

Supporting information

In-situ element permeation constructed highly endurable Li-LLZO interface at high current density

Yang Lu,^{a,b} Xiao Huang,^{a,b} Yadong Ruan,^{a,b} Qingsong Wang,^{a,b} Kun Rui,^{a,b} Jianhua Yang,^a Zhaoyin Wen^{a,b*}

^a CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, P. R. China

^b University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

Experimental section

Synthesis of powder of garnet solid electrolyte (Ta doped $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$)

The powder of garnet solid electrolyte was synthesized by solid state reaction. $\text{LiOH} \cdot \text{H}_2\text{O}$ (AR), La_2O_3 (99.99%), ZrO_2 (AR) and Ta_2O_5 (99.99%) were mixed by ball milling in stoichiometric ratio. Isopropanol was solution for ball milling. In the starting material powder, 2% excessive $\text{LiOH} \cdot \text{H}_2\text{O}$ was added to compensate the Li loss in subsequent sintering process. The mixture of the starting material powder was calcined at 950°C for 6h in alumina crucible to obtain the cubic phase LLZTO powder. The XRD result for LLZTO powder is shown in Figure S1.

Synthesis of sintering aid $\text{La}_2\text{Zr}_2\text{O}_7$ (LZO)

La_2O_3 and ZrO_2 were mixed by ball milling in stoichiometric ratio. The mixture was calcined at 1500°C for 6 h in alumina crucible to obtain the pure phase LZO.

LLZTO pellets preparation

4 wt% LZO as sintering aid was added into the LLZTO powder and fully ball milled at 275 rpm for 10 h. The mixed powder was pressed into $\Phi 18 \text{ mm} \times 1.5 \text{ mm}$ pellets. The pellets were sintered at 1240 °C for 30 min in platinum crucible filled by bed power with 15% excessive Li resource. The as-synthesized pellets are shown in Figure S2, S3.

Synthesis of Li-Al alloy

Li foil and Al foil were stacked and pressed together and heated at 250°C. Then the Li foil and Al foil will fuse together spontaneously.

Modification of garnet SSE by Li-Al alloy

The Li-Al alloy was melted in stainless steel container, then one side of raw LLZTO-LZO pellets was emerged in the molten alloy for 5 min. Then the alloy will spontaneously adhere on one side of the LLZTO-LZO pellets.

Preparing of LiFePO_4 (LFP) cathode and sulfur cathode

The LFP cathodes were prepared by slurry coating procedure. The LFP powder, super P electronic conductive carbon and poly vinylidene fluoride (PVDF) as binder in weight ratio of 8:1:1 were mixed in N-methylpyrrolidone (NMP) by ball milling. After fully mixing for 6 h, the slurry was coated on Al foil by blade casting and dried under vacuum. The cathode was cut into $\Phi 18 \text{ mm}$ pellets. The mass loading of LFP was about 4.5-5 mg cm^{-2} .

The sulfur cathodes were also prepared by slurry coating technique. The Kejten Black (KB) carbon and sulfur in weight ratio of 1:4 were mixed and heated at 155 °C to synthesize the KB/S composite. Then the KB/S composite, super P as conductive carbon and styrene-butadiene rubber (SBR)- carboxymethyl cellulose (CMC) as binder in weight ratio of 8:1:1 were mixed in water by ball milling. The fully mixed slurry were coated on Al foil and dried under vacuum. The mass loading of sulfur was about 1-1.5 mg cm^{-2} .

Assembly of symmetric and full cells

The Li-Al alloy was heated to 250 °C to molten state. Then the molten alloy was coated on one side or both side of LLZTO directly. The one side Li-Al coated garnet electrolytes were prepared for the assembly of full cells. The two side Li-Al coated garnet electrolytes were prepared for the assembly of symmetric cells. All the cells were assembled in CR2032 coin cells. The assembly of LFP full cell was finished in the following processes: fresh Li foil was firstly melted on Li-Al coated LLZTO to provide enough Li for the whole battery system. 10 μL of EC/DMC electrolyte was dropped on LFP cathode, then the Li-Al coated LLZTO with melted Li was placed upon the liquid electrolyte. The assembly of

Li-S full cell was finished in the following processed: 50 μL of the solution containing 10 wt% LiTFSI and 20 wt% Polyethylene oxide (PEO) in acetonitrile was added on the sulfur cathode, then the solvent was evaporated at 80 $^{\circ}\text{C}$ at vacuum.

Characterization

X-ray diffraction (XRD Rigaku) analysis were conducted to ensure the phase component of Li-Al alloy and LLZTO ceramics. The measurement for Li-Al alloy was conducted in following process. The samples were prepared in argon-filled glove box to get rid of the influence of moisture and oxygen. Kapton tapes were utilized to protect Li-Al alloy in the ambient atmosphere during the XRD analysis. The microstructure images were achieved by scanning electron microscope (SEM, Hitachi, S-3400N) and field emission scanning microscopy (FESEM, Magellan-400) equipped with energy dispersive X-ray analysis system (EDS Horiba250).

