Electronic Supplementary Information (ESI)

## Surface Modification of Garnet Solid Electrolytes with Amorphous SnO<sub>2</sub> via Atomic Layer Deposition

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Fig. S1 Density and packing density of LLCZN before and after sintering.



Fig. S2 TGA curve of the LLCZN powders with no obvious weight loss.



**Fig. S3** (a) SEM image of the cross section of LLCZN pellets and (b,c) EDS mapping of La and Zr which are uniformly distributed.



**Fig. S4** XPS of LLCZN and SnO<sub>2</sub> coated LLCZN. (a) Full spectra of Li, C, O, Sn, La, and Zr; (b,c,d) spectral lined of La, Zr, and Sn of pristine LLCZN; (e,f,g) spectral lines of La, Zr, and Sn of SnO<sub>2</sub> coated LLCZN.



**Fig. S5** (a) Dark field TEM image of as-scratched SnO<sub>2</sub> powders, (b) HRTEM image of the red box area, and (c) SAED pattern. (d) Overall EDS mapping images of Zr, La and Sn.



**Fig. S6** AFM image of the pristine LLCZN pellet, which shows a rough surface with a fluctuation of over 100 nm.



**Fig. S7** Specific capacity and coulombic effeciency of Li|liquid electrolyte|LLCZN cells with the cut-off voltage from 0.5 V to 4.2 V.



Fig. S8 EIS images of lithium symmetric cell of different thickness of  $SnO_2$ .



Fig. S9 EIS of the symmetric cell before and after cycling.



Fig. S10 CV curve of Li/LLCZN ALD SnO<sub>2</sub>/Li cells at the voltage range of -0.5-5V with the scan rate of 1 mV s<sup>-1</sup>.



Fig. S11 XPS of after-cycled  $SnO_2$  coated LLCZN. (a) Full spectra of Li, C, O, Sn, La, and Zr; (b) spectral lined of Li 1s; (c) spectral lines of Sn  $3d_{5/2}$ .