Supporting information

for

Dendrite-free lithium deposition *via* fumed silica interlayer as electron inhibitor in all-solid-state batteries

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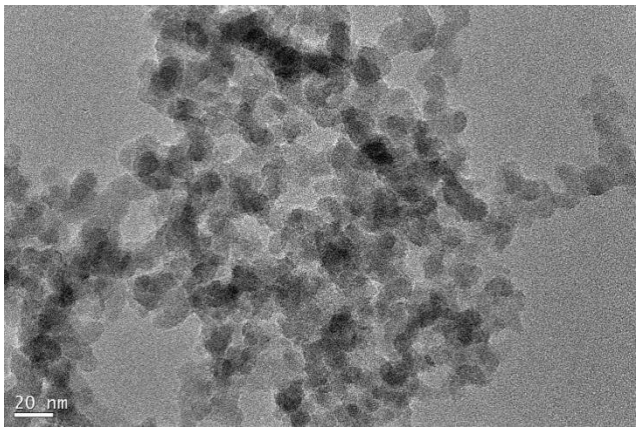

Figure S1. The TEM image of fumed silica used in current research

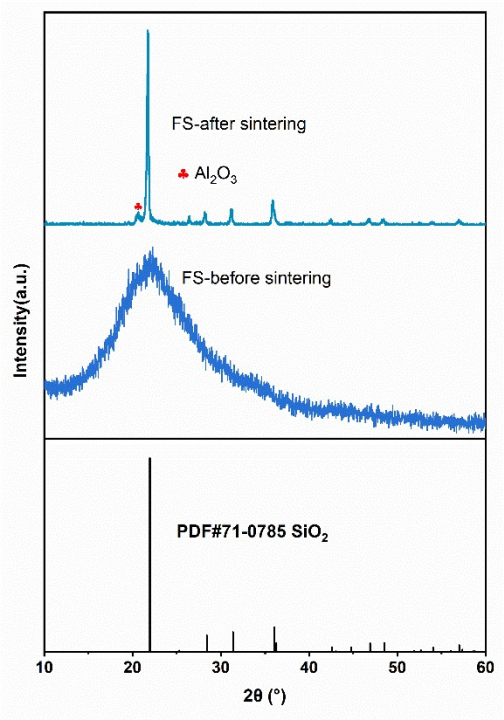

Figure S2. The XRD spectra for fumed silica before and after sintering

