

## Support Information

# Halide-sulfide bilayer electrolytes for LiFePO<sub>4</sub>-based all-solid-state batteries

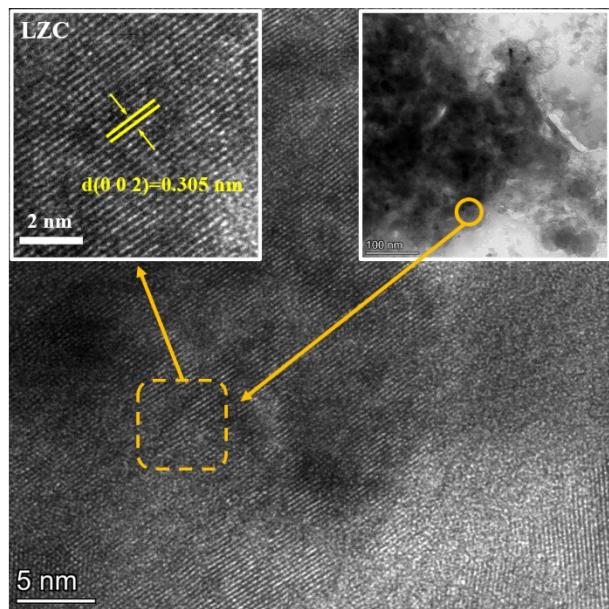
Guoyao Zhang <sup>a</sup>, Xixi Shi <sup>a</sup>, Qili Su <sup>b</sup>, Yiming Sun <sup>c</sup>, Yong Lu <sup>b</sup>, Kai Liu <sup>a\*</sup>, Zhe Li <sup>b\*</sup>,  
Haijing Liu <sup>b\*</sup>, Lianqi Zhang <sup>a\*</sup>

<sup>a</sup> School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China

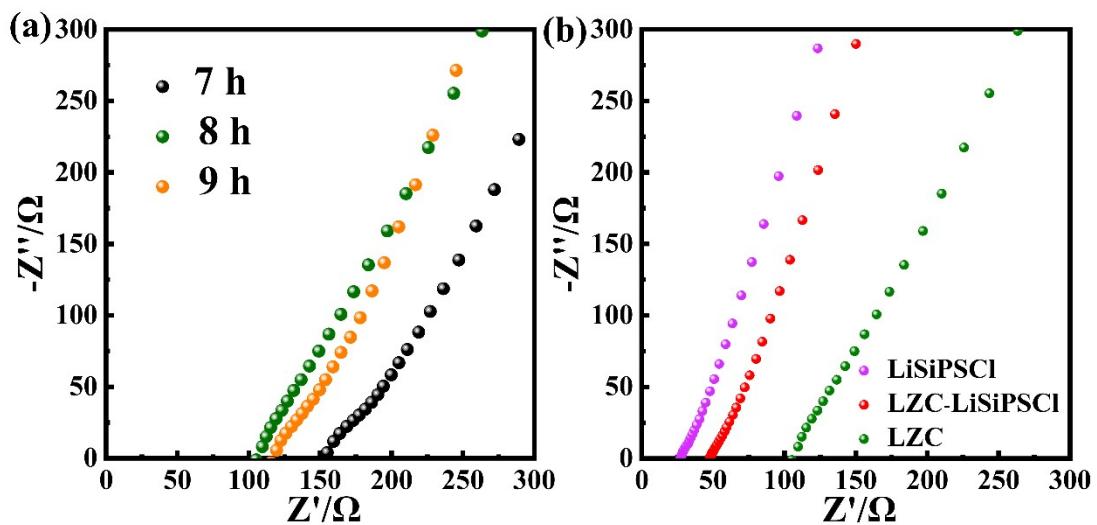
<sup>b</sup> China Science Lab, General Motors Global Research & Development, Shanghai 201206, China

<sup>c</sup> School of Materials Science and Engineering, Tianjin University, Tianjin 300350, China