Electrochemical measurement

All the assembled batteries were tested on battery test system (LAND CT2001A China). The electrochemical impedance spectroscopy (EIS) were measured on Electrochemical workstation (Autolab PGSTAT302N Netherland). The ionic conductivity is calculated in following formula: $R=L/(\Sigma*A)$ R is total impedance exhibited in EIS plot. L is the thickness of SSE pellets. A is the effective area of SSE pellets. After substituting the known parameters into the formula, the ionic conductivity Σ will be calculated by the aforementioned formula. The assessment on critical current density at room temperature were measured in current steps of 0.1 mA cm^{-2} from 0.2 mA cm^{-2} to 1.3 mA cm^{-2} . The charge and discharge periods in every step are 10 minutes for 20 cycles. The same assessments for critical current density at 60 $^{\circ}\text{C}$ were conducted at a gradient current steps of 0.13, 0.2, 0.33 mA cm^{-2} . The times for charge and discharge period were same as that in room temperature. Besides, CCD measurement in 30 min per period are also conducted in current step of 0.05 mA cm^{-2} per cycle starting from 0.1 mA cm^{-2} at RT.

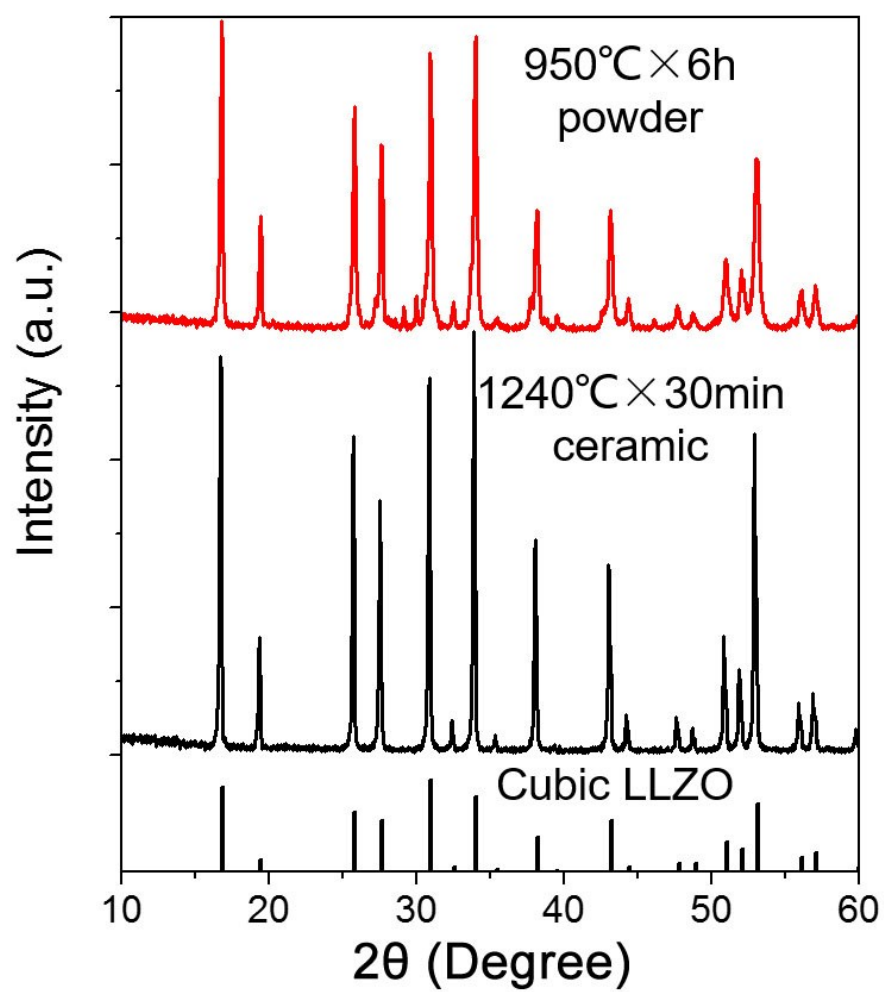


Figure S1 XRD patterns of the synthesized garnet solid electrolyte powder and pellets.



Figure S2 Digital photo representation for pellets sintering in Pt crucible.

