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Solution-processable glass LiI-Li₄SnS₄ superionic conductors for all-solid-state Li-ion batteries

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Conventional lithium-ion batteries (LIBs) have important large-scale energy storage applications, such as electric vehicles and energy storage systems.^[1] However, these applications are limited by the safety concerns arising from the flammability of liquid electrolytes used in LIBs.^[1-2] As a promising solution to this issue, all-solid-state lithium batteries (ASLBs) with inorganic solid electrolytes (SEs) have attracted considerable attention.^[3] Bulk-type ASLBs, in which the composite electrode consists of a particulate mixture of active materials, SEs, and conductive additives, are considered particularly promising because of their high energy density and scalable fabrication.^[3a,3b,3d,3e,3g] Sulphide SEs are highly desirable because of their high ionic conductivities (e.g. Li₁₀GeP₂S₁₂ (LGPS):^[3a] $1.2 \times 10^{-2} \text{ S cm}^{-1}$, Li₃P₇S₁₁:^[4] $1.7 \times 10^{-2} \text{ S cm}^{-1}$, Li₆PS₅X^{[5])} and

deformability.^[3a,3b,3g] The latter enables the fabrication of two-dimensional contacts with active materials by simple cold-pressing.

Most efforts on the development of SEs thus far have placed a strong emphasis on the high ionic conductivity of the SEs.^[3a,3g,4-6] However, there is a huge discrepancy between the high ionic conductivities of sulphide SEs and the below-par performance of bulk-type ASLBs,^[3g,7] which originates from the limited ionic contact between the active materials and SEs.^[3a,3b,3d,3g] For example, cold-pressed composite electrodes have exhibited porosities as high as 20–30%, reflecting poor surface coverage of SEs on the active materials.^[7b] Therefore, the fabrication of composite electrodes with more intimate ionic contacts should be a prime objective for future development.^[3g,7b,8] However, this development has been inhibited by the drawbacks associated with the conventional protocols of synthesizing sulphide SEs, such as solid-state reactions^[3a,5] and mechanochemical methods.^[4]

An alternative architecture of SEs for composite electrodes was demonstrated by depositing a SE (80Li₂S-20P₂S₅) thin film on active materials by pulsed laser deposition.^[8-9] In theory, direct SE coatings on active materials can solve the problem of poor ionic contact in bulk-type ASLBs, thus increasing the power and energy densities at the electrode and cell levels.^[9-10] However, the vacuum deposition method might be prohibitive for commercialization. In contrast, a scalable solution-based coating method could provide the necessary breakthrough for developing better sulphide SEs and ASLBs. It was reported that Thio-LISICON (Li_{3.25}Ge_{0.25}P_{0.75}S₄) showing $1.82 \times 10^{-4} \text{ S cm}^{-1}$ can be prepared by using anhydrous hydrazine.^[11] However, the use of extremely dangerous anhydrous hydrazine excludes interests for further development. Liang and coworkers reported the synthesis of β -Li₃PS₄ with an ionic conductivity of $1.6 \times 10^{-4} \text{ S cm}^{-1}$ by using tetrahydrofuran^[12] and Li₇P₂S₈I with an ionic conductivity of $6.3 \times 10^{-4} \text{ S cm}^{-1}$ by using acetonitrile.^[13] In both cases, however, the solutions are neither homogeneous nor environmentally friendly. The

Tatsumisago group reported that N-methylformamide (b.p. = 182.6 °C) can dissolve Li_3PS_4 (LPS) to form a homogenous solution, and LPS with a conductivity of $2.6 \times 10^{-6} \text{ S cm}^{-1}$ can be recrystallized.^[14] The same group later showed that argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$ with an ionic conductivity of $1.4 \times 10^{-5} \text{ S cm}^{-1}$ can be prepared by using ethanol.^[15] It is also worth mentioning that Li_4SnS_4 with an ionic conductivity of $7 \times 10^{-5} \text{ S cm}^{-1}$ was prepared at 320 °C from aqueous solution, where water was used to obtain a high-purity crystalline phase.^[16] A major challenge in developing solution-processable sulphide SEs is the simultaneous fulfilment of all the following requirements: forming a homogeneous solution for the coatable process, using nontoxic and safe solvents with low boiling points, and ensuring sufficiently high ionic conductivities ($>10^{-4} \text{ S cm}^{-1}$). Another critical issue regarding sulphide SEs is their instability in air.^[17] As-substituted Li_4SnS_4 exhibiting stability in air and high conductivity ($1.39 \times 10^{-3} \text{ S cm}^{-1}$) was recently prepared by a solid-state reaction at 450 °C.^[18] However, the application of this SE may be hindered owing to the use of arsenic, which is extremely toxic.

