

Supplementary Information

Manipulating $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ Mixed Discharge Products of All-Solid-State Lithium

Sulfur Batteries for Improved Cycle Life

Jung Tae Kim¹, Adwitiya Rao², Heng-Yong Nie^{3,4}, Yang Hu¹, Wei Han Li¹, Feipeng Zhao¹, Sixu Deng¹, Xiaoge Hao¹, Jiamin Fu¹, Jing Luo¹, Hui Duan¹, Chandra Veer Singh^{2,*}, Changhong Wang^{5,*}, and Xueliang Sun^{1,5*}

¹ Department of Mechanical and Materials Engineering, University of Western Ontario, 1151 Richmond St, London, Ontario, N6A 3K7, Canada.

² Department of Materials Science and Engineering, University of Toronto, Ontario, M5S 3E4 Canada.

³ Surface Science Western, University of Western Ontario, 999 Collip Circle, London, Ontario, N6A 3K7, Canada.

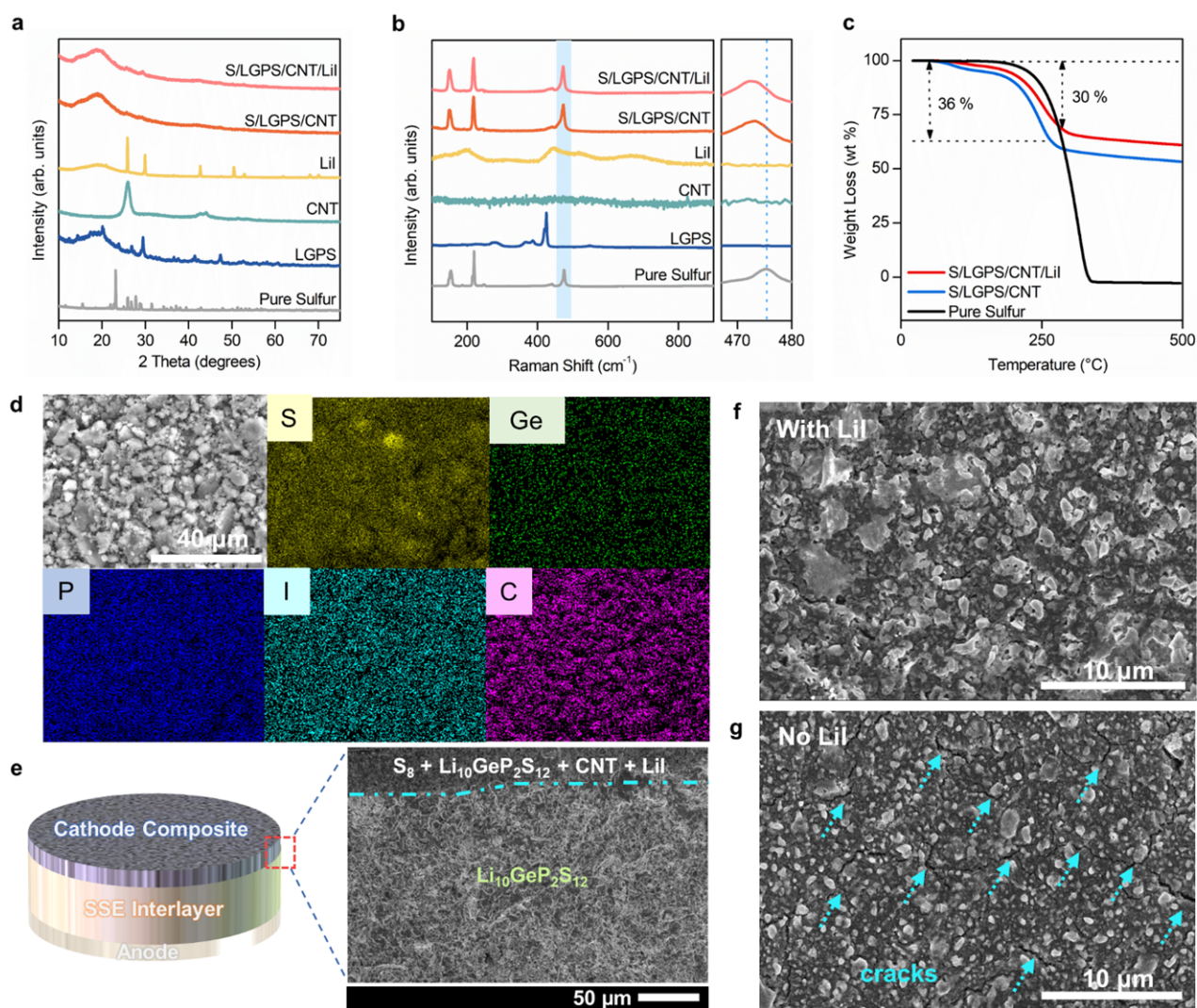
⁴ Department of Physics and Astronomy, University of Western Ontario, 1151 Richmond St, London, Ontario, N6A 3K7, Canada.

⁵ Eastern Institute for Advanced Study, Ningbo 315201, China

* Corresponding email: chandraveer.singh@utoronto.ca, changhongwang@eias.ac.cn and xsun9@uwo.ca