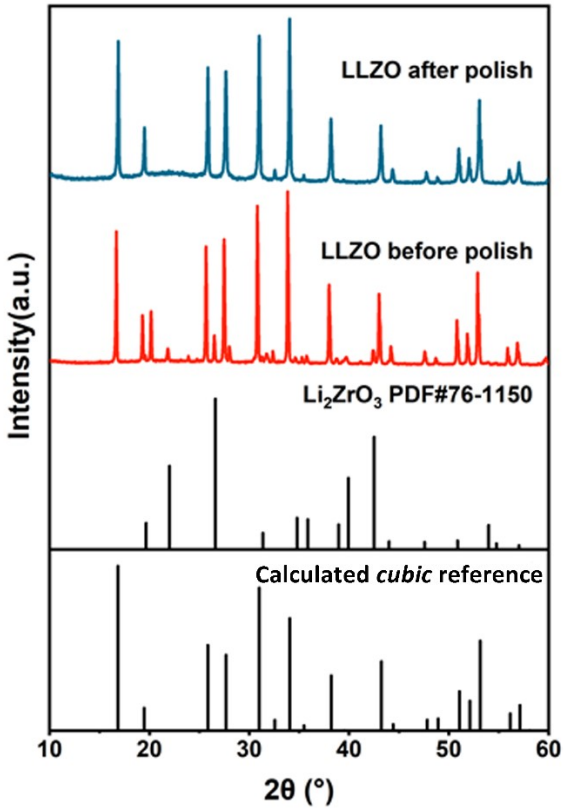

Figure S3. The XRD patterns of the LLZO pellet before and after polish

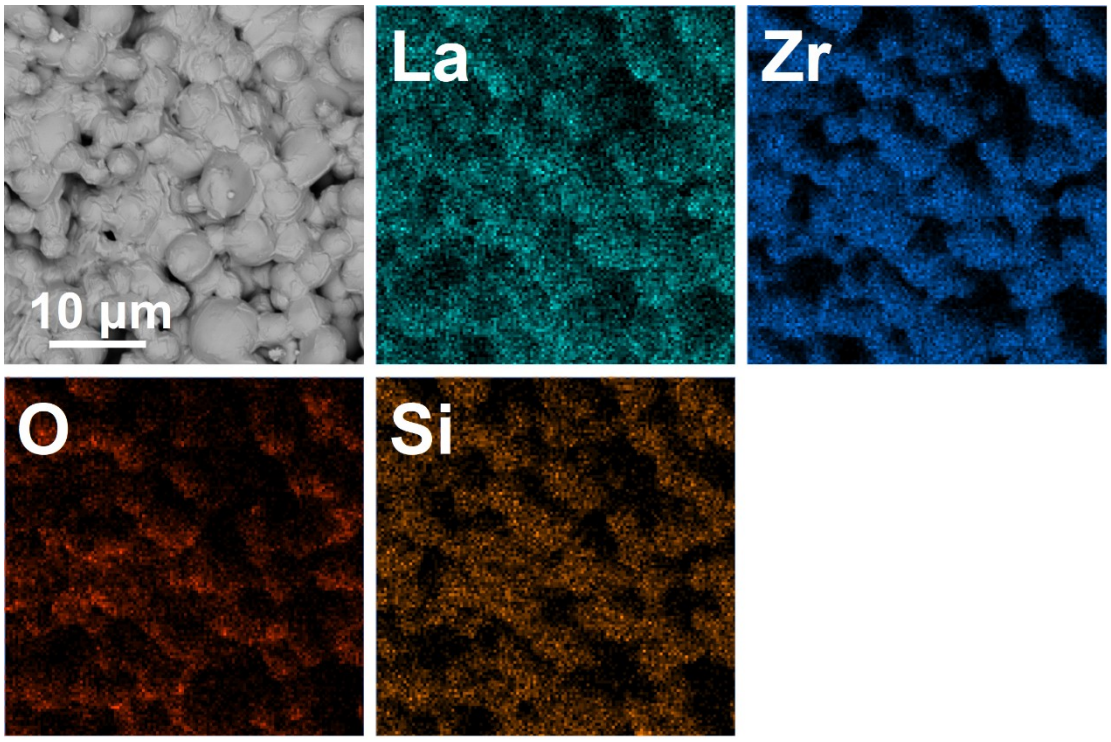

Figure S4. The surface SEM image of the FS-LLZO solid electrolyte and corresponding EDS mappings for La, Zr and O

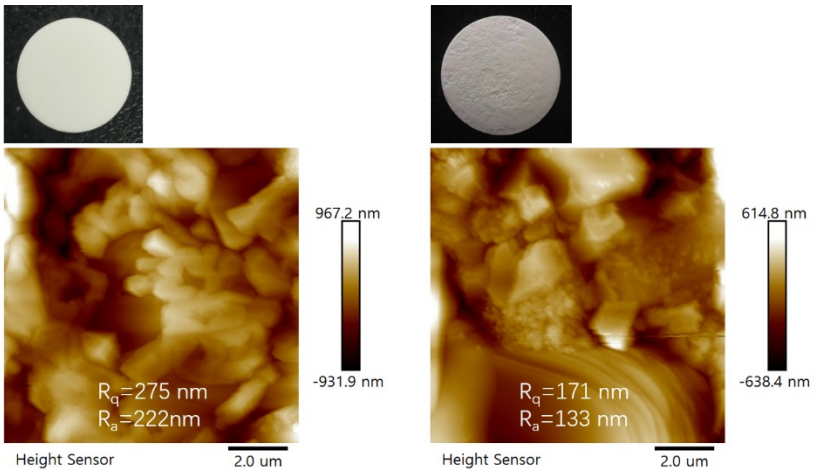

Figure S5. The optical image and the AFM results for pristine LLZO (left) and FS-LLZO (right)