Here, we report the development of a new class of solution-coatable superionic conductor, $\text{LiI-Li}_4\text{SnS}_4$, which enables us to achieve direct ionic contacts on active materials with highly conductive solidified electrolyte coating. Glass $0.4\text{LiI-}0.6\text{Li}_4\text{SnS}_4$ is prepared at 200 °C from a homogenous MeOH solution to exhibit high ionic conductivity ($4.1 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C), excellent deformability, and dry-air-stability. The conductivity of $4.1 \times 10^{-4} \text{ S cm}^{-1}$ is the highest among all inorganic SEs prepared from homogeneous solution. We find that the deformability and ionic conductivity of the solution-processed Li_4SnS_4 are significantly enhanced at lower preparation temperature and by the addition of LiI. Importantly, the solution-processed 15 wt% $0.4\text{LiI-}0.6\text{Li}_4\text{SnS}_4$ coating on LiCoO_2 ensures much higher surface coverage on LiCoO_2 (81%) than that for conventional mixture electrodes (31%), thus allowing a significant enhancement of the rate capabilities. Our results represent

the first demonstration of the high potential of ASLBs fabricated by a scalable and coatable solution process.

For the synthesis of $x\text{LiI}-(1-x)\text{Li}_4\text{SnS}_4$ ($0.0 \leq x \leq 5.0$), solutions were prepared by dissolving both LiI and Li_4SnS_4 together into anhydrous MeOH. **Figure 1a** shows the homogenous MeOH solution containing fully dissolved LiI and Li_4SnS_4 (0.46 M of a formula unit of $0.4\text{LiI}-0.6\text{Li}_4\text{SnS}_4$, 100 mg mL^{-1}). Powders obtained by drying the as-prepared solution under vacuum at room temperature were subjected to thermogravimetric analysis (TGA) under N_2 , as shown in **Figure 1b**. Owing to its low boiling point (64.7°C), MeOH was removed below 160°C , based on which three different heat-treatment (HT) temperatures (200°C , 320°C , and 450°C) were selected. Hereafter, $x\text{LiI}-(1-x)\text{Li}_4\text{SnS}_4$ prepared at a temperature of y ($^\circ\text{C}$) is referred to as “ $x\text{LiI}-(1-x)\text{LSS}-y$ ”.

Figures 1c, d show the X-ray diffraction (XRD) patterns and ionic conductivities at 30°C with activation energies for $x\text{LiI}-(1-x)\text{Li}_4\text{SnS}_4$ samples ($0.0 \leq x \leq 5.0$) prepared at different temperatures. The sample prepared at 450°C exhibits a pure crystalline Li_4SnS_4 .^[16] As the HT temperature is decreased to 320°C , the XRD pattern shows lowered crystallinity. Decreasing the HT temperature further to 200°C results in an almost amorphous feature. The ionic conductivities of cold-pressed pellets prepared under 370 MPa were measured using Li-ion blocking c-Al/SE/c-Al cells (c-Al: carbon-coated Al foil) by the AC impedance method (Nyquist and Arrhenius plots are shown in Figure S1). Li_4SnS_4 prepared at 450°C exhibits a conductivity of $1.0 \times 10^{-5} \text{ S cm}^{-1}$. Surprisingly, decreasing the HT temperature leads to an increase in the conductivity ($2.1 \times 10^{-5} \text{ S cm}^{-1}$ at 320°C and $8.9 \times 10^{-5} \text{ S cm}^{-1}$ at 200°C). Considering that a minimum temperature of 320°C is required for complete dehydration when using an aqueous solution,^[16] the significantly enhanced conductivity at 200°C in this work highlights the exceptional benefit of using the low-boiling-point MeOH. As x in $x\text{LiI}-(1-x)\text{Li}_4\text{SnS}_4$ increases up to 0.4, the XRD-amorphous features are retained and the

conductivity increases gradually, with the highest conductivity value reaching $4.1 \times 10^{-4} \text{ S cm}^{-1}$ and the lowest activation energy reaching 41.6 kJ mol^{-1} . Subsequently, the conductivity is decreased at $x = 0.5$, at which the segregated crystalline LiI (JCPDS No. 71-3746) is observed (**Figure 1c**). Apart from one exception ($x = 0.0$ vs. 0.1), the activation energies inversely follow the trend of ionic conductivities. Consistent with the results from the AC impedance method, the activation energy obtained from motional narrowing of the ^7Li nuclear magnetic resonance (NMR) data^[19] also confirms the lower activation energy of 0.4LiI-0.6LSS-200 (24.7 kJ mol^{-1}) compared to that of LSS-200 (27.3 kJ mol^{-1}) (see Supporting Information for details, Figure S2). The difference in the activation energy values from the AC impedance and the ^7Li NMR stem from the different time windows of sensing.^[20] While NMR is sensitive to local Li-ion hopping, AC impedance is sensitive to the overall contributions of Li-ion movements, such as grain boundary resistance. Increasing HT temperature for 0.4LiI-0.6Li₄SnS₄ to 450 °C resulted in the formation of SnI₄ and a decrease in conductivity ($4.0 \times 10^{-6} \text{ S cm}^{-1}$, Figure S3). Overall, it is evident that both the composition (the inclusion of LiI) and the structure (whether XRD-amorphous or crystalline as well as whether crystalline LiI is segregated or not) affect the ionic conductivities.