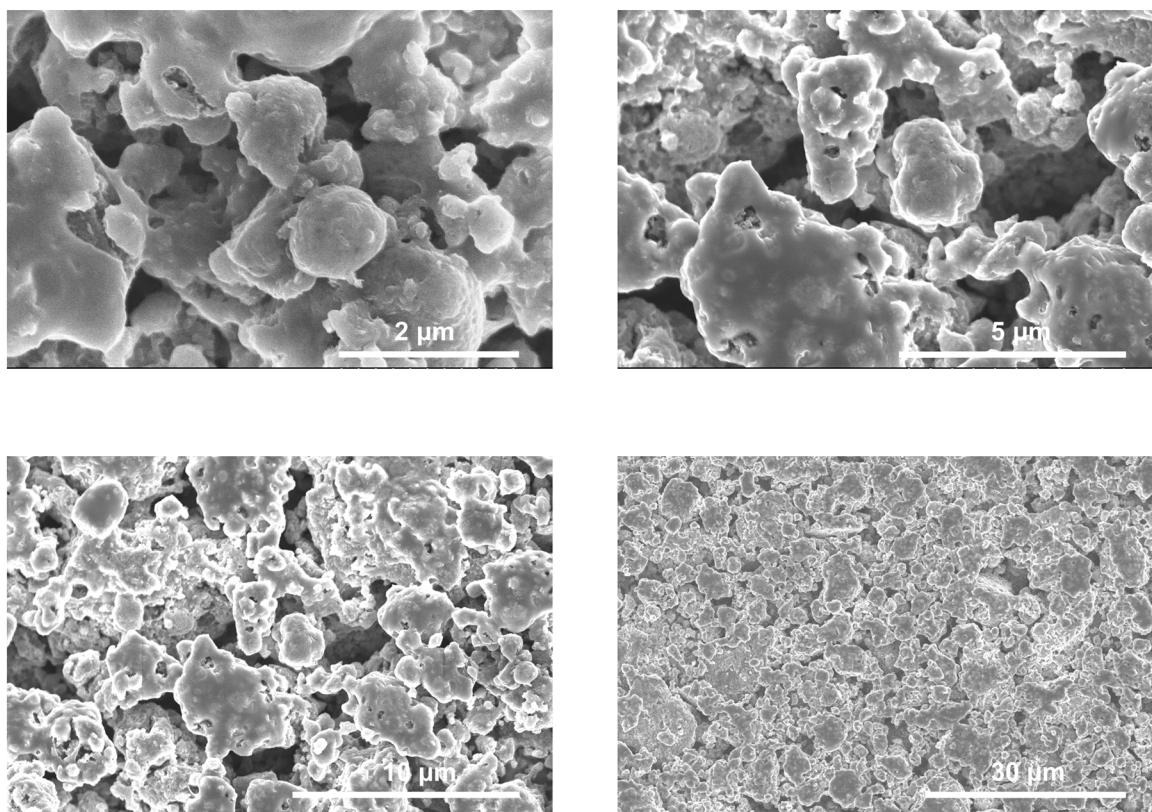
Sulfur content (wt %)	Solid-state electrolyte content (wt %)	Carbon additive content (wt %)	Reference
40	40	20	Sakuda et al. ¹
40	50	10	Sun et al. ²
30	60	10	Han et al. ³
20	40	20	Hou et al. ⁴
30	50	20	Zhang et al. ⁵
30	50	20	Yao et al. ⁶
20	40	20	Zhu et al. ⁷
24	60	16	Wang et al. ⁸
25	60	15	Zhang et al. ⁹

Supplementary Table 1. Summary of the sulfur, solid-state electrolyte, and carbon additive ratio used in recent studies to fabricate the composite electrode of ASSLSBs.

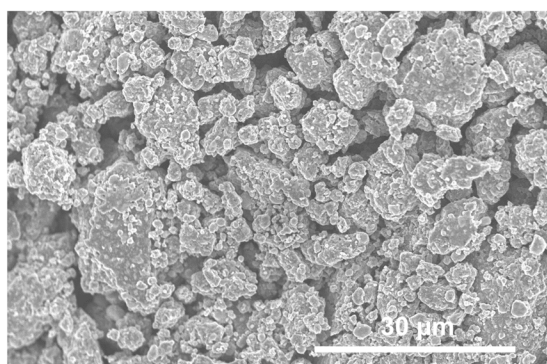
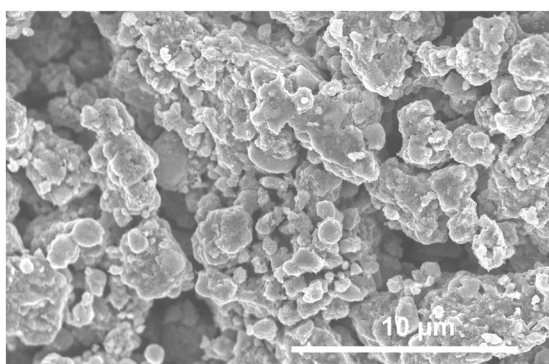
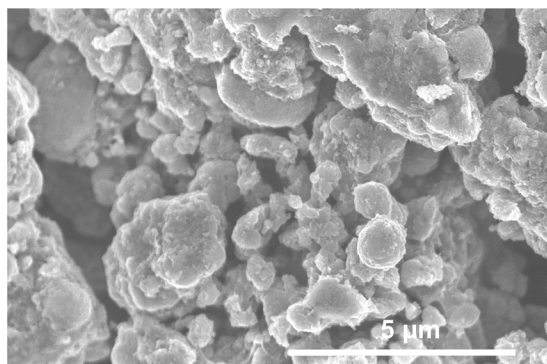
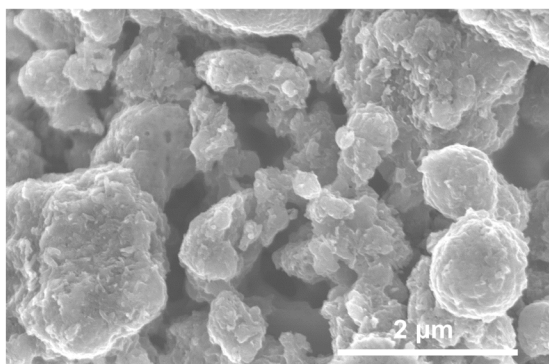


Supplementary Figure 1. Structural characterization of S composite electrodes with and without Lil. (a) XRD patterns of S composite electrodes with and without Lil compared against S, LGPS, CNT, and Lil. (b) Raman spectra of S composite electrodes with and without Lil compared against S, LGPS, CNT, and Lil. (c) TGA curves of S composite electrodes with and without Lil against S. (d) SEM image of the Lil-incorporated S composite electrode after the ball-milling process with corresponding EDX mapping of S, Ge, P, I, and C elements. (e) Schematic illustration and cross-sectional SEM image of the interface between the Lil-incorporated S composite electrode and SSE