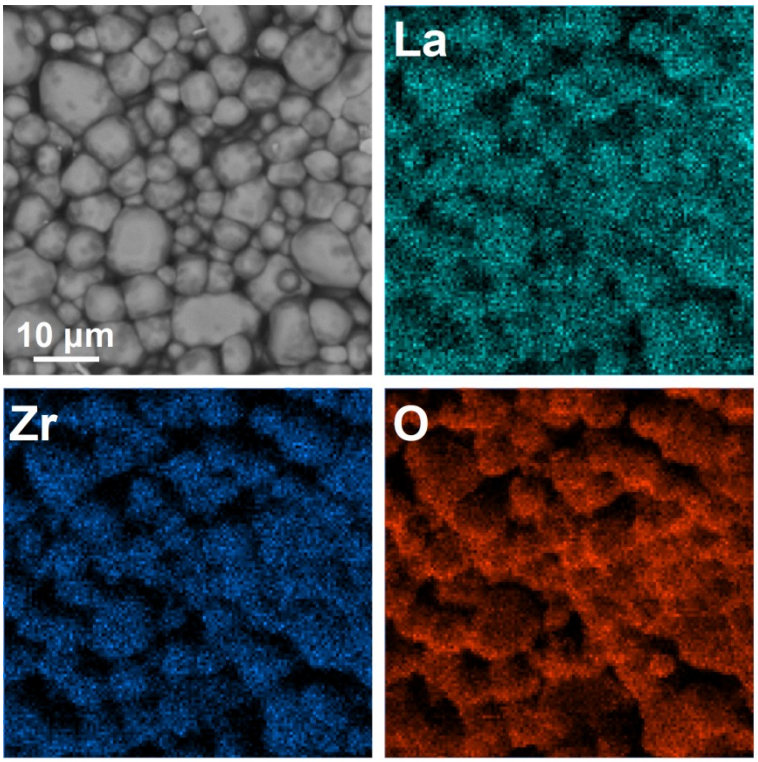

Figure S6. The surface SEM image of the LLZO solid electrolyte and corresponding EDS mappings for La, Zr and O