As the first step to elucidate the microstructures of LiI-Li₄SnS₄, high-resolution transmission electron microscopy (HRTEM) analyses were carried out. **Figures 1e, f** exhibit HRTEM images and their corresponding selected-area electron diffraction (SAED) patterns for LSS-200 and 0.4LiI-0.6LSS-200, respectively. Contrary to the XRD-amorphous feature in **Figure 1c**, the LSS-200 here appears to consist of nanometre-sized crystallites. The lattice fringes and the SAED patterns in the inset of **Figure 1e** unequivocally indicates that the nanocrystallites belong to orthorhombic Li₄SnS₄.^[16] In sharp contrast, the HRTEM image and the featureless SAED pattern in **Figure 1f** reveal a completely amorphous structure for 0.4LiI-0.6LSS-200, indicating that the added LiI acts as the glass former by dissolving into Li₄SnS₄. The aberration-corrected scanning TEM (STEM) image and its corresponding

energy dispersive X-ray spectroscopy (EDXS) elemental maps of Sn, S, and I for 0.4LiI-0.6LSS-200 in Figure S4 show homogeneous composition all over the particle. The homogeneous distribution of Li is also confirmed by the STEM image and its corresponding electron energy loss spectroscopy (EELS) map in Figure S5. The Raman spectra for LSS-450, LSS-200, and 0.4LiI-0.6LSS-200 (**Figure 1g**) show the strong peaks centred at 345 cm^{-1} originating from SnS_4^{4-} .^[21] This result implies that the SnS_4^{4-} polyanion is intact regardless of the HT temperature and the inclusion of LiI, which is also corroborated by the similar ^{119}Sn magic angle spinning (MAS) NMR signatures centred at $\sim 59\text{ ppm}$ for LSS-200 and 0.4LiI-0.6LSS-200 (Figure S6).^[16] Further, Sn K-edge extended X-ray absorption fine structure (EXAFS) spectra for LSS-450, LSS-200, 0.1LiI-0.9LSS-200, 0.3LiI-0.7LSS-200, and 0.4LiI-0.6LSS-200 exhibit the main peaks at an identical radial distance that are attributed to Sn-S bonds from SnS_4^{4-} (Figure S7). X-ray absorption near edge structure (XANES) spectra for Sn K-edge and I L-edge show no noticeable difference among the samples (Figure S8). However, a subtle difference between LSS-200 and 0.4LiI-0.6LSS-200 is observed in the ^{119}Sn NMR signatures (Figure S6), where the 0.4LiI-0.6LSS-200 exhibits a slight negative shift in the peak at 59 ppm as compared to LSS-200, indicating the influence of iodide ions in the proximity of SnS_4^{4-} . From the combined spectroscopic analyses, the microstructure of the solution-processed LiI- Li_4SnS_4 prepared at $200\text{ }^\circ\text{C}$ is considered to be a disordered matrix consisting of SnS_4^{4-} and I^- anions around which Li^+ cations occupy the interstitial sites.

Several factors can be considered to account for the enhancement in conductivity after adding LiI to Li_4SnS_4 (0.4LiI-0.6LSS-200: $4.1 \times 10^{-4}\text{ S cm}^{-1}$ vs. LSS-200: $8.9 \times 10^{-5}\text{ S cm}^{-1}$). As a naïve consideration, the concentration of Li may be related to the conductivity.^[22] However, the change in the concentration of Li from Li_4SnS_4 to $x\text{LiI}-(1-x)\text{Li}_4\text{SnS}_4$ is marginal (45.2 atomic % for $x = 0.4$ vs. 44.4 atomic % for $x = 0.0$). The increased conductivities at higher x in $x\text{LiI}-(1-x)\text{Li}_4\text{SnS}_4$ can be explained by highly open frameworks owing to the large ionic radii of iodide ions (0.206 nm)^[23] and/or the lower energy barriers for Li-hopping due to

the highly polarizable nature of iodide ions,^[22,24] which is supported by the fact that the activation energy decreases as x increases from 0.1 to 0.4 (**Figure 1d**). The decrease in conductivity by replacing the iodide ion by a smaller and less polarizable bromide ion ($0.4\text{LiBr}-0.6\text{Li}_4\text{SnS}_4$, $r = 0.182$ nm, 1.4×10^{-4} S cm⁻¹) is also in line with the aforementioned explanation. We also need to explain why the nanocrystalline Li_4SnS_4 prepared at 200 °C exhibits much higher conductivity (8.9×10^{-5} S cm⁻¹) than the highly crystalline one prepared at 450 °C (1.0×10^{-5} S cm⁻¹). Apart from bulk conductivity, the deformability of SEs could also account for the measured conductivity since it influences the grain boundary or interfacial contact resistances.^[4b]