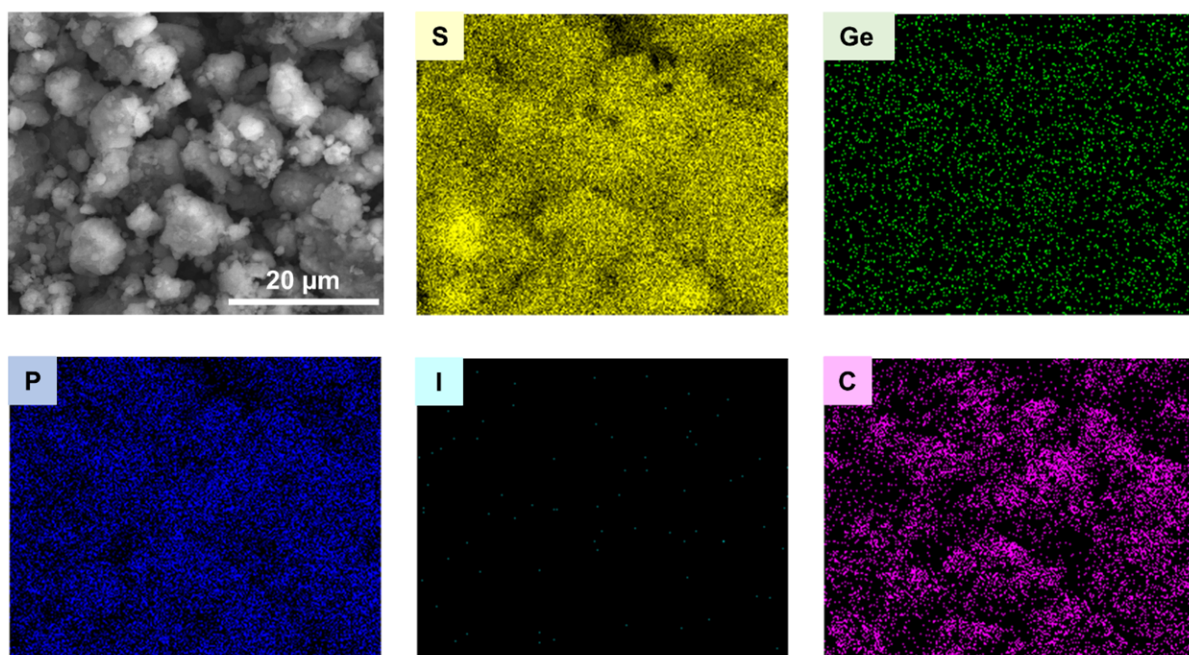
interlayer pelletized at 350 MPa. (f) SEM image (top view) of the Lil-incorporated S composite electrode pelletized at 350 MPa. (g) SEM image (top view) of the S composite electrode without Lil pelletized at 350 MPa.



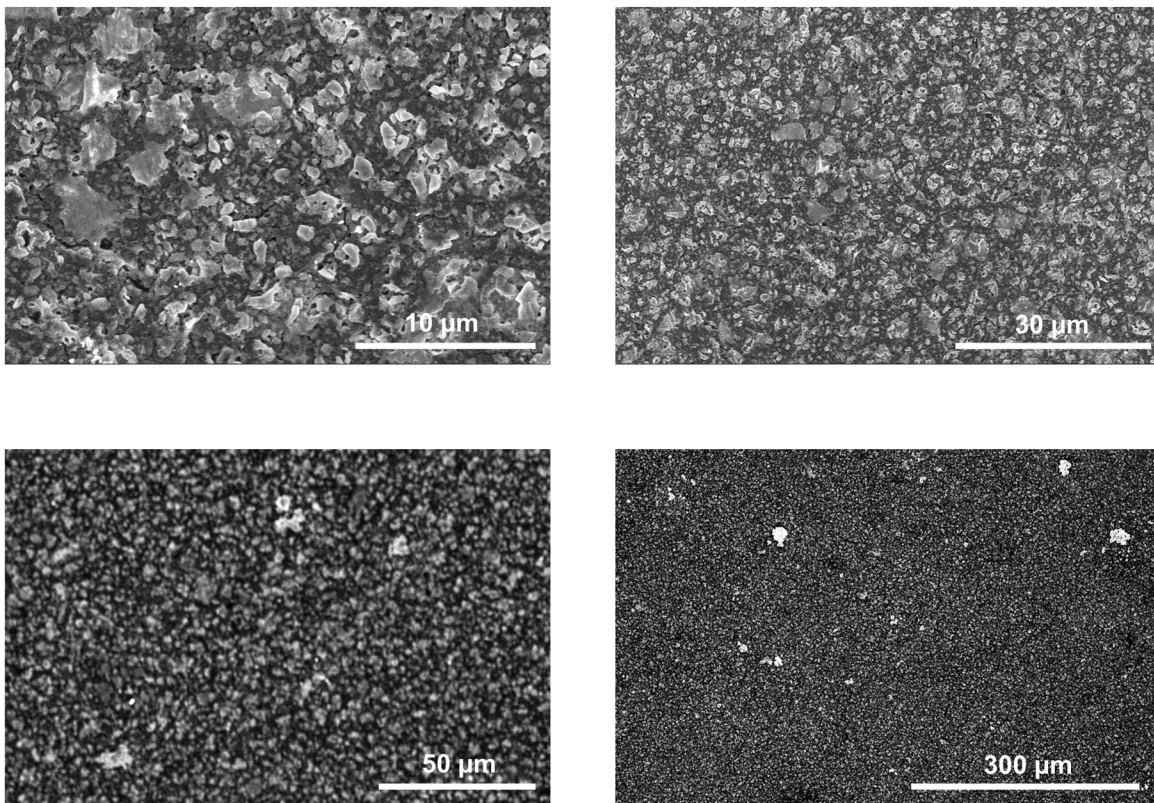
Supplementary Figure 2. SEM images of the Lil-incorporated S composite electrode after ball-milling under different magnification.



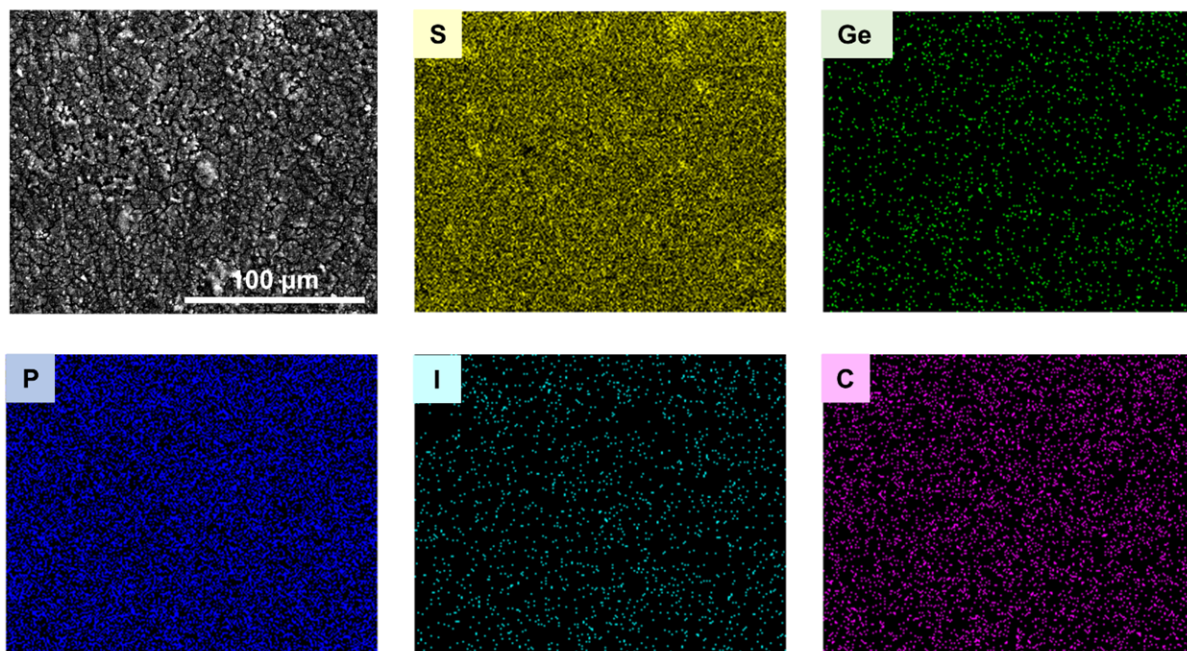
Supplementary Figure 3. SEM images of the S composite electrode without LiI after ball-milling under different magnification.