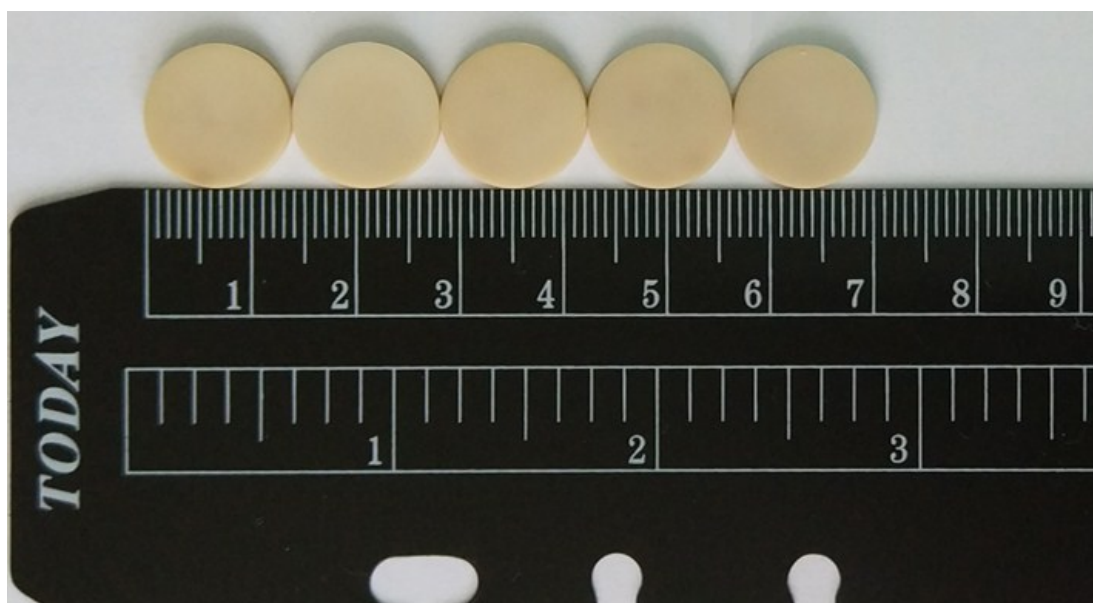


Figure S3 Digital photo of as-synthesized LLZTO-LZO pellets

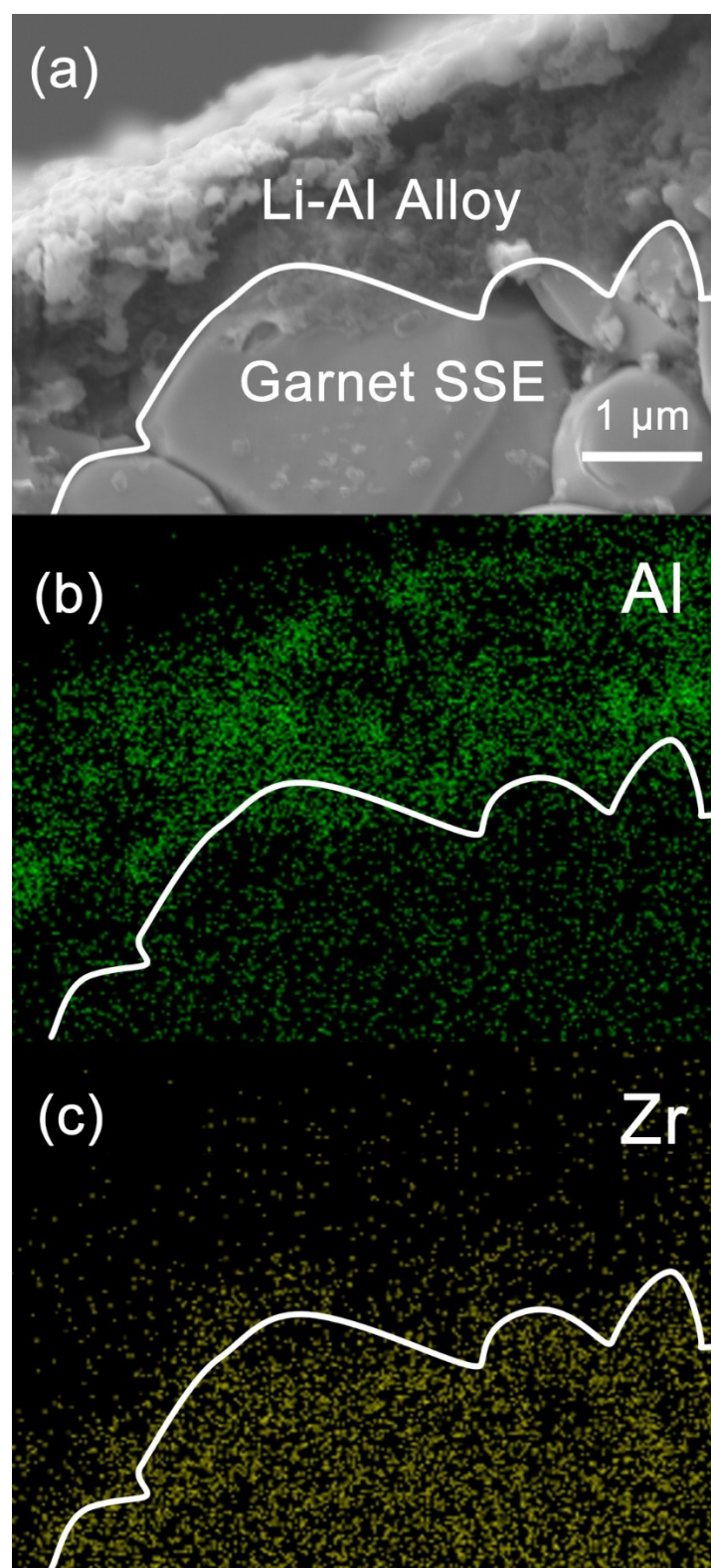


Figure S4 (a) SEM images and corresponding EDS mapping of cross section of Li-Al/LLZTO on (b) Al and (c) Zr

In order to consolidate the results, we fitted and simulated the EIS curve of the symmetric cells and calculated the interfacial impedance carefully. Accurately coupling each section of the plot to appropriate model is essential before fitting the plot. And the core area of this scaled up curves have been shown in Figure S5. In Ta doped LLZO system, the $R_{\text{grain boundary}}$ can't be detected under the measurement frequency less than 1 MHz. The intercept point at X axis is attributed to bulk resistance of SSEs. The interfacial process should be ascribed to the semi-circle exhibited