Figures 2a–c show fracture cross-sectional images of the cold-pressed pellets of LSS-450 and LSS-200, and $0.4\text{LiI}-0.6\text{LSS}-200$, respectively. For the highly crystalline LSS-450 pellet (**Figure 2a**), the particles are not deformed/merged well. Decreasing the HT temperature to 200 °C (LSS-200) results in a smoothened cross-sectional surface (**Figure 2b**), indicating enhanced deformability. Therefore, the main source for the lower conductivity of LSS-450 compared to that of LSS-200 is considered to be the poor interfacial contacts between the particles and grains. The low bond energy at the interfaces between nanocrystallites and/or the defect-rich nanostructures could be responsible for the superior deformation of nanocrystalline Li_4SnS_4 (LSS-200) compared to the highly crystalline one (LSS-450).^[8,25] More importantly, for $0.4\text{LiI}-0.6\text{LSS}-200$, an almost poreless fracture cross-sectional surface is observed (**Figure 2c**). The excellent deformability of $0.4\text{LiI}-0.6\text{LSS}-200$ can be explained by its completely amorphous structure and the presence of iodide ions. Following Fajans' rule, the large size and the high polarizability of iodide ions lead to more covalent nature, resulting in the enhanced deformability.^[8,23] The better deformability of $0.4\text{LiI}-0.6\text{LSS}-200$ compared to that of LSS-200 is also confirmed by measurements of density and conductivity as a function of applied pressure. As shown in **Figure 2d**, the

density and the conductivity are saturated at far lower pressures for 0.4LiI-0.6LSS-200 than for LSS200. When the electrodes are prepared by mixing LiCoO₂ with 30 wt% of these SEs and assembled as LiCoO₂/Li-In cells, the variations in the electrochemical performances appear dramatic. **Figures 2e, f** show the voltage profiles at 0.11 mA cm⁻² (0.1C) and the associated rate capabilities, respectively. The better performances of the lower overpotential and the higher capacity are achieved for the SEs in the order of 0.4LiI-0.6LSS-200, LSS-200, and LSS-450, thus highlighting the importance of both ionic conductivity and deformability. The excellent deformability of LiI-Li₄SnS₄ would also be advantageous for buffering the volume change of active materials upon repeated charge and discharge.^[8] Further exploration on incorporation of other highly polarizable elements and alio-/iso-valent substitutions for Sn and S of Li₄SnS₄ along with fine control of microstructure by solution-process may open opportunities to achieve higher conductivities (>10⁻³ S cm⁻¹) than that for 0.4LiI-0.6Li₄SnS₄.

0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ powders were obtained from the LiI- and Li₄SnS₄-dissolved MeOH solution in the presence of LiCoO₂ particles. Since the SE precursor solution wets any exposed surfaces (even porous surfaces) of the LiCoO₂ particles and is solidified, it is possible to achieve direct ionic contacts comparable to those in the case of conventional LIBs using liquid electrolytes. **Figure 3a** shows an field-emission scanning electron microscopy (FESEM) image of the coated LiCoO₂ particle and its corresponding EDXS elemental maps, which confirm uniform SE coatings and their homogeneous composition. (The EDXS elemental map for iodine is shown in Figure S9.) Direct visualization of the SE coating layer was achieved by HRTEM using a focused ion beam (FIB) cross-sectioned sample as seen in **Figure 3b**. An amorphous SE layer of approximately 100 nm thickness covers the LiCoO₂, which is also corroborated by an annular dark field (ADF) STEM image and its corresponding EDXS elemental maps (Figure S10). The direct coating of SEs on active materials offers significant advantages over the conventional mixture electrodes, such as intimate ionic contacts and better spatial distribution of SEs. **Figures 3c,**

d show FESEM images of the surface of the LiCoO₂ composite electrodes prepared by cold-pressing a mixture of LiCoO₂ and 0.4LiI-0.6Li₄SnS₄ powders and that of the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ electrode. While voids are seen between particles in the mixture electrode, the SE-coated LiCoO₂ electrode exhibits a smooth and flat surface. Upon cold-pressing, the soft SEs are deformed by the hard LiCoO₂ particles and are squeezed to fill the voids between the LiCoO₂ particles. The voids observed in the mixture electrode (**Figure 3c**) reflect poor spatial distribution of SEs and their limited contacts with LiCoO₂ particles (**Figure 3d**). In sharp contrast, a cross-sectioned FESEM and the corresponding EDXS elemental maps for the SE-coated LiCoO₂ electrode in **Figure 3e** show that the SEs are well distributed by filling the spaces between the LiCoO₂ particles without noticeable voids, thus implying excellent ionic conduction pathways. (The EDXS elemental map for iodine is shown in Figure S11.) This is also consistent with much lower porosity for the 0.4LiI-Li₄SnS₄-coated LiCoO₂ electrode (7%) than that for the conventional mixture electrode (12%). (See Supporting Information for details.)