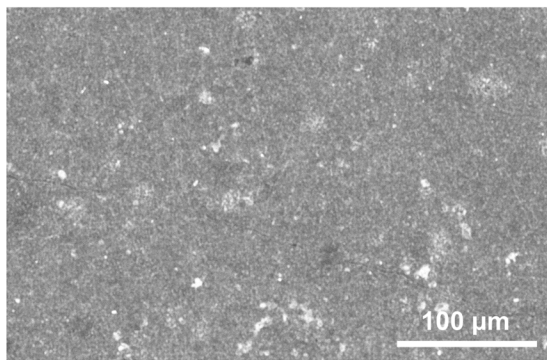
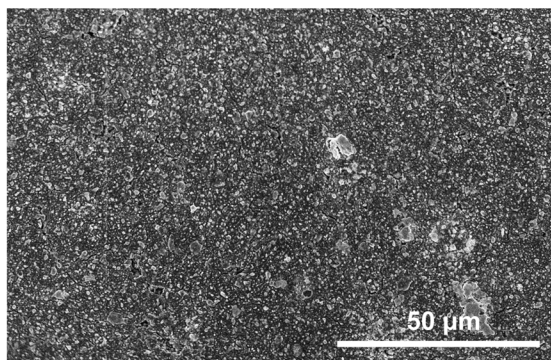
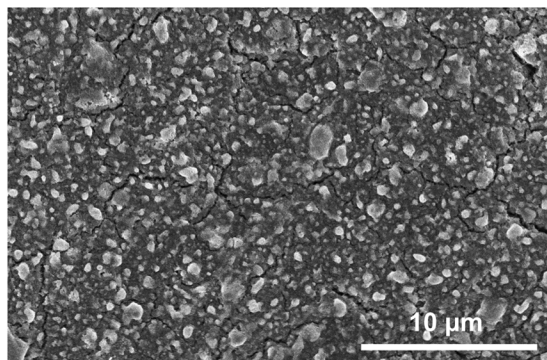
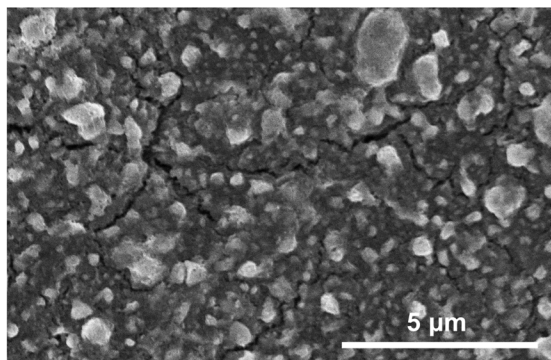
Supplementary Figure 4. SEM image and EDX mapping of the S composite electrode without LiI after ball-milling.



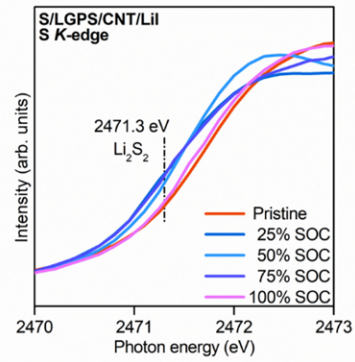
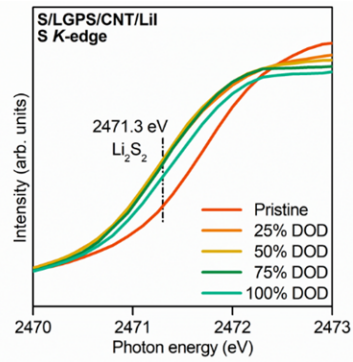
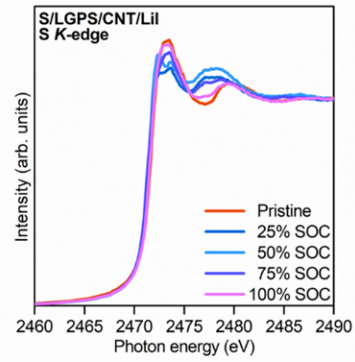
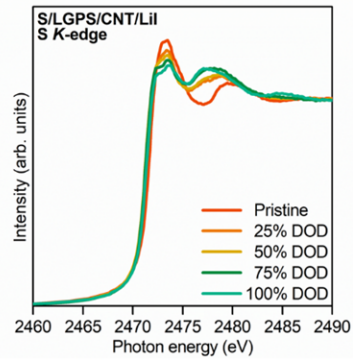
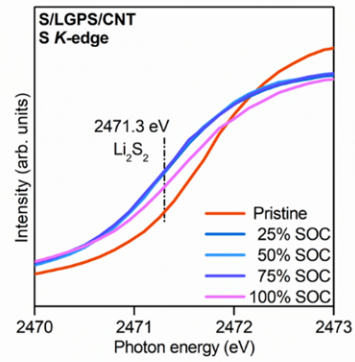
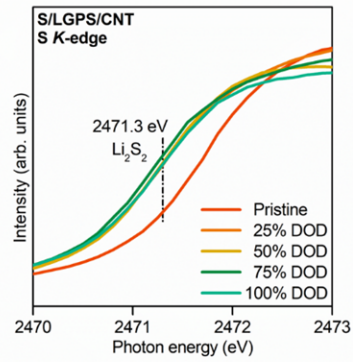
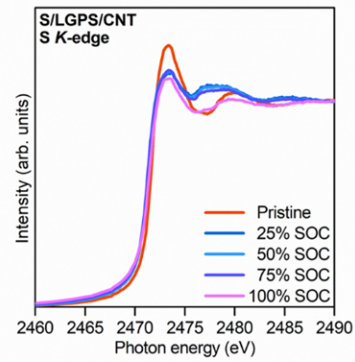
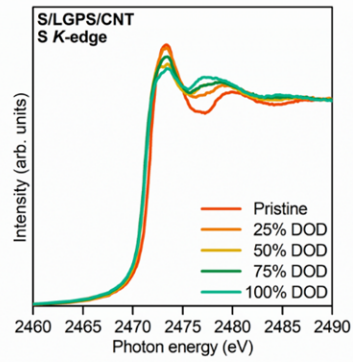
Supplementary Figure 5. Top view SEM images of the LiI-incorporated S composite electrode pelletized at 350MPa under different magnification.