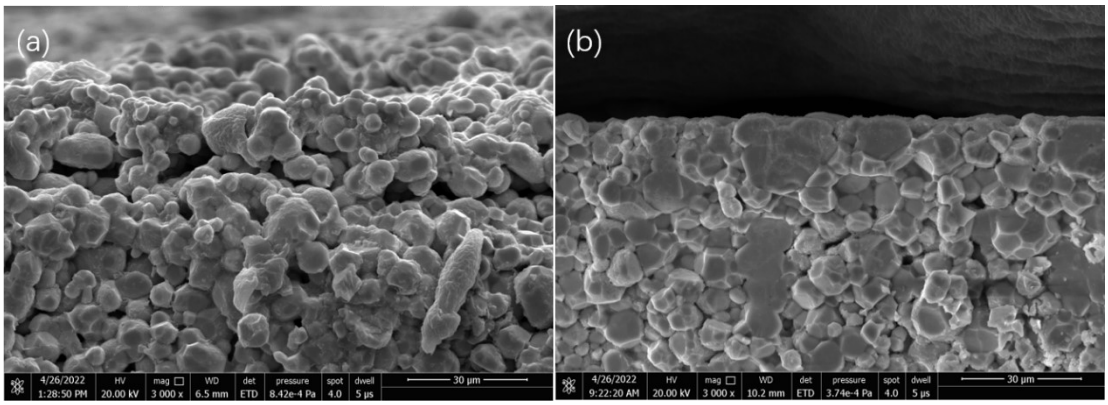

Figure S7. The Cross-sectional SEM images for (a) LLZO and (b) FS modified LLZO

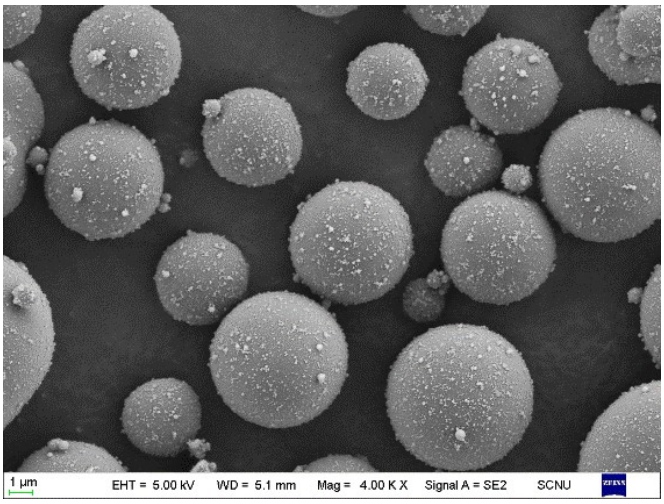

Figure S8. The SEM images of the commercial SiO_2

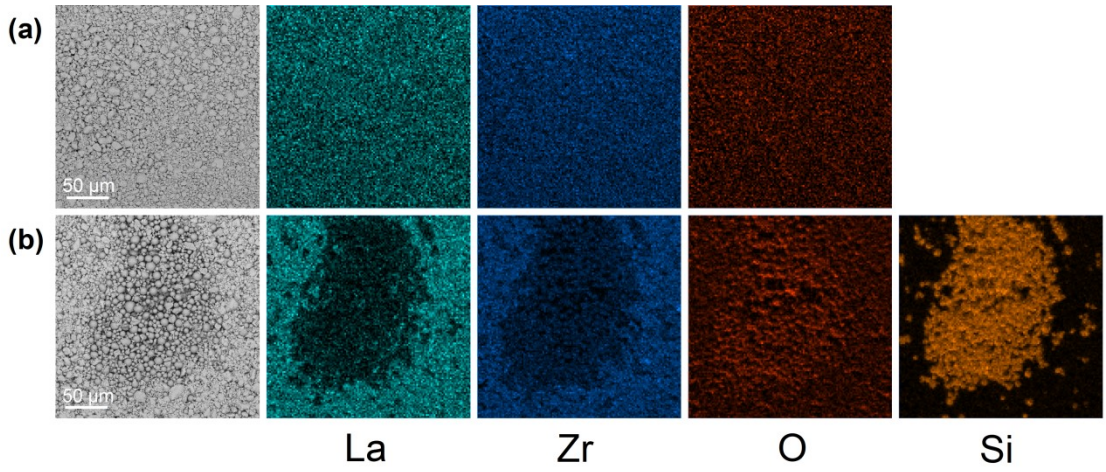

Figure S9. The surface SEM images of the LLZO (a) and S-LLZO (b) pellets and corresponding EDS mappings