The advantage in ionic contacts by SE coatings on active materials is evaluated by comparing the electrochemical performances of LiCoO₂/Li-In cells made of the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ electrode with the ones made of the conventional mixture electrode (**Figure 4**). The weight fraction of SE was 15 wt%. A diagnostic electrochemical analysis was first carried out by comparing the electrochemical impedance spectroscopy (EIS) responses for LiCoO₂/LPS/Li-In cells (Configuration is depicted in Figure S12a.). The Nyquist plots in **Figure 4a** show one semicircle followed by the Warburg tail. The intercept values at the x-axis and the size of the semicircle are assigned as the resistance of LPS SE layer (~54 Ω) and the interfacial resistance, respectively.^[10] The semicircle for SE-coated LiCoO₂ electrode (~16 Ω) is smaller than half that of the mixture electrode (~39 Ω), which can be explained by its much superior ionic contacts. **Figure 4b** compares the discharge capacities varied by the current densities for LiCoO₂/LPS/Li-In cells. Consistent with the EIS

results in **Figure 4a**, a pronounced improvement in the rate capability for the SE-coated LiCoO₂ electrode over the mixture electrode is observed. The performance of the mixture electrode is affected by mixing conditions. The mixture electrode obtained using a vortex mixer shows even inferior performance compared to the manually mixed electrode. This result indicates that the use of SE-coated active materials can lessen the need of process control for mixing during electrode fabrication. Considering the higher conductivity of LPS ($1.0 \times 10^{-3} \text{ S cm}^{-1}$) than that of 0.4LiI-0.6LSS-200 ($4.1 \times 10^{-4} \text{ S cm}^{-1}$), the poor performance of the LiCoO₂/LPS mixture electrode (open square) implies the importance of ionic contacts (and deformability) over conductivity on the overall performance of bulk-type ASLBs. When the LPS/LGPS bilayer having lower resistance ($\sim 13 \text{ } \Omega$, LGPS: $6.0 \times 10^{-3} \text{ S cm}^{-1}$) replaces the LPS SE layer ($\sim 54 \text{ } \Omega$) (Configuration is depicted in Figure S12b.), a more dramatic improvement of the SE-coated LiCoO₂ electrode over the mixture electrode is achieved (**Figure 4c**). The SE-coated LiCoO₂ electrode shows the capacity retention of 83.3% at 1C (113 mA h g⁻¹) as compared to the capacity at 0.1C (135 mA h g⁻¹) while the mixture electrode shows only 46.0% (60 mA h g⁻¹). In the discharge voltage profiles for the LiCoO₂/(LPS/LGPS)/Li-In cells in **Figure 4d**, the SE-coated LiCoO₂ electrode shows a much lower polarization and the resulting higher capacities compared to the mixture electrode. Moreover, the 0.4LiI-0.6LSS-coated LiCoO₂ electrode also outperforms the LiCoO₂/LGPS mixture electrode (**Figures 4c**, S13). This result is surprising in that the conductivity of LGPS ($6.0 \times 10^{-3} \text{ S cm}^{-1}$) is more than one order of magnitude higher than that for 0.4LiI-0.6LSS ($4.1 \times 10^{-4} \text{ S cm}^{-1}$), which again highlights the decisive role of intimate ionic contacts over ionic conductivity on the overall performance of bulk-type ASLBs. Further optimization of the rate performance would be possible by a combination of 0.4LiI-0.6LSS-coated LiCoO₂ and LGPS powders, which can synergize the intimate ionic contacts by the 0.4LiI-0.6LSS coating and the extremely fast ionic transport through the LGPS. This strategy will be our

next mission. As shown in the inset in **Figure 4c**, the 0.4LiI-0.6LSS-coated LiCoO₂ electrode cycled at 1C also exhibits the excellent cycleability (Capacity retention of 95.7% after 80 cycles).

Finally, the galvanostatic intermittent titration technique (GITT) was employed to track the polarization.^[26] Transient voltage profiles and polarization curves for LiCoO₂/LPS/Li-In cells are plotted in **Figure 4e**. The whole range shows a higher polarization for the mixture electrode than that for the SE-coated LiCoO₂ electrode. Moreover, the interfacial contact areas between LiCoO₂ and the SEs were extracted by analysing the transient voltage profiles (**Figures 4e**, S14) (see Supporting Information for details).^[27] Notably, the surface coverage of SEs over the LiCoO₂ in the SE-coated LiCoO₂ electrode (81%) turns out to be 2.6 times higher than that in the mixture electrode (31%). **Figure 4f** shows schematic diagrams illustrating the uneven spatial distribution of SEs and the poor ionic contacts in the mixture electrode as compared to the SE-coated LiCoO₂ electrode, which is confirmed by the surface images of electrodes (**Figures 3c, d**) and the porosity values (7% for the SE-coated LiCoO₂ electrode and 12% for the mixture electrode). These features are responsible for the resulting electrochemical behaviours shown in **Figures 4a-e**. The improved performance by solution-processed coating on active materials was also demonstrated for Li₄SnS₄-coated Li₄Ti₅O₁₂ as the anode material (Figure S15). A 2.7 wt% coating of Li₄SnS₄ on Li₄Ti₅O₁₂ resulted in increase in the reversible capacity at 0.2C from 90 mA h g⁻¹ to 140 mA h g⁻¹. Overall, all the electrochemical results unequivocally demonstrate the superiority of the electrode fabricated from the SE-coated active materials over the mixture electrode, thus revealing the importance of intimate ionic contacts in bulk-type ASLBs. Practical bulk-type ASLBs would require the inclusion of organic components, such as polymeric binders^[28] and nonwoven scaffolds^[10], that provide flexibility and/or better adhesion. However, ionic blockage by those organic components would result in a significant trade-off in the rate performance. The direct ionic contact between active materials and