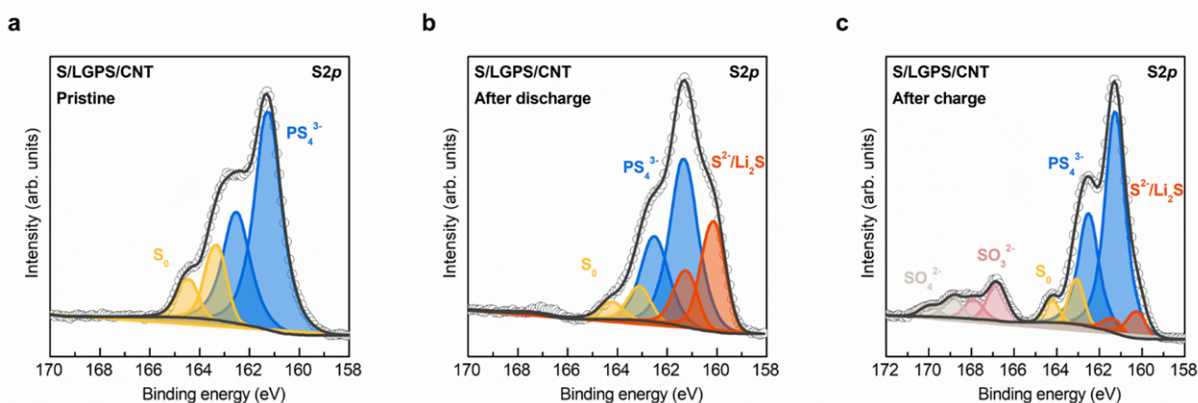
Supplementary Figure 6. Top view SEM image and EDX mapping of the Lil-incorporated S composite electrode pelletized at 350MPa.



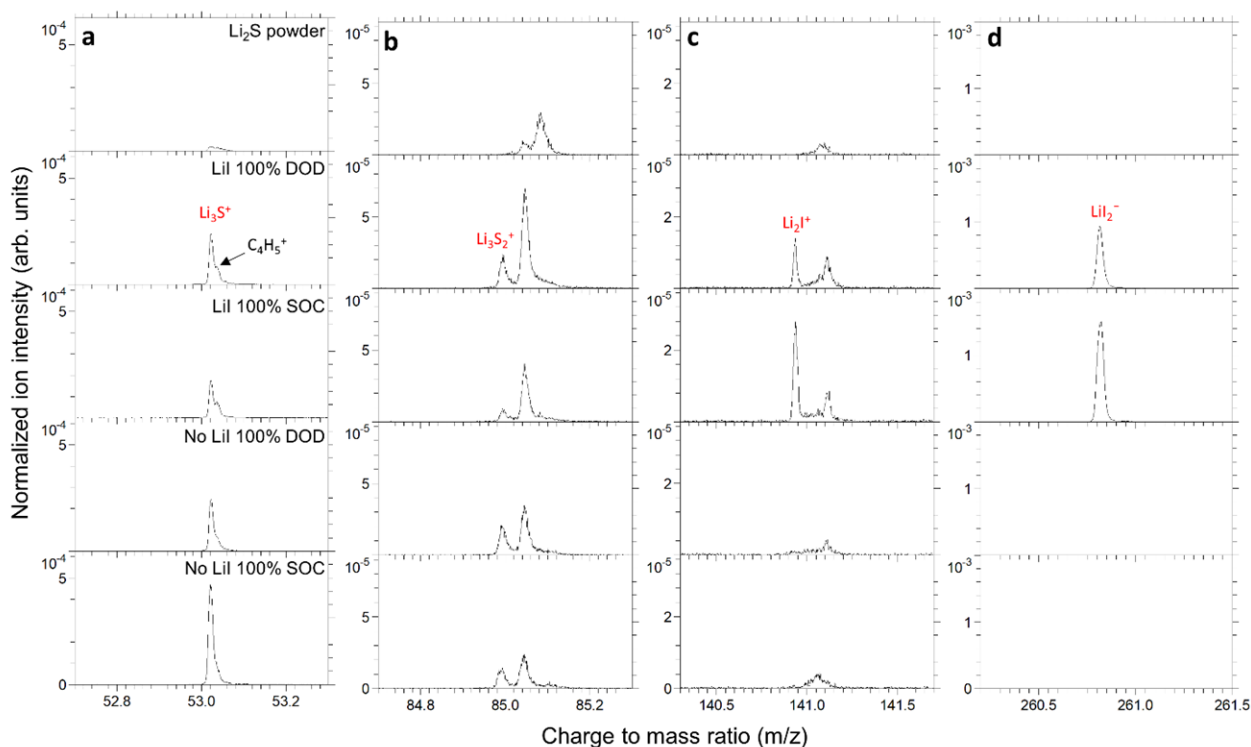
Supplementary Figure 7. Top view SEM images of the S composite electrode without Lil pelletized at 350MPa under different magnification.



Supplementary Figure 8. XANES spectra of ASSLSBs with and without Lil at different discharge/charge states.

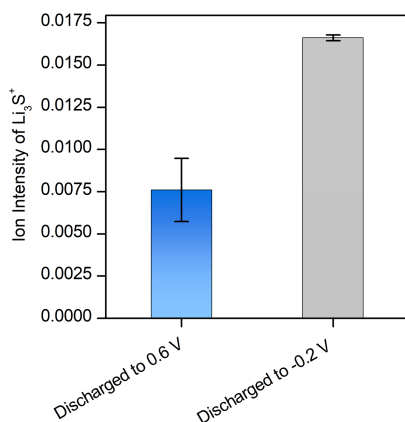


Supplementary Figure 9. S 2p XPS Spectra of ASSLSBs (a) before cycling, (b) after full discharge, and (c) after full charge. The S 2p_{3/2} binding energies of S₀, PS₄³⁻, and S²⁻/Li₂S, are 163.3 eV, 161.3 eV, and 1601.1 eV, respectively.

