

To improve the ionic conductivity of Li<sub>2</sub>O–LiI solid electrolytes, Li<sub>2</sub>O–LiI–MoO<sub>3</sub> solid electrolytes were prepared by adding MoO<sub>3</sub> to Li<sub>2</sub>O–LiI solid electrolytes. Then, amorphous-like samples were prepared using a mechanochemical process. MoO<sub>3</sub> was incorporated into the amorphous structure and MoO<sub>4</sub><sup>2-</sup> was partially formed in the amorphous components. The addition of MoO<sub>3</sub> to the Li<sub>2</sub>O–LiI solid electrolytes was



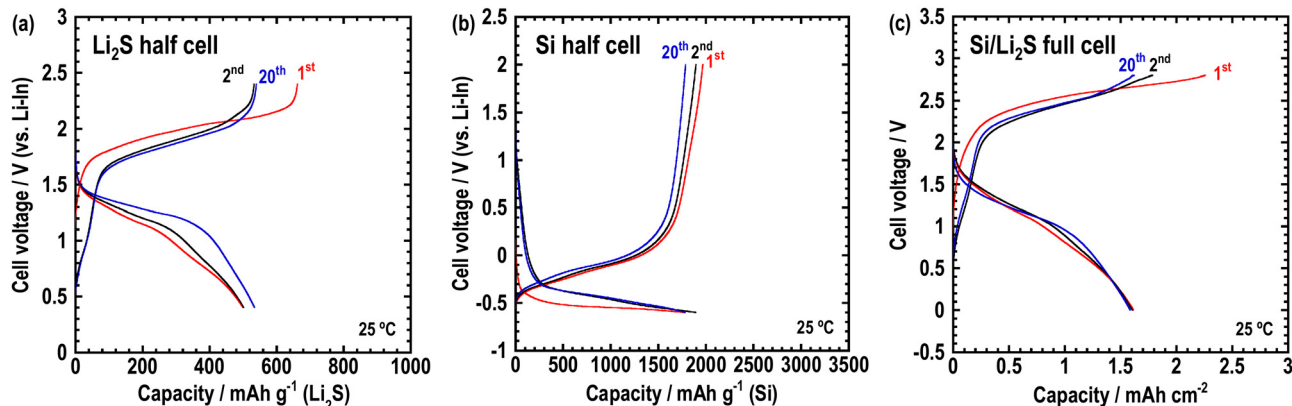


Fig. 10 Charge-discharge curves of the cell at 25 °C (a) (Li-In/Li<sub>3</sub>PS<sub>4</sub>/Li<sub>2</sub>S-VGCF-63Li<sub>2</sub>O-32LiI-5MoO<sub>3</sub>), (b) (Li-In/Li<sub>3</sub>PS<sub>4</sub>/Si-VGCF-63Li<sub>2</sub>O-32LiI-5MoO<sub>3</sub>), and (c) (Si-VGCF-63Li<sub>2</sub>O-32LiI-5MoO<sub>3</sub>/63Li<sub>2</sub>O-32LiI-5MoO<sub>3</sub>/Li<sub>2</sub>S-VGCF-63Li<sub>2</sub>O-32LiI-5MoO<sub>3</sub>).

found to improve the ionic conductivity. The Li<sub>2</sub>O-LiI-MoO<sub>3</sub> solid electrolytes were stable to Li metal and full cells that used them worked reversibly at 25 °C, which proved that Li<sub>2</sub>O-LiI-MoO<sub>3</sub> solid electrolytes were suitable for application in all-solid-state batteries. This work will contribute to the further study of solid oxide electrolytes.

## Author contributions

Y. F. wrote the manuscript. Y. F. synthesized and characterized the samples. T. A. fabricated and measured Li-symmetric cells. T. O. subjected the samples to NMR and RIR and analyzed the data. D. J., H. T., and S. M. analyzed the samples using TEM. A. S. and A. H. supervised the study. All authors discussed the results and reviewed and approved the final manuscript.

## Data availability

The information to confirm the reproducibility of the experiments is basically presented in the figures and tables of the main text.

## Conflicts of interest

There are no conflicts to declare.

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