highly conductive 0.4LiI-0.6Li₄SnS₄ is thus expected to considerably affect the performance of practical bulk-type ASLBs.

Finally, the dry-air-stability of 0.4LiI-0.6Li₄SnS₄ was tested. The conductivity after exposing the 0.4LiI-0.6Li₄SnS₄ powders to dry air for 24 h at 30 °C was still high (from $4.1 \times 10^{-4} \text{ S cm}^{-1}$ to $2.6 \times 10^{-4} \text{ S cm}^{-1}$). This is in sharp contrast to the LPS powders, whose conductivity decreased by more than two orders of magnitude (from $1.0 \times 10^{-3} \text{ S cm}^{-1}$ to $8.0 \times 10^{-6} \text{ S cm}^{-1}$) (Figure S16). The changes in the electrochemical performances of LiCoO₂/LPS/Li-In cells fabricated from the LPS/LiCoO₂ mixture electrodes and the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ electrodes before and after exposure to dry air for 24 h at 30 °C are also compared. When cycled at 0.11 mA cm^{-2} (0.1C), after exposure to dry air, the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ electrode shows negligible decrease in capacity, whereas the LPS/LiCoO₂ mixture electrode exhibits significantly increased polarization and decreased capacity (**Figures 5a, b**), indicating that the solution-processable LiI-Li₄SnS₄ has potential compatibility with practical applications.^[29] The inertness of 0.4LiI-0.6Li₄SnS₄ against dry air is confirmed by the negligible change in the Sn K-edge EXAFS signature (**Figure 5c**). The excellent stability of 0.4LiI-0.6Li₄SnS₄ is in line with the results of previous works for As-substituted Li₄SnS₄^[18] and Li₂SnS₃,^[30] and is explained by adopting the hard and soft acid and base (HSAB) theory.^[7b,18] The soft acid, Sn, is less vulnerable toward attack by the hard base, O, than the hard acid, P.

Similar to the case of LGPS, one drawback of Li₄SnS₄-based SEs is their poor reduction stability at <1 V (vs. Li/Li⁺) because Sn acts as a reducing centre.^[31] However, it does not neutralize the promising advantages of LiI-Li₄SnS₄. In contrast to conventional LIBs using a single liquid electrolyte, configuring with more than one SE is a significant benefit for ASLBs. For example, 3LiBH₄·LiI-coated As-substituted Li₄SnS₄ is operable with Li metal,^[18] and TiS₂/(LGPS/LPS)/Li-In cell maximizes the rate capability with retaining

reversibility.^[10,31b] The latter is also the case for the results of (0.4LiI-0.6LSS-coated LiCoO₂)/(LGPS/LPS)/Li-In cell shown in **Figures 4c, d**, S12b.

In summary, we successfully demonstrated the application of a new, highly conductive, highly deformable, and dry-air-stable glass 0.4LiI-0.6Li₄SnS₄ prepared at 200 °C from a homogeneous MeOH solution for the scalable solution coating with intimate ionic contacts. The combined spectroscopic and electrochemical analyses revealed the importance of the microstructure and the inclusion of LiI on the properties of SEs (conductivity and deformability). Importantly, the comprehensive electron microscopy and electrochemical analyses revealed the significant impact of intimate ionic contacts between the active materials and SEs for the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ electrodes, as compared to the conventional mixture electrodes. The excellent capacity retention of the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ electrode upon exposure to dry air is also very promising for ASLB applications. It should be emphasized that this solution-processable LiI-Li₄SnS₄ unprecedentedly satisfies both high performance and high potential for practical applications. We believe that our results provide new insight into the design/synthesis of ionic conductors as well as a breakthrough for the scalable fabrication of practical all-solid-state batteries.