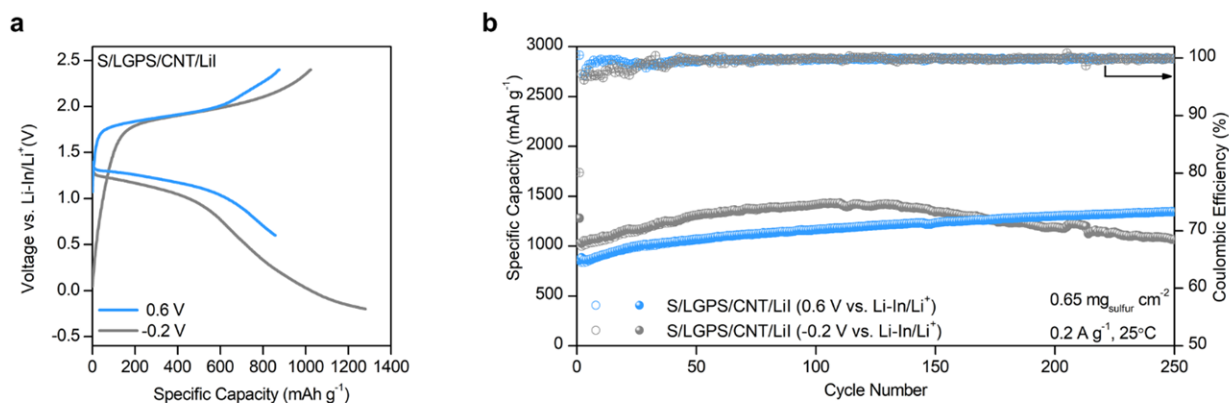


Supplementary Figure 10. ToF-SIMS secondary ion mass spectra in the mass ranges for ions (a) Li₃S⁺, (b) Li₃S₂⁺, (c) Li₂I⁺ and (d) LiI₂⁻ for fully discharged (100% DOD) and

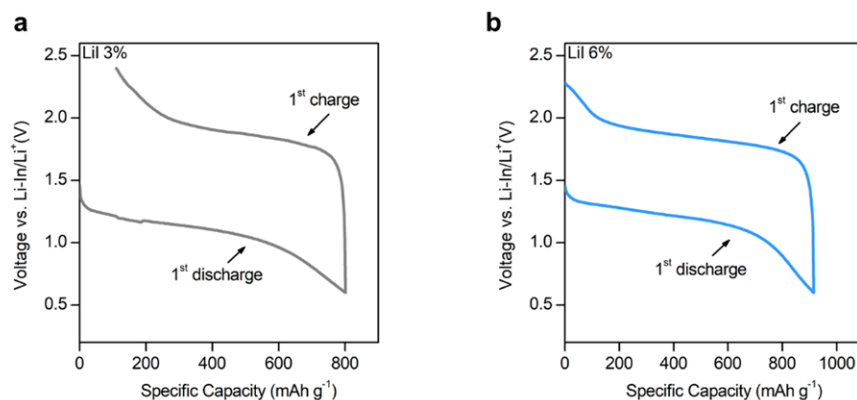
fully charged (100% SOC) products of ASSLSBs with and without LiI. The spectra are normalized to their total ion intensity for comparison purposes.



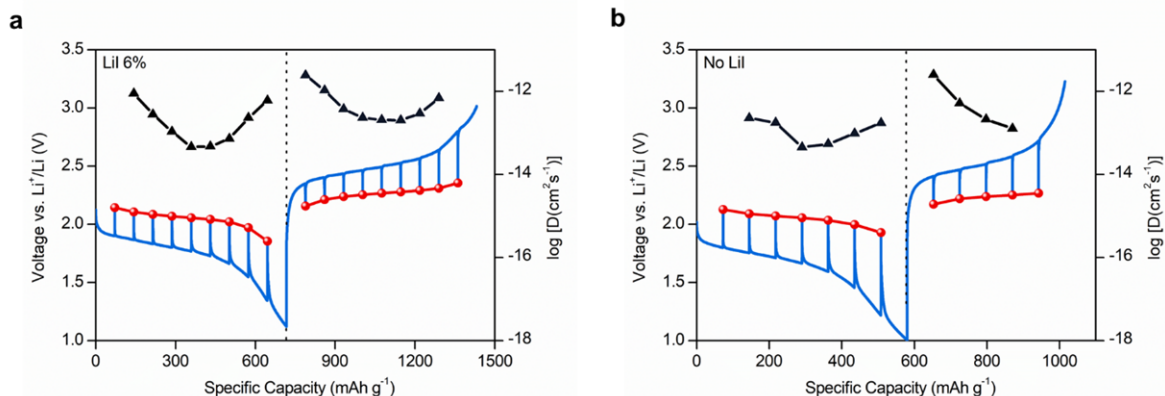
Supplementary Figure 11. Ion intensity of Li_3S^+ for ASSLSBs discharged to 0.6 V (vs. Li-In/Li^+) and 0.2 V (vs. Li-In/Li^+). The Li_3S^+ ion intensity is normalized to the total ion intensity. The error bars represent the standard deviation of the measured intensity ratio and were produced using five independent measurements.



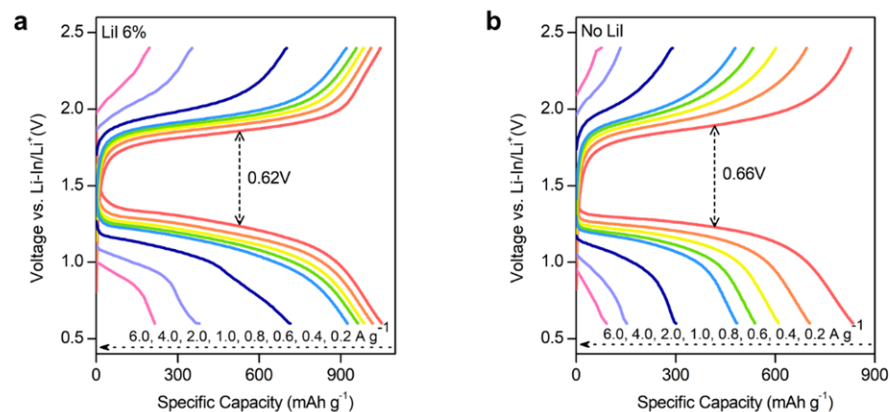
Supplementary Figure 12. (a) Voltage profile of ASSLSBs tested using different lower limit potentials. (b) Corresponding cycling performance of ASSLSBs tested at 0.2 A g^{-1} and 25°C.



