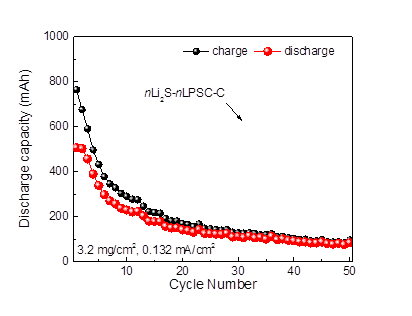
**Supplementary information**

**Quantifying the local Li-ion diffusion over the grain boundaries of a protective coating, revealing the impact on the macroscopic Li-ion transport in an all-solid-state battery**

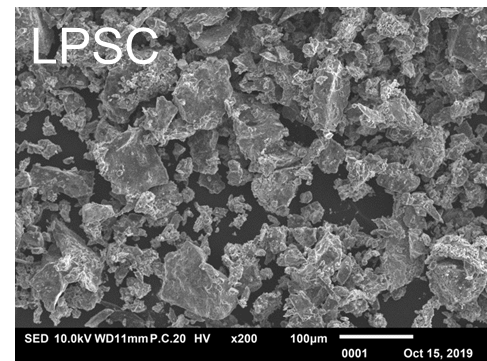
Ming Liua, Chao Wanga, Chenglong Zhaoa,b, Eveline van der Maasa, Kui Linb, Violetta A. Arszelewskaa, Baohua Lib, Swapna Ganapathya\* and Marnix Wagemakera\*

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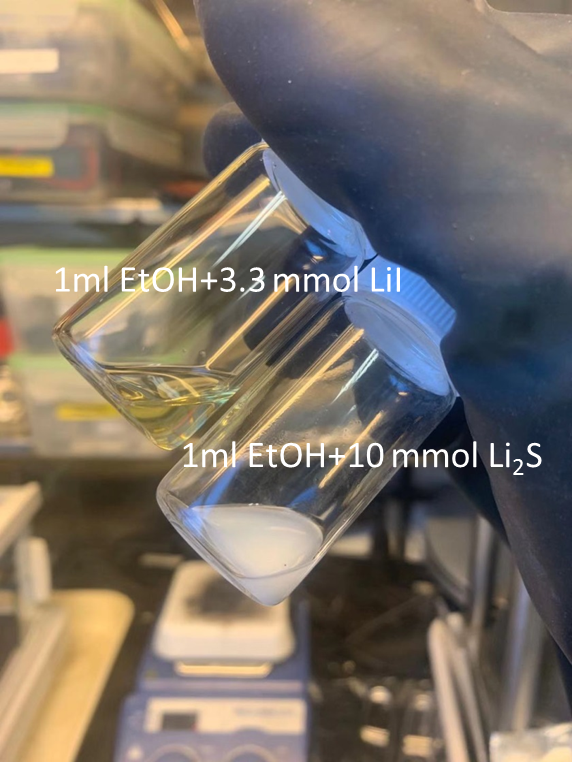
b Key Laboratory on Power Battery Research and Shenzhen Geim Graphene Center, Tsinghua Shenzhen International Graduate School, Tsinghua University, Guangdong 518055, China.