Experimental Section

Preparation of materials: Crystalline Li₄SnS₄ powders as precursors for the solution process were prepared by heat-treatment of 2 g of a pelletized stoichiometric mixture of Li₂S (99.9%, Alfa Aesar) and SnS₂ (99.999%, American elements) at 450 °C in a quartz ampoule sealed under vacuum. For the solution-based synthesis of LiI-Li₄SnS₄, a stoichiometric amount of the as-prepared Li₄SnS₄ and LiI (99.95%, Alfa Aesar) was dissolved into anhydrous MeOH (99.8%, Sigma-Aldrich) under dry Ar. For typical preparation, 0.36–0.49 M solution (concentration for xLiI-(1-x)Li₄SnS₄ or 100 mg (mL of MeOH)⁻¹) was used. After the

powders were obtained under vacuum at room temperature, further heat-treatment under vacuum at designated temperatures (200 °C, 320 °C, and 450 °C) resulted in the final samples. The solution-processable LiBr-Li₄SnS₄ powders were prepared by using LiBr (99.95%, Alfa Aesar) and Li₄SnS₄ by following the same procedure as that for LiI-Li₄SnS₄. The 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ powder was prepared by the same solution process in the presence of LiCoO₂ powders with a HT temperature of 200 °C; In order to mitigate undesirable side reactions, 0.3 wt% LiNbO₃-coated LiCoO₂ powders were used.^[3a,3g,32] The entire preparation procedure was carried out without exposure to air. The LPS (1.0×10^{-3} S cm⁻¹ at 30 °C) and LGPS (6.0×10^{-3} S cm⁻¹ at 30 °C) powders were prepared by ball-milling followed by HT at 243 °C for 1 h and by solid-state reaction at 550 °C, respectively, as described in our previous reports.^[7b,10]

Materials characterization: The TGA profile was obtained from 25 °C to 600 °C at 0.167 °C s⁻¹ under N₂ using a SDT Q600 (TA Instrument Corp.). XRD cells containing hermetically sealed LiI-Li₄SnS₄ samples with a beryllium window were mounted on a D8-Bruker Advance diffractometer equipped with Cu K_α radiation (0.154056 nm), and were subjected to measurements at 40 kV and 40 mA using a continuous scanning mode at 0.025° s⁻¹. The Raman spectra were measured using a Raman spectrometer (Alpha300R, WITec) with a 532-nm He-Ne laser. The HRTEM and EDXS elemental mapping images were obtained using JEM-2100F (JEOL). The HRTEM images were obtained with 200 kV of acceleration voltage. The EDXS elemental mapping images were obtained using 80 mm² X-Max silicon drift detector (energy resolution = 128 eV) and the INCA software from Oxford Instruments. The aberration-corrected STEM (Hitachi 2700C) was operated at 200 keV, and the corresponding EDXS elemental maps were acquired using a 5030 EDX detector from Bruker. The FESEM images were obtained using the S-4800 (Hitachi Corp.). The cross-sectioned FESEM images and EDXS elemental maps for the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂

electrode were obtained using a JSM-7000F (JEOL) after polishing the cross-sectioned surface at 5 kV for 13 h with an Ar ion beam (JEOL, SM-0910). The weight fraction of the SE coating layer for the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ powders was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using the 720-ES (Varian Corp.). The SE and composite electrode pellets used for characterization were prepared under a pressure of 370 MPa.

Electrochemical characterization: After the LiI-Li₄SnS₄ pellets were prepared by cold-pressing at 370 MPa, the Li-ion conductivity was measured by an AC impedance method using an Iviumstat (IVIUM Technologies Corp.) with symmetric Li-ion blocking c-Al/SE/c-Al cells, in which the carbon coating layers face the SE. All-solid-state cells were fabricated as follows: Composite electrodes were prepared from the LiI-Li₄SnS₄/LiCoO₂ mixture or the LiI-Li₄SnS₄-coated LiCoO₂. Li_{0.5}In prepared by mixing In (99%, Sigma Aldrich) and Li (FMC Lithium Corp.) powders were used as the counter and reference electrode materials. After the SE layer was formed by pelletizing 150 mg of LPS powders by pressing at 74 MPa, 15 mg of the as-prepared composite electrodes was spread, followed by pressing at 370 MPa. Then, 100 mg of the as-prepared Li_{0.5}In was attached on the other side of SE layer by pressing at 370 MPa. All procedures were performed in a polyaryletheretherketone (PEEK) mould (diameter = 1.3 cm) with two Ti metal rods as current collectors. All processes for preparing the SEs and fabricating the all-solid-state cells were performed in an Ar-filled dry box. Galvanostatic charge–discharge cycling test was performed at 30 °C with current densities of 0.11, 0.22, 0.55, 0.77, and 1.10 mA cm⁻². The same current density was applied for charge and discharge. The Nyquist plots for the LiCoO₂/Li-In cells were obtained after charging at 0.11 mA cm⁻² (0.1C) to 30 mA h g⁻¹ and resting for more than 3 h. The GITT measurements were carried out with a pulse current of 0.55 mA cm⁻² for 60 s and rest for 2 h. For the dry-air-stability test, 250 mg of LPS or the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ powders was kept under a flow of dry air (a mixture of O₂ and N₂ with 21/79 vol. ratio).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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Figure 1. Preparation and characterization of solution-processable $x\text{LiI}-(1-x)\text{Li}_4\text{SnS}_4$. a) Photograph of LiI - and Li_4SnS_4 -dissolved MeOH. b) TGA profile under N_2 for the powders obtained by drying the solution under vacuum at room temperature. c) XRD patterns of $x\text{LiI}-(1-x)\text{Li}_4\text{SnS}_4$. The preparation temperatures are given. d) Conductivities of $x\text{LiI}-(1-x)\text{Li}_4\text{SnS}_4$ at 30 $^\circ\text{C}$ and activation energies as a function of x in $x\text{LiI}-(1-x)\text{Li}_4\text{SnS}_4$. HRTEM images of e) Li_4SnS_4 and f) $0.4\text{LiI}-0.6\text{Li}_4\text{SnS}_4$ prepared at 200 $^\circ\text{C}$. The SAED patterns are provided in the insets. g) Raman spectra for LSS-450, LSS-200, and $0.4\text{LiI}-0.6\text{LSS}-200$.