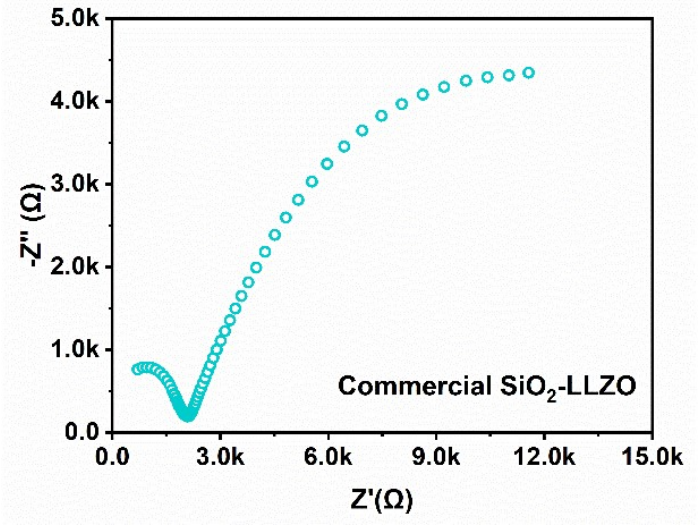

Figure S10. The ionic conductivity of LLZO modified by commercial SiO_2

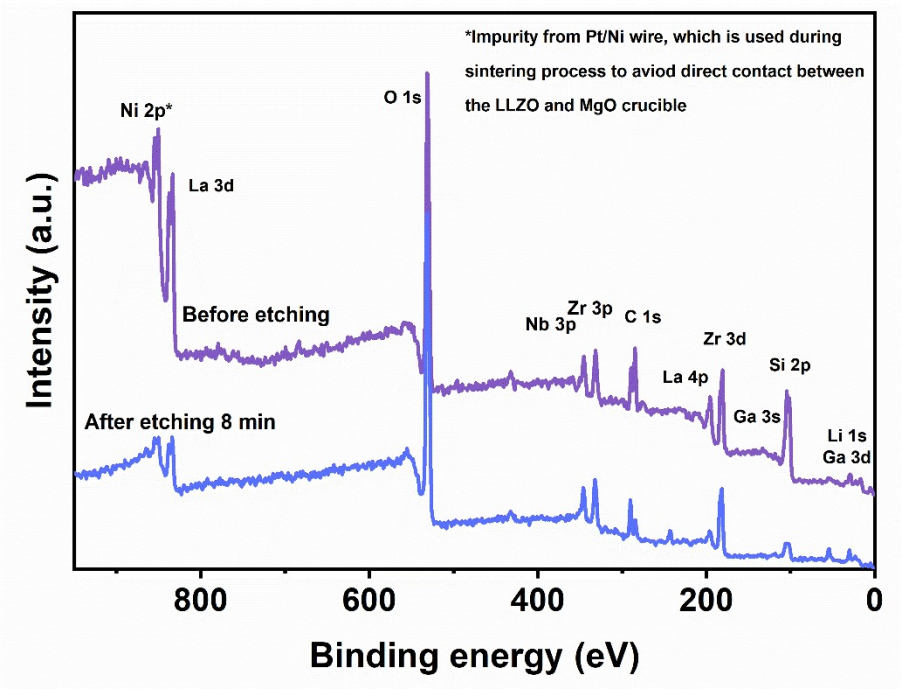

Figure S11. The XPS survey spectra obtained from the FS-LLZO pellet