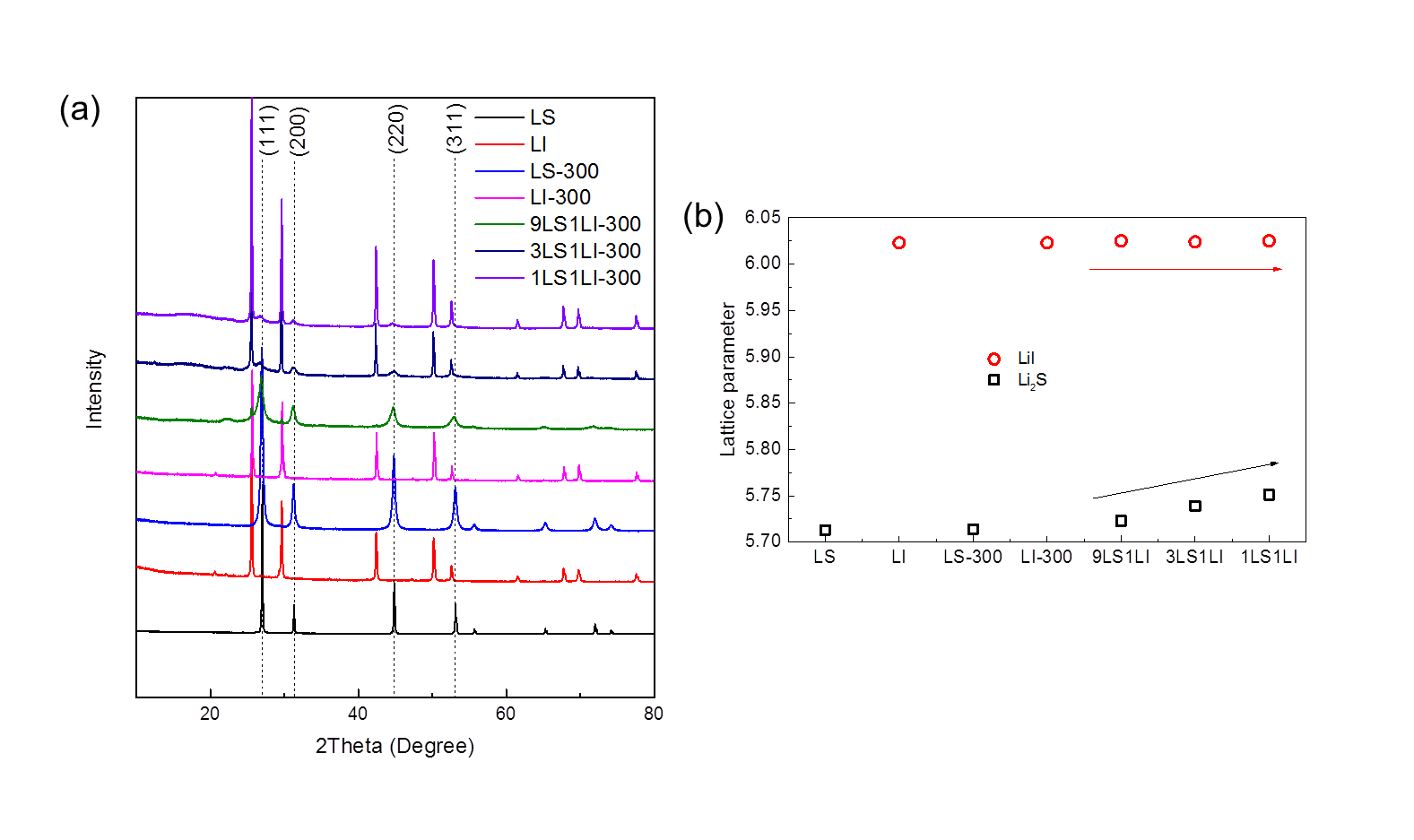
**Figure S1|** Cycle performance of battery with *n*Li2S-*n*LPSC-C cathode.