in EIS plot. At the end of the EIS plot, obvious short oblique line don't represent the interfacial process, which have been mentioned in many published papers.¹⁻³ The oblique line could be attributed to a weak lithium ion diffusion process. Hence the model of the symmetric cell could be divided in following parts, the bulk resistance of SSEs, two interfacial resistance and weak Li diffusion process. The interfacial impedance is calculated by the fitted semi-circle, which is ascribed to $2 \times R_{\text{int Li-Al/LLZTO}}$. The total interfacial impedance is calculated as $1.81 \Omega \text{ cm}^{-2}$. Hence a single interfacial impedance is affirmed as $0.9 \Omega \text{ cm}^{-2}$.

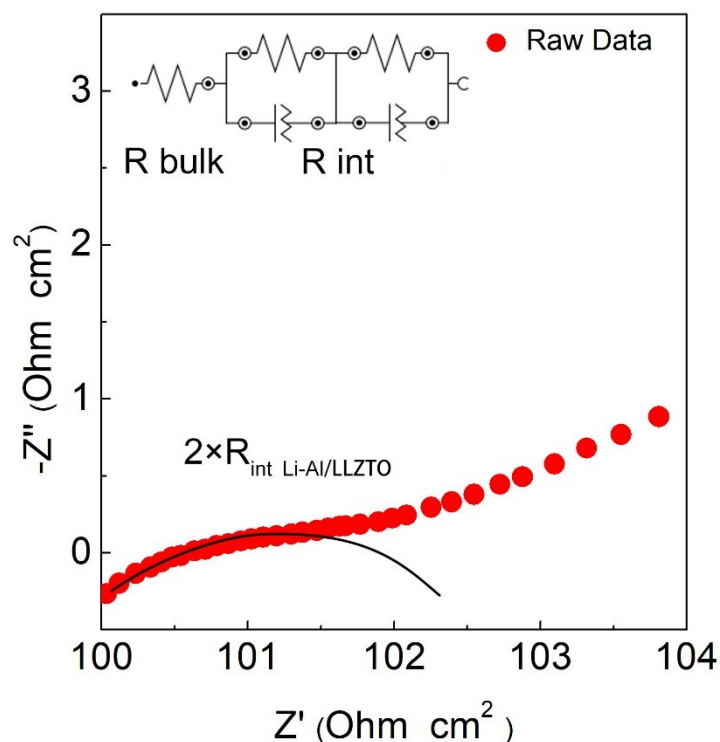


Figure S5 EIS spectrum and corresponding fitting results of symmetric cells assembled with Li enriched alloy at RT