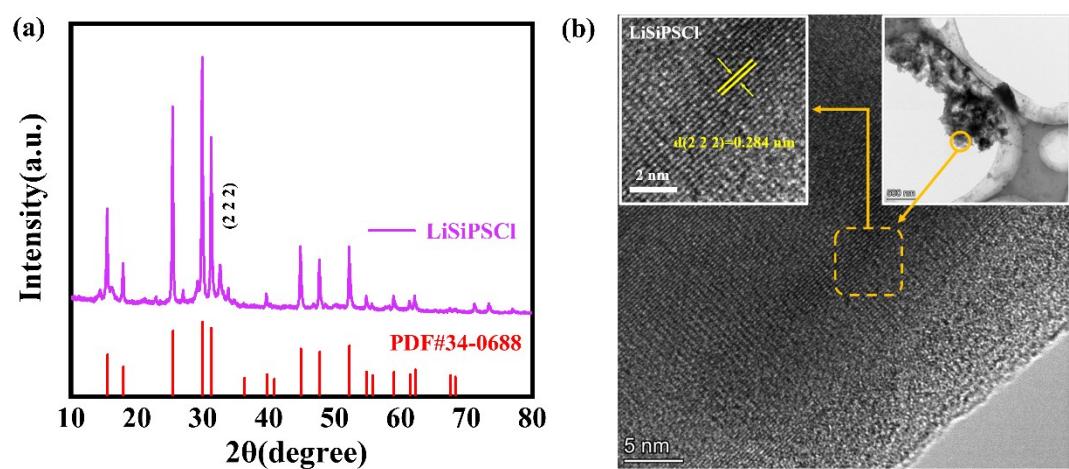
\* Corresponding author. E-mail: [liukai\\_tju\\_edu\\_cn@163.com](mailto:liukai_tju_edu_cn@163.com) (K. Liu), [zhe.4.li@gm.com](mailto:zhe.4.li@gm.com) (Z. Li),  
[helen.liu@gm.com](mailto:helen.liu@gm.com) (H. Liu), [tianjinzhanglq@163.com](mailto:tianjinzhanglq@163.com) (L. Zhang)