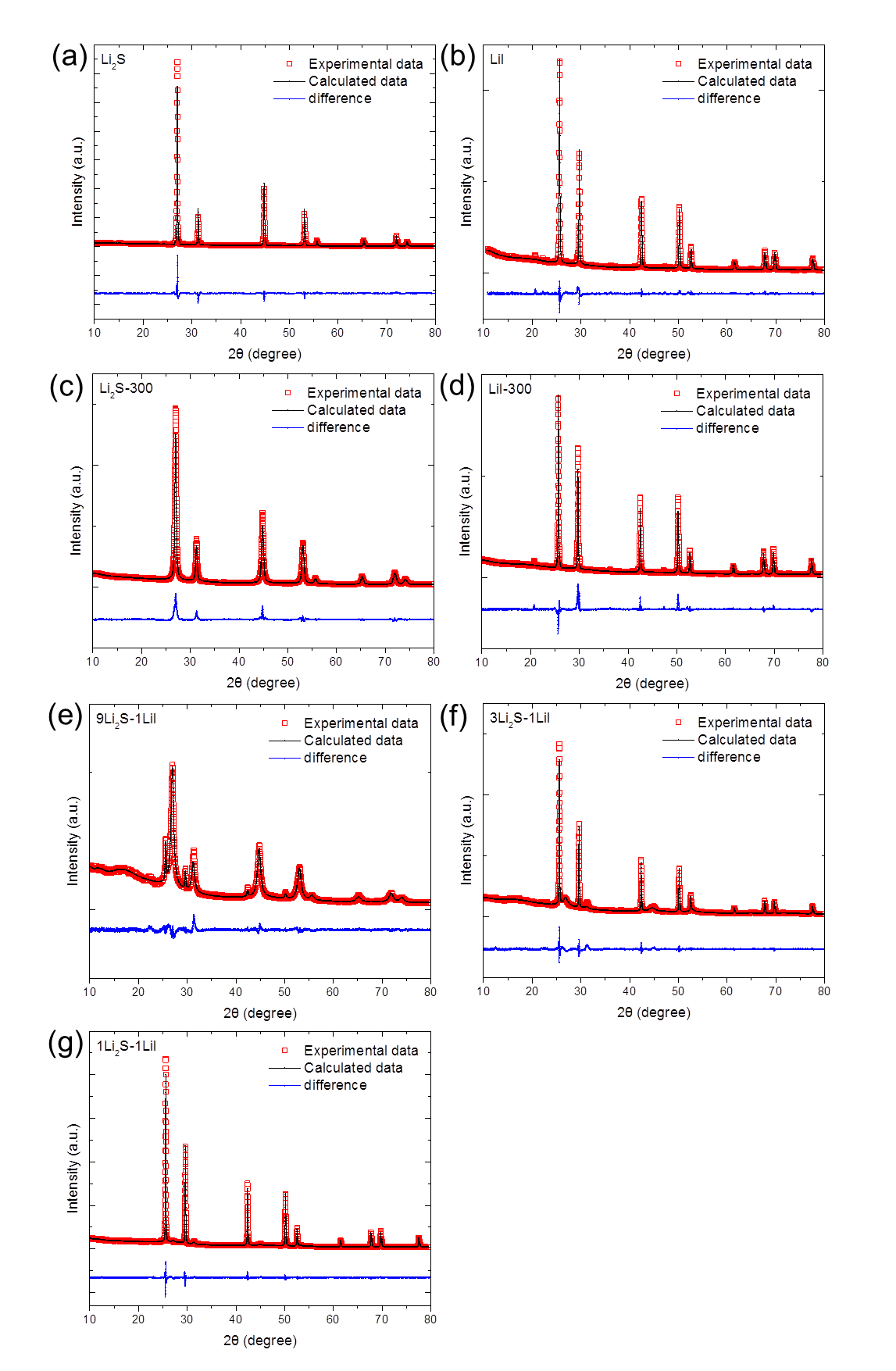
**Figure S2|** SEM images of micron sized LPSC.



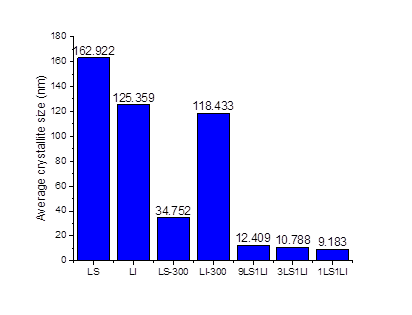
**Figure S3|** Optical image of 3.3 mmol fully dissolved LiI and 10 mmol partially dissolved Li2S in 1 ml ethanol respectively.