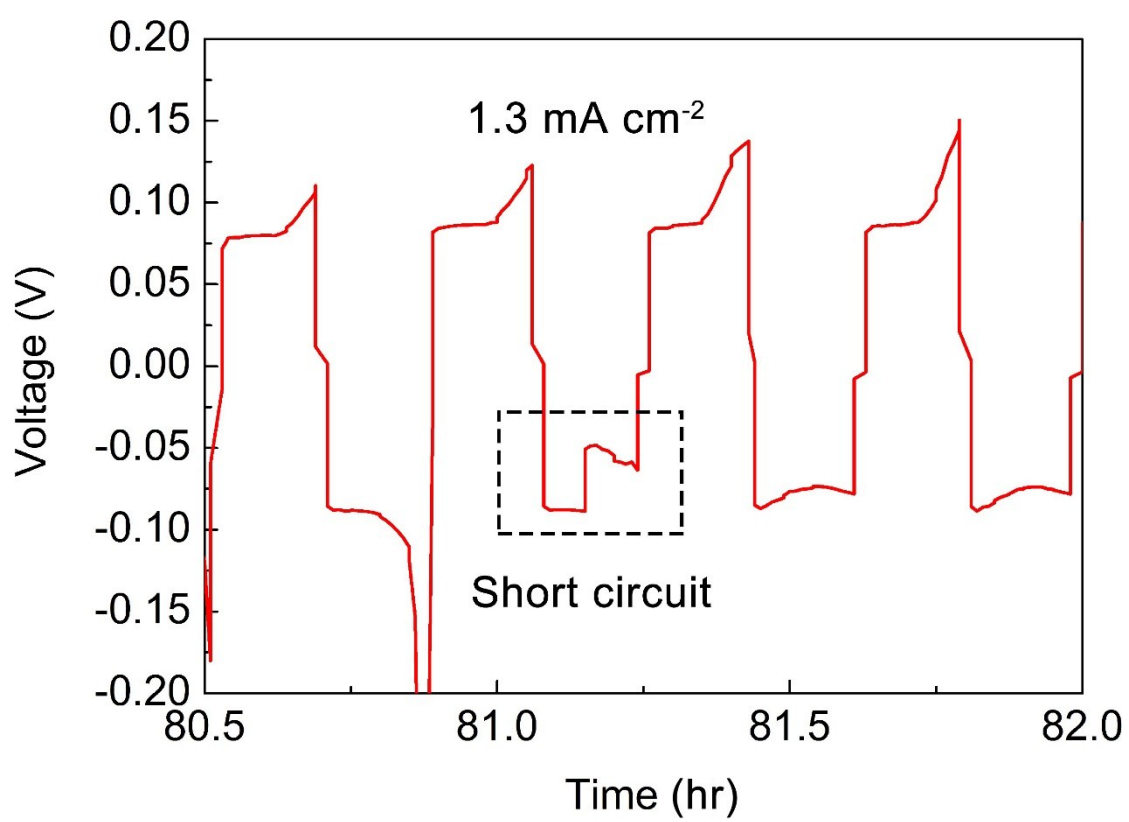


Figure S6 Complete short circuit phenomenon of Li-Al/LLZTO-LZO/Li-Al in Figure 3a at current density of 1.3 mA cm^{-2}

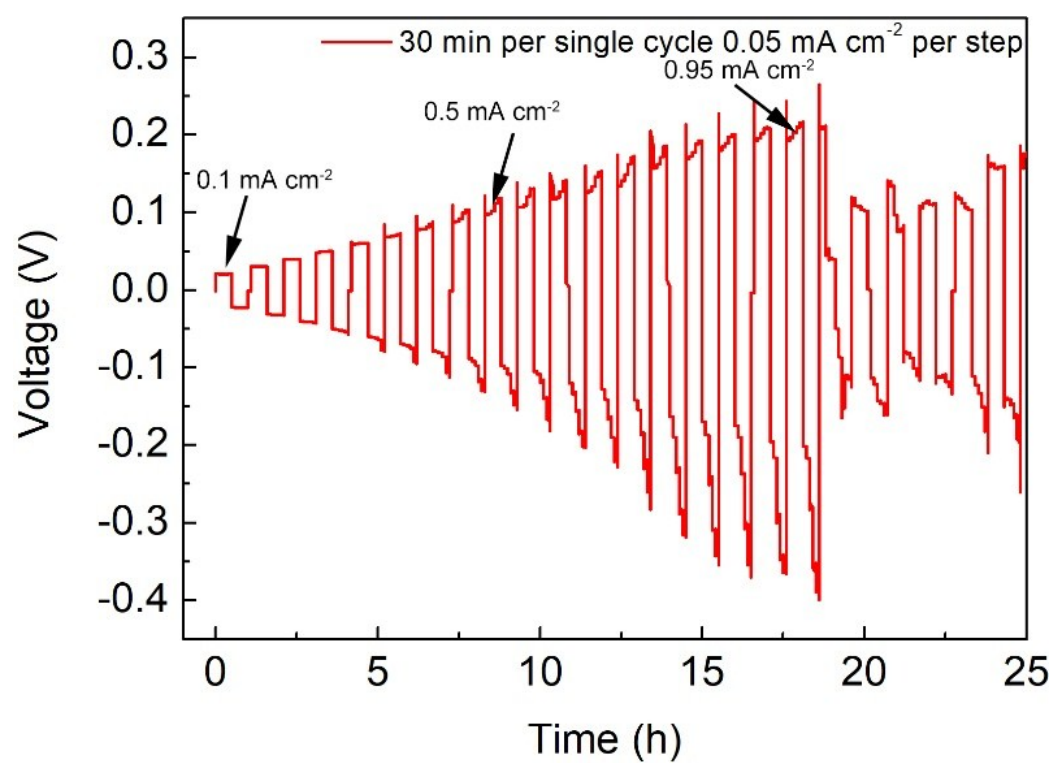


Figure S7 CCD results of Li-Al/LLZTO/Li-Al symmetric cell measured at 30 min per period with current step of 0.05 mA cm⁻²