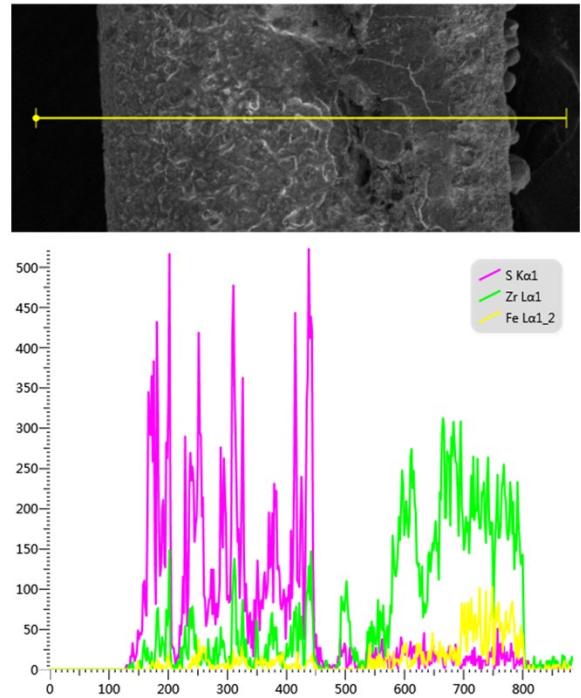
**Fig. S1.** HRTEM plots of LZC



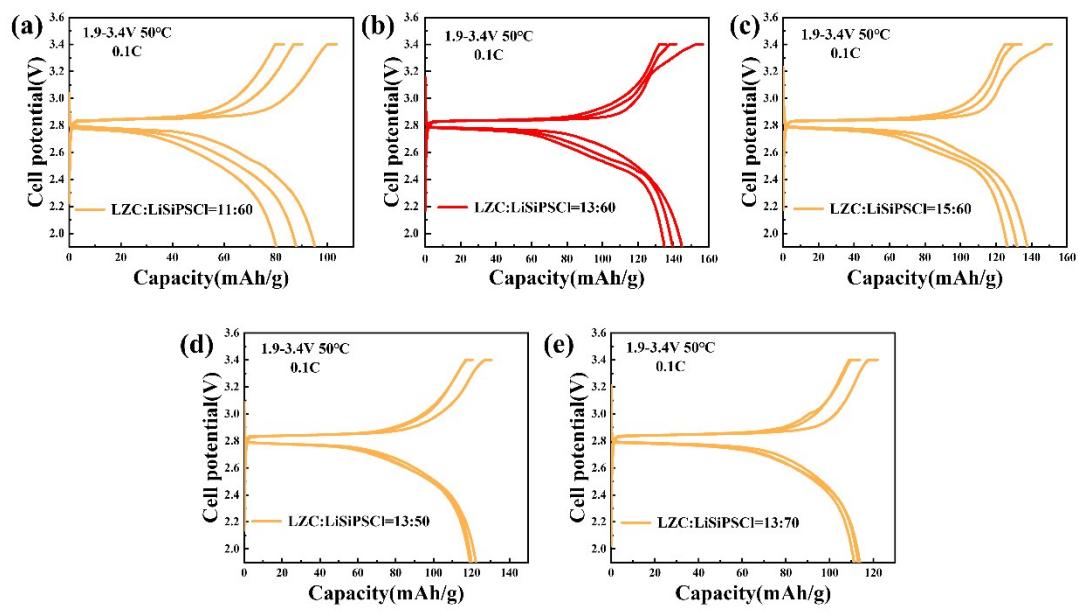
**Fig. S2.** Nyquist plots of (a) LZO after different ball milling times, (b) LiSiPSCl and LZO-LiSiPSCl at room temperature.



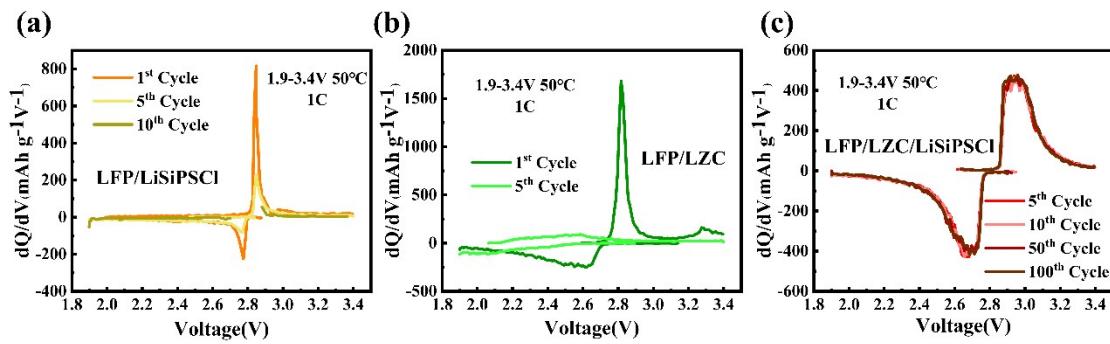
**Fig. S3.** (a) XRD and (b) HRTEM plots of LiSiPSCl