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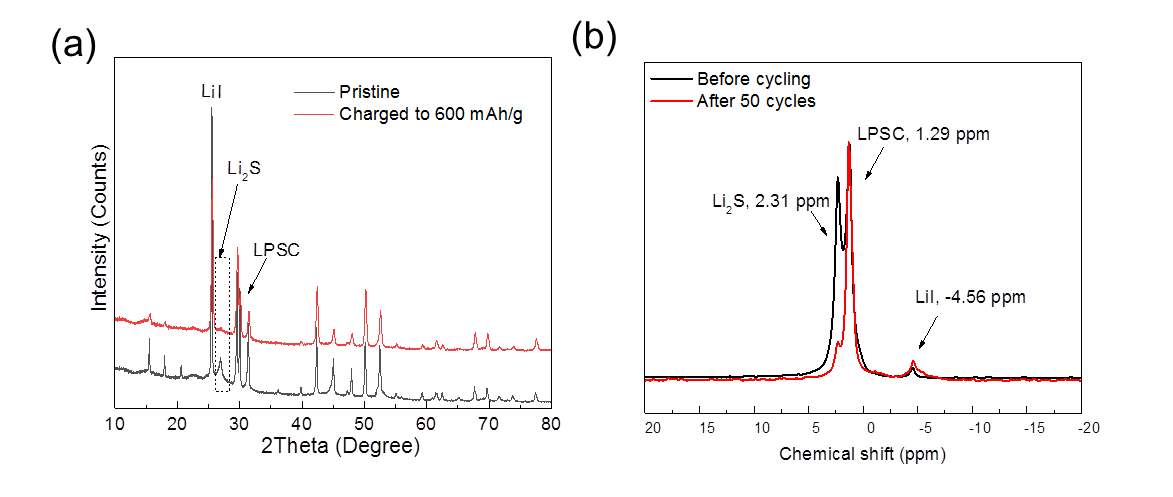
**Figure S4|** (a) XRD patterns and (b) fits lattice parameter of the Li2S, LiI and Li2S-LiI materials. All the patterns are fit with the Rietveld method as implemented in GSAS.



**Figure S5|** Rietveld refinement of Li2S, LiI and Li2S-LiI based on diffraction patterns given in **Figure S4**.



**Figure S6|** Average crystallite size of Li2S, LiI and Li2S in Li2S-LiI based on the Rietveld refinement in **Figure S5**.



**Figure S7|** Post mortem (a)XRD and (b) NMR analysis of the *m*Li2S(LiI)-*m*LPSC-C active materials after activation to 600 mAh/g and after 50 cycles to 600 mAh/g under charged state.

**Table S1|** Activation voltage and over potential in our work compared with open literature as shown in **Figure 4d**.

|  |  |  |  |
| --- | --- | --- | --- |
| Title | Activation platform | Over-potential | Reference number |
| Accessing the bottleneck in all-solid state batteries, lithium-ion transport over the solid-electrolyte electrode interface | ~1.8 V vs. In-Li | ~400 mV | 1 |
| Li2S-Based Solid Solutions as Positive Electrodes with Full Utilization and Super long Cycle Life in All-Solid-State Li/S Batteries | ~2.4 V vs. In-Li | ~500 mV | 2 |
| In Situ Generated Li2S−C Nanocomposite for High-Capacity and Long-Life All-Solid-State Lithium Sulfur Batteries with Ultrahigh Areal Mass Loading | ~1.85 V vs. In-Li | ~300 mV | 3 |
| High-Performance All-Solid-State Lithium−Sulfur Battery Enabled by a Mixed-Conductive Li2S Nanocomposite | ~2 V vs. In-Li | ~700 mV | 4 |
| High performance all-solid-state lithium-sulfur battery using a Li2S-VGCF nanocomposite | ~2.5 V vs. In-Li | ~600 mV | 5 |
| Cathode-Supported All-Solid-State Lithium–Sulfur Batteries with High Cell-Level Energy Density | ~2.4 V vs. In-Li | ~500 mV | 6 |
| Carbon-coated Li2S cathode for improving the electrochemical properties of an all-solid-state lithium-sulfur battery using Li2S-P2S5 solid electrolyte | ~2.5 V vs. In-Li | ~200 mV | 7 |
| This work | 1.69 V vs. In-Li | ~100 mV | 8 |

**References**

1 Yu, C. *et al.* Accessing the bottleneck in all-solid state batteries, lithium-ion transport over the solid-electrolyte-electrode interface. *Nat Commun* **8**, 1086 (2017).

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