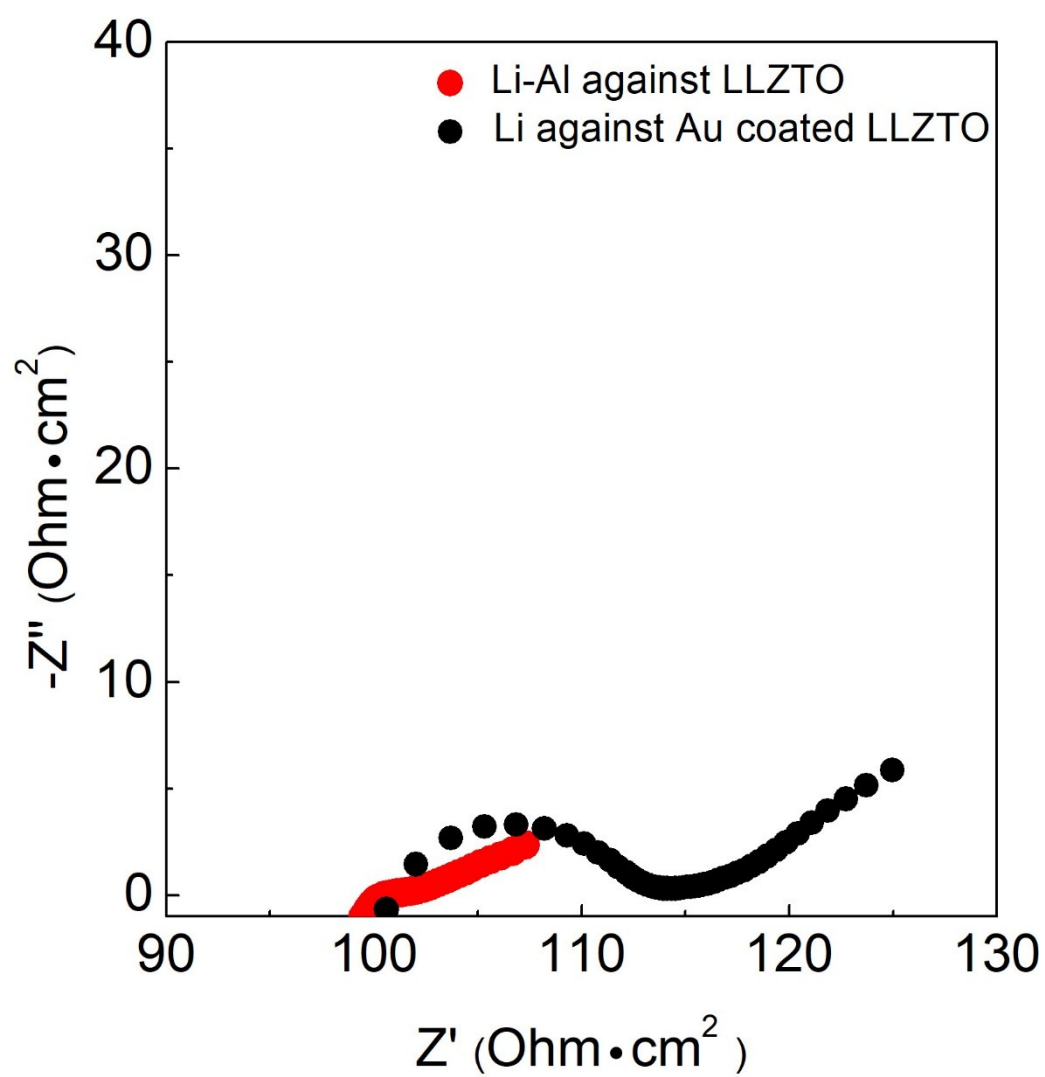


Figure S8 Comparing of impedance on Al permeation induced interface and Au coated interface in LLZTO symmetric cells.