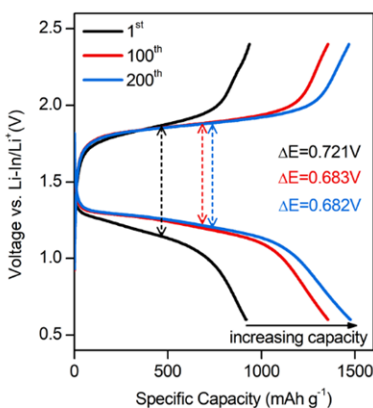
Supplementary Figure 13. (a) Voltage profile showing the reversibility of ASSLSBs in the first cycle with 3 wt% LiI. (b) Voltage profile showing the reversibility of ASSLSBs in the first cycle with 6 wt% LiI.



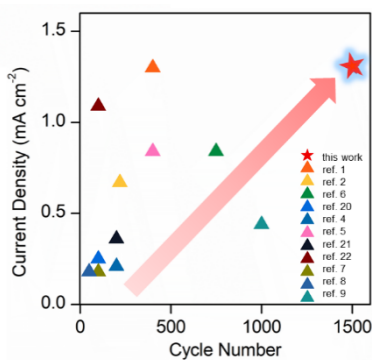
Supplementary Figure 14. GITT curve of ASSLSBs with and without LiI in the first cycle. 0.2 A g⁻¹ current pulses are used for 20-minute increments followed by a 2 h relaxation.



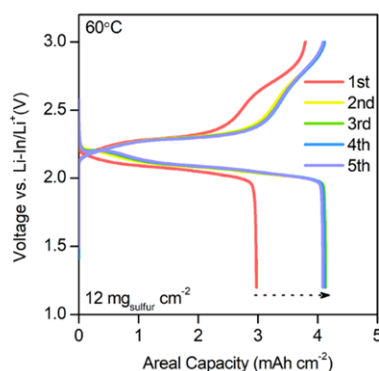
Supplementary Figure 15. Voltage profiles of ASSLSBs with and without LiI cycled over a current density range of 0.2 to 6.0 A g⁻¹.



Supplementary Figure 16. Voltage profile of ASSLSB at 1st, 100th, and 200th cycle.



Supplementary Figure 17. Plot depicting the cycling behavior demonstrated in this work compared to recent ASSLSB reports.



Supplementary Figure 18. Voltage profile of ASSLSBs with active material loading of 12 mg cm⁻².

Supplementary Note 1

Density Functional Theory (DFT) Calculations

The formation energies of Li₂S₂, Li₂S and S were calculated in vacuum and on the Lil surface to provide atomic level insights regarding the catalytic mechanism of Lil. An energy correction of -0.503 eV/atom for anionic sulfur in the structure was utilized based on a previous study conducted by Persson et al.¹⁰ The calculated formation energy values for Li₂S₂, Li₂S and S in vacuum are in close agreement with the data available in the Materials Project database.¹¹ A slight difference was observed due to the use of GGA in this work, as compared to a mixture of GGA and GGA+U in the Materials Project Database for modelling exchange-correlation.¹² The calculated values for formation energies in vacuum are also in good agreement with a previous study conducted by Wang et al.¹³ In vacuum, Li₂S has a formation energy of approximately -1.59 eV/atom and is shown to exist in the bulk phase rather than the molecular phase. This indicates that Li₂S is very stable and requires a large activation potential to facilitate its electrochemical oxidation back to S during charge. The calculated formation energy of Li₂S₂ and Li₂S on

the LiI(100) surface suggests that the compounds are thermodynamically stable in their molecular form on LiI(100), as compared to the compounds in vacuum. In contrast, the formation energy of S₈ on the LiI(100) surface is calculated to be approximately +0.02 eV/atom. This indicates that the S₈ molecule breaks off to form a bulk sulfur phase after it has been oxidized from Li₂S to S on the LiI(100) surface. These results demonstrate that LiI can facilitate the electrochemical oxidation of Li₂S₂ and Li₂S during charge.

To understand the delithiation process of Li₂S₂ and Li₂S during charging, the energy required to extract one lithium atom from bulk Li₂S and adsorbed Li₂S₂ and Li₂S was computed using DFT. Barrier to Li removal could not be calculated for bulk Li₂S₂ because it is meta-stable (energy above convex hull = 0.315 eV/atom), resulting in immediate structural decomposition.¹⁴ For the adsorbed substrate, one Li atom was removed from the adsorbed Li₂S and Li₂S₂ molecule as per the following reaction: (1) Li₂S → Li-S* + Li* and (2) Li₂S₂ → Li-S-S* + Li*, respectively. The lithium extraction energy for the adsorbed Li₂S₂ and Li₂S molecules were calculated using the following expression: $E_{\text{ext}} = E(\text{Li-S}^*/\text{Li-S-S}^*) - E(\text{Li}_2\text{S}_{(\text{ads})}/\text{Li}_2\text{S}_{2(\text{ads})})$. The lithium vacancy formation energy of a bulk Li₂S crystal was calculated using a large supercell of 96 atoms for bulk Li₂S, using the following expression: $E_{\text{vac}} = E(\text{Li}_2\text{S}_{(\text{bulk with 1 Li vacancy})}) - E(\text{Li}_2\text{S}_{(\text{bulk})})$. The lithium extraction energy was calculated to be +4.10 eV and +3.78 eV for the adsorbed Li₂S and Li₂S₂ molecule, respectively, while the lithium vacancy formation energy of the bulk Li₂S crystal was calculated to be +5.75 eV per Li atom. After accounting for the energy required to form Li₂S on the LiI surface, the overall activation peak was lowered by 0.65 eV/atom, which indicates that the energy required for delithiation of Li₂S becomes lower in the

presence of Lil as compared to bulk Li_2S . On Lil(100) surface, the overall activation peak for Li_2S_2 as compared to Li_2S was 0.42 eV/atom lower.