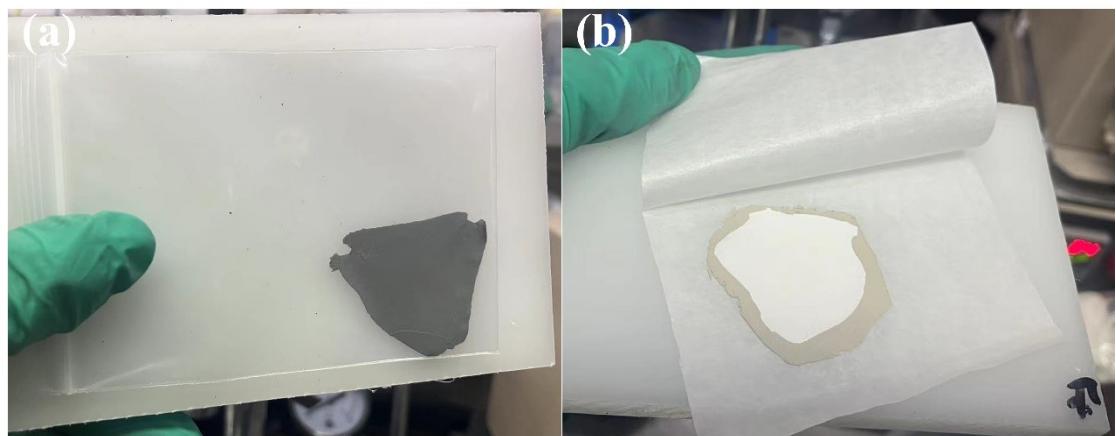
**Fig. S4.** Cross-sectional line scan of LFP-LZC/LZC/LiSiPSCl/Li-In ASSBs.



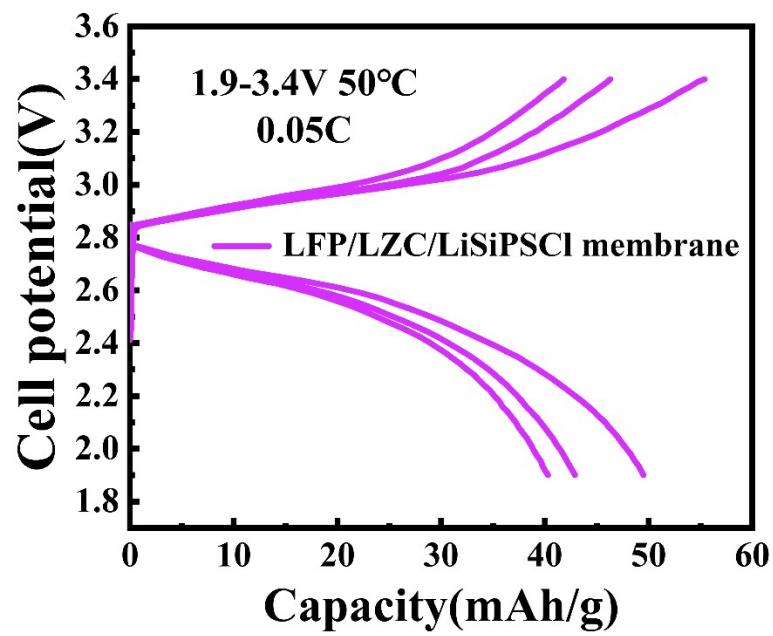
**Fig. S5.** Electrochemical performance of all-solid-state batteries assembled with different ratios of LZC solid-state electrolytes and LiSiPSCl solid-state electrolytes



**Fig. S6.** dQ/dV curves for different number of cycles for (a) LiSiPSCl, (b) LZC and (c) LZC-LiSiPSCl cells.



**Fig. S7.** (a) LFP composite positive electrode and (b) LZC-LiSiPSCl bilayer electrolyte prepared as lamellar membrane.



**Fig. S8.** Electrochemical performance of LFP all-solid-state membrane batteries.

**Table. S1.** Fitting data for LiSiPSC1, LZC and LZC-LiSiPSC1 cycle EIS and error values.

Composite	Cycle	Resistance ( $\Omega$ )			$\delta$ (%)
		SSE/Bulk	SEI	CT	
LFP/LiSiPSC1	1 <sup>st</sup>	12	47	278	0.136
	100 <sup>st</sup>	20	212	3800	0.203
LFP/LZC	1 <sup>st</sup>	69	21	\	0.145
	100 <sup>st</sup>	140	493	\	0.167
LFP/LZC/LiSiPSC1	1 <sup>st</sup>	29	9	\	0.138
	100 <sup>st</sup>	28	33	\	0.120