Figure 2. Comparison of deformability of $x\text{LiI}-(1-x)\text{Li}_4\text{SnS}_4$ and electrochemical performances for LiCoO₂/Li-In cells. Fracture cross-sectional FESEM images of a) LSS-450, b) LSS-200, and c) 0.4LiI-0.6LSS-200. d) Normalized densities and conductivities at 30 °C for LSS-200 and 0.4LiI-0.6LSS-200 as a function of pressure. e) Voltage profiles at 0.1C (0.11 mA cm⁻²) and f) rate capabilities for LiCoO₂/Li-In cells in which the electrodes were prepared by mixing LiCoO₂ with LSS-450, LSS-200, and 0.4LiI-0.6LSS-200 with a LiCoO₂:SE weight ratio of 70:30.

Figure 3. 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂. a) FESEM image of 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ particle and its corresponding EDXS elemental maps. b) HRTEM image of FIB-cross-sectioned 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ particle. FESEM surface images of c) 0.4LiI-0.6Li₄SnS₄/LiCoO₂ mixture electrode and d) 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ electrode. The arrows indicate void spaces. e) Cross-sectional FESEM image of 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ electrode and the corresponding EDXS elemental maps. The LiCoO₂:SE weight ratio was 85:15.

Figure 4. Comparative electrochemical characterization of mixture electrode and 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ electrode. a) Nyquist plots for LiCoO₂/LPS/Li-In cells. Rate capabilities of LiCoO₂/SE/Li-In cells when the SE layer is b) Li₃PS₄ (LPS) (Figure S12a) and c) LGPS/LPS bilayer (Figure S12b). Two mixture electrodes, one prepared by manual mixing and one using a vortex mixer, are compared in b. The results of the LPS/LiCoO₂ (b) and the LGPS/LiCoO₂ mixture electrode (c) are also shown for comparison. Cycle performance at 1C for the 0.4LiI-0.6LSS-coated LiCoO₂ electrode is shown in the inset in c. d) Discharge voltage profiles for LiCoO₂/(LGPS/LPS)/Li-In cell. e) Transient discharge voltage profiles and their corresponding polarization plots obtained by GITT for LiCoO₂/LPS/Li-In cell. The enlarged view is shown in the inset. The polarization curves were plotted by subtracting CCV from QOCV in the transient voltage profiles. The LiCoO₂:SE weight ratio was 85:15. f) Schematic illustration of the mixture electrode and the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ electrode. The dark blue and yellow regions indicate LiCoO₂ and SE, respectively.

Figure 5. Dry air stability of 0.4LiI-0.6Li₄SnS₄. Voltage profiles of LiCoO₂/LPS/Li-In cells in which the LiCoO₂ composite electrodes are the LPS/LiCoO₂ mixture electrode or the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ electrode a) before and b) after exposure of the LPS powders and the 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ powders to dry air for 24 h. The C-rate was 0.1C (0.11 mA cm⁻²). c) Sn K-edge EXAFS spectra for 0.4LiI-0.6Li₄SnS₄-coated LiCoO₂ powders before and after exposure to dry air. The LiCoO₂:SE weight ratio was 85:15.

The new, highly conductive ($4.1 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C), highly deformable, and dry-air-stable glass $0.4\text{LiI}-0.6\text{Li}_4\text{SnS}_4$ is prepared using a homogeneous methanol solution. The solution process enables the wetting of any exposed surface of the active materials with highly conductive solidified electrolytes ($0.4\text{LiI}-0.6\text{Li}_4\text{SnS}_4$), resulting in considerable improvements in electrochemical performances of these electrodes over conventional mixture electrodes.

Batteries, Solid electrolytes, Electrodes, Composites, Nanostructures

K. H. Park, D. Y. Oh, Y. E. Choi, Y. J. Nam, L. Han, J.-Y. Kim, H. Xin, F. Lin, S. M. Oh*, Y. S. Jung*

Solution-processable glass $\text{LiI}-\text{Li}_4\text{SnS}_4$ superionic conductors for all-solid-state Li-ion batteries