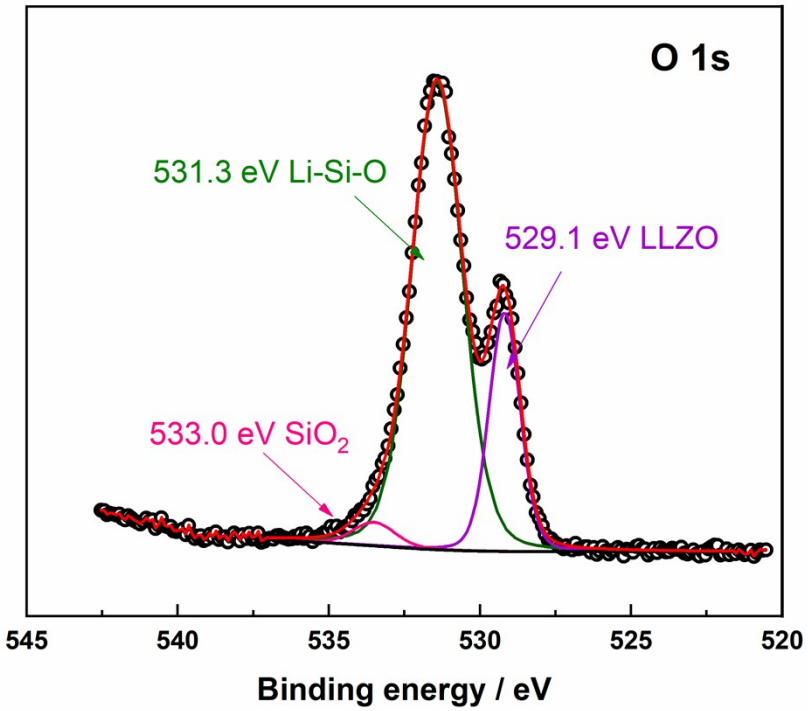

Figure S12. The O 1s spectra collected on the FS-LLZO

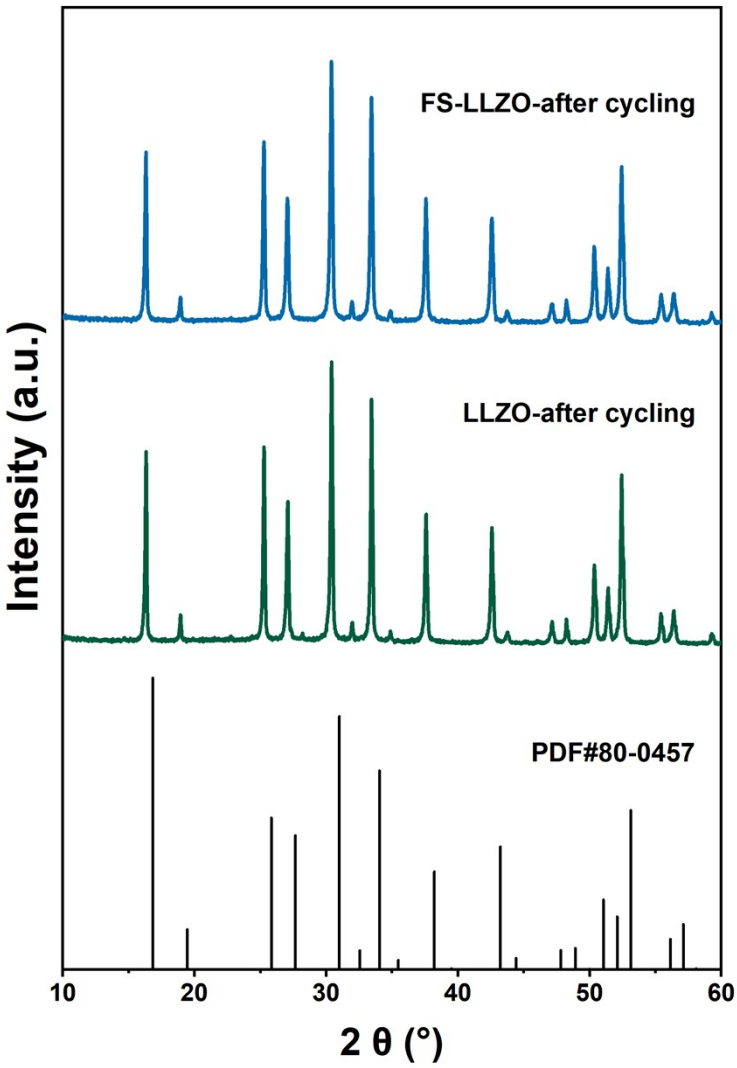

Figure S13. The XRD patterns of the LLZO and FS-LLZO solid electrolyte after cycling

Experimental Section:

Preparation of solid electrolytes. The solid electrolyte, $Li_{6.35}Ga_{0.15}La_3Zr_{1.8}Nb_{0.2}O_{12}$ (LLZO) was prepared according to our previous papers[1]. In detail, stoichiometric materials, Li_2CO_3 (Macklin), La_2O_3 (Macklin), ZrO_2 (Aladdin) , Ga_2O_3 (Macklin), and Nb_2O_3 (Macklin), were ball mixed for 24 h using isopropanol as solvent. Next, the mixture was pressed into pellets and subjected to sintering at 950 ºC for 12 h. After cooling down, the pellets were grounded in a mortar and sieved to get fine powders, the powders were pressed into pellets again and sintered at 1150 ºC for 6 h to get the solid electrolytes, during the sintering process, Pt/Ni wires were used in order to avoid the direct contact of LLZO pellet and the MgO crucible. For preparing the fumed silica modified solid electrolyte (FS-LLZ), a mass ratio of 1% fumed silica (purchased from the company and used directly) was weighed and added to the surface of the LLZO pellets and then subjected to a 10 MPa pressure for 3 min before sintering. The detailed process was illustrated in the following **Figure S14**.

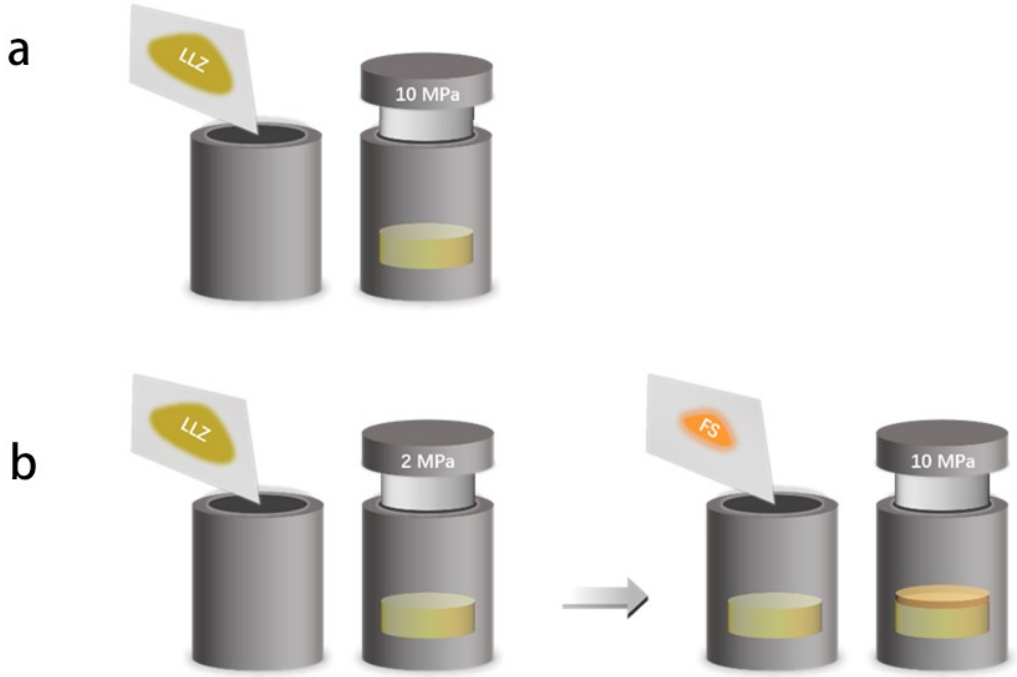

Figure S14. Preparation of solid electrolytes during tablet pressing, (a) LLZO and (b) FS-LLZO

Cell assembly. Different types of cells were assembled and tested to evaluate the performance using LLZO and FS-LLZO electrolytes, namely, Au | LLZO | Au blocking cell to get the ionic conductively of the pellets, Li | LLZO | Li symmetrical cell to obtain the plating/strapping properties of Li metal and Li | LLZO | $LiFePO_4$ cells to acquire the energy storage properties, while during preparing Li | LLZO | $LiFePO_4$ cells, the mass load of $LiFePO_4$ in each electrode was controlled at around 2 mg cm^{-2}, and 20 µL liquid electrolyte was employed to wet the LLZO/$LiFePO_4$ interface. All the cells were assembled and disassembled in an argon-filled glove box.

Characterization. The crystal structure