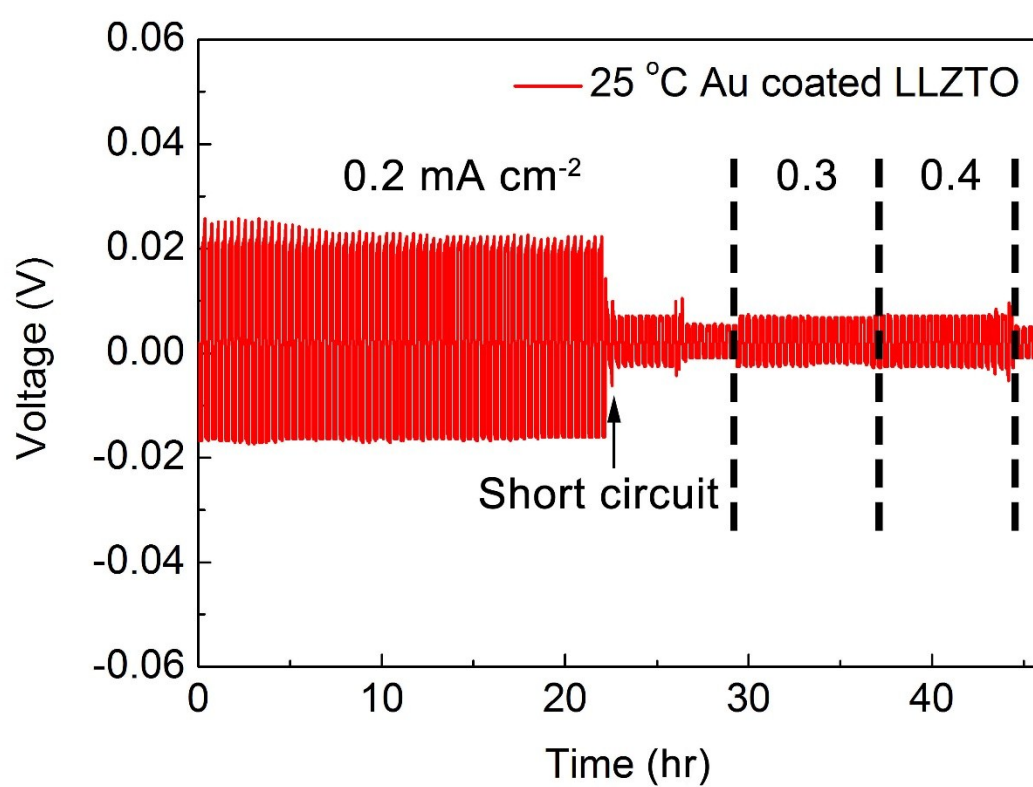


Figure S9 Galvanostatic cycling of the Li/LLZTO-LZO/Li symmetric cell with Au sputtered LLZTO-LZO

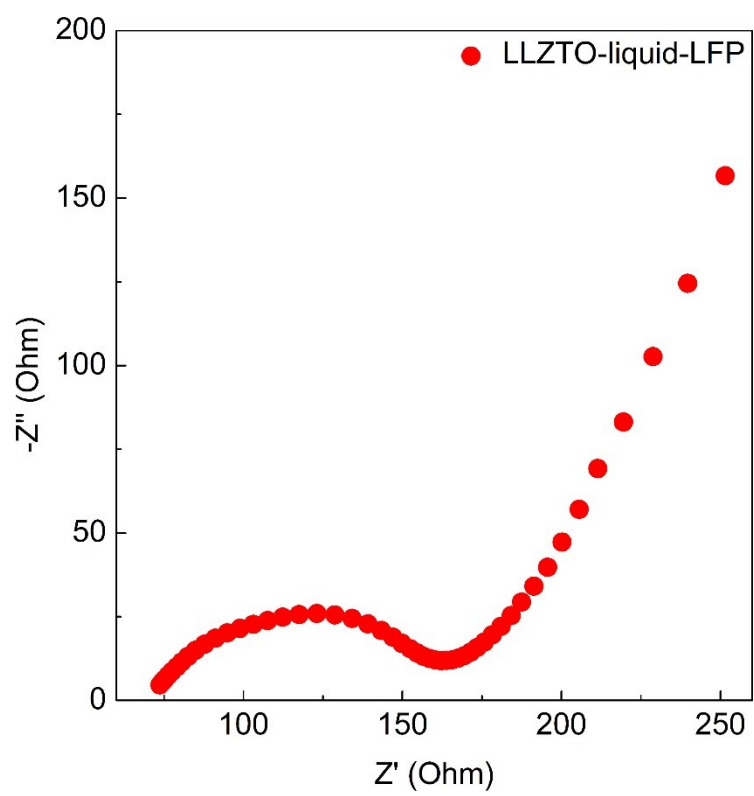


Figure S10 Initial impedance of garnet SSE based quasi solid state battery in Figure 5b.