Supplementary Note 2

Structural Characterization of Cathode Composites With and Without Lil

Two cathode composites with and without Lil were prepared by mixing sulfur (S), $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) SSE, carbon nanotubes (CNTs), and lithium iodide (Lil) using a ball-milling method. The absence of diffraction peaks in the XRD patterns for both the cathode composites with and without Lil indicates that the incorporated materials were homogeneously mixed after the ball-milling process (Supplementary Fig. 1a). The Raman spectra in Supplementary Fig. 1b shows that the peak at 472 cm^{-1} representative of the S-S bonds in elemental sulfur shows a slight redshift for both the composites with and without Lil. This implies a reduced interaction between S-S bonds, which is most likely caused by the CNTs and/or Lil.¹⁵ The sulfur content in the cathode composites with and without Lil was approximately 30 and 36 wt%, respectively, as determined by thermogravimetric analysis (TGA) (Supplementary Fig. 1c). Interestingly, the sublimation temperature of sulfur in both cathodes slightly accelerates, in comparison to pure sulfur. This can be attributed to the high thermal conductivity of the CNTs, which accelerates sulfur sublimation during heating.¹⁶ As Lil exhibits a lower thermal conductivity when compared to carbon, the sulfur in the Lil-incorporated cathode composite begins to sublime at a slightly higher temperature than its counterpart. The morphology of the ball-milled cathode composites with and without Lil are shown by the scanning electron microscopy (SEM) images in Supplementary Fig. 1d, Supplementary Fig. 2, and

Supplementary Fig. 3. Energy dispersive X-ray spectroscopy (EDX) confirms a homogenous distribution of S, Ge, P throughout both cathode composites and I for the composite with Lil (Supplementary Fig. 1d and Supplementary Fig. 4). The cross-sectional SEM image confirms that the Lil-incorporated cathode composite establishes good contact with the SSE interlayer (Supplementary Fig. 1e). Iodine ions have a larger ionic radius ($r_{\text{I}^-} = 206 \text{ pm}$) compared to sulfur ions ($R_{\text{S}^{2-}} = 170 \text{ ppm}$), which means that Li-I has a longer ionic bond length and higher polarizability, indicating high Li^+ mobility and soft mechanical properties.^{15,17} Top view SEM images of the pelletized cathode composites were taken to provide information about the surface morphology of the samples. The pellet with Lil exhibits a dense and compact morphology, indicating intimate contact between particles (Supplementary Fig. 1f and Supplementary Fig. 5). EDX mapping confirms the even distribution of elements (Supplementary Fig. 6). In contrast, the pellet without Lil has several cracks on the surface (Supplementary Fig. 1g and Supplementary Fig. 7). It can be inferred that Lil can improve contact at the tri-phase interface between sulfur, LGPS, and CNTs in the cathode composite. This phenomenon is consistent with other studies that have incorporated halide materials such as fluorine.^{18,19}

References

1. Sakuda, A., Sato, Y., Hayashi, A. & Tatsumisago, M. Sulfur-Based Composite Electrode with Interconnected Mesoporous Carbon for All-Solid-State Lithium–Sulfur Batteries. *Energy Technol* **7**, 1900077 (2019).
2. Sun, X. *et al.* High Surface Area N-Doped Carbon Fibers with Accessible Reaction Sites for All-Solid-State Lithium-Sulfur Batteries. *Small* **18**, 2105678 (2022).
3. Han, Q. *et al.* Outstanding cycle stability and rate capabilities of the all-solid-state Li-S battery with a Li₇P₃S₁₁ glass-ceramic electrolyte and a core-shell S@BP2000 nanocomposite. *J Mater Chem A Mater* **7**, 3895–3902 (2019).
4. Hou, L.-P. *et al.* Improved interfacial electronic contacts powering high sulfur utilization in all-solid-state lithium–sulfur batteries. *Energy Storage Mater* **25**, 436–442 (2020).
5. Zhang, Q. *et al.* CNTs@S composite as cathode for all-solid-state lithium-sulfur batteries with ultralong cycle life. *J Energy Chem* **40**, 151–155 (2020).
6. Yao, X. *et al.* High-Performance All-Solid-State Lithium–Sulfur Batteries Enabled by Amorphous Sulfur-Coated Reduced Graphene Oxide Cathodes. *Adv Energy Mater* **7**, (2017).
7. Zhu, G. L. *et al.* A Self-Limited Free-Standing Sulfide Electrolyte Thin Film for All-Solid-State Lithium Metal Batteries. *Adv Funct Mater* **31**, (2021).
8. Wang, S. *et al.* High-Conductivity Argyrodite Li₆PS₅Cl Solid Electrolytes Prepared via Optimized Sintering Processes for All-Solid-State Lithium-Sulfur Batteries. *ACS Appl Mater Interfaces* **10**, 42279–42285 (2018).
9. Zhang, Y. *et al.* High-performance all-solid-state lithium-sulfur batteries with sulfur/carbon nano-hybrids in a composite cathode. *J Mater Chem A Mater* **6**, 23345–23356 (2018).
10. Wang, A. *et al.* A framework for quantifying uncertainty in DFT energy corrections. *Sci Rep* **11**, 15496 (2021).
11. Jain, A. *et al.* Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Mater* **1**, 011002 (2013).
12. Jain, A. *et al.* Formation enthalpies by mixing GGA and GGA
$$E_{\text{form}} = \frac{1}{N} \sum_i E_i - U$$
 calculations. *Phys Rev B* **84**, 045115 (2011).
13. Gao, G., Zheng, F., Pan, F. & Wang, L. Theoretical Investigation of 2D Conductive Microporous Coordination Polymers as Li–S Battery Cathode with Ultrahigh Energy Density. *Adv Energy Mater* **8**, 1801823 (2018).
14. The Materials Project. *Materials Data on LiS by Materials Project*. United States: N. p., 2020. Web. doi:10.17188/1666639.
15. Wan, H. *et al.* Understanding LiI–LiBr Catalyst Activity for Solid State Li₂S/S Reactions in an All-Solid-State Lithium Battery. *Nano Lett* **21**, 8488–8494 (2021).

16. Kumanek, B. & Janas, D. Thermal conductivity of carbon nanotube networks: a review. *J Mater Sci* **54**, 7397–7427 (2019).
17. Asano, T. *et al.* Solid Halide Electrolytes with High Lithium-Ion Conductivity for Application in 4 V Class Bulk-Type All-Solid-State Batteries. *Adv Mater* **30**, 1803075 (2018).
18. Zhang, S. *et al.* Advanced High-Voltage All-Solid-State Li-Ion Batteries Enabled by a Dual-Halogen Solid Electrolyte. *Adv Energy Mater* **11**, 2100836 (2021).
19. Mo, F. *et al.* Inside or Outside: Origin of Lithium Dendrite Formation of All Solid-State Electrolytes. *Adv Energy Mater* **9**, 1902123 (2019).
20. Alzahrani, A. S. *et al.* Confining Sulfur in Porous Carbon by Vapor Deposition to Achieve High-Performance Cathode for All-Solid-State Lithium–Sulfur Batteries. *ACS Energy Lett* **6**, 413–418 (2021).
21. Pan, H. *et al.* Carbon-free and binder-free Li-Al alloy anode enabling an all-solid-state Li-S battery with high energy and stability. *Sci. Adv* **8**, eabn4372 (2022).
22. Zhu, X. *et al.* Exploring the concordant solid-state electrolytes for all-solid-state lithium-sulfur batteries. *Nano Energy* **96**, (2022).