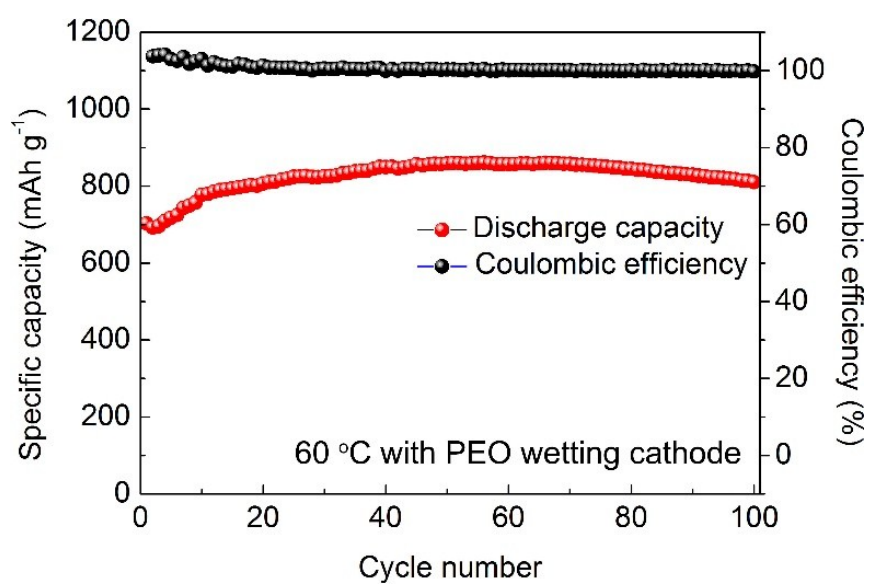


Figure S11 Performance of LLZO/Li-alloy metal based full cell with PEO-sulfur cathode

Table S1 State-of-the-art on anodic modification on garnet based SSE by different methods comparing to our works

Solid electrolyte/sintering method	Modification method	Special apparatus requirement	Operation temperature	Critical current (mA cm ⁻²)	Stability (RT) (mA cm ⁻² /hour)	reference
LLZO(0.4Ta)* Hot press sintering	Sputtering Au	sputter	25°C	0.5	0.08/150	⁴
LLZO(0.25Ca,Nb) Conventional sintering	Sputtering Al	evaporator	25°C	0.2	0.2/42	⁵
LLZO(0.25Ca,Nb) Conventional sintering	PECVD for Si	PECVD	25°C	0.2	0.1/225	¹
LLZO(0.25Ca,Nb) Conventional sintering	ALD Al ₂ O ₃	Atomic layer deposition	25°C	0.2	0.2/90	²
LLZO(0.25Al) Hot press sintering	Heating treatment	Hot press technique	25°C	0.3	0.2/200	⁶
LLZO(0.5Ta) SPS sintering	Grain boundary modification	Spark plasma sintering	25°C	0.6	N/A	⁷
LLZO(0.5Ta-4%LZO) Conventional sintering	Li-Al alloy induced SEI	No special technique	25°C 60°C	>0.9 2.3	0.2/3000	This work

*LLZO(0.4Ta)= Li₇La₃Zr₂O₁₂ doped by 0.4Ta₂O₅(Li_{6.6}La₃Zr_{1.6}Ta_{0.4}O₁₂)

References

1. W. Luo, Y. Gong, Y. Zhu, K. K. Fu, J. Dai, S. D. Lacey, C. Wang, B. Liu, X. Han, Y. Mo, E. D. Wachsman and L. Hu, *J. Am. Chem. Soc.*, 2016, **138**, 12258-12262.
2. X. Han, Y. Gong, K. K. Fu, X. He, G. T. Hitz, J. Dai, A. Pearse, B. Liu, H. Wang, G. Rubloff, Y. Mo, V. Thangadurai, E. D. Wachsman and L. Hu, *Nat Mater*, 2017, **16**, 572-579.
3. R. Inada, S. Yasuda, H. Hosokawa, M. Saito, T. Tojo and Y. Sakurai, *Batteries*, 2018, **4**, 26.
4. C. L. Tsai, V. Roddatis, C. V. Chandran, Q. Ma, S. Uhlenbruck, M. Bram, P. Heitjans and O. Guillon, *ACS Appl. Mater. Interfaces*, 2016, **8**, 10617-10626.
5. K. K. Fu, Y. H. Gong, B. Y. Liu, Y. Z. Zhu, S. M. Xu, Y. G. Yao, W. Luo, C. W. Wang, S. D. Lacey, J. Q. Dai, Y. N. Chen, Y. F. Mo, E. Wachsman and L. B. Hu, *Sci. Adv.*, 2017, **3**, 11.
6. A. Sharafi, E. Kazyak, A. L. Davis, S. Yu, T. Thompson, D. J. Siegel, N. P. Dasgupta and J.

Sakamoto, *Chem. Mater.*, 2017, **29**, 7961-7968.

7. R. Hongahally Basappa, T. Ito, T. Morimura, R. Bekarevich, K. Mitsuishi and H. Yamada, *J. Power Sources*, 2017, **363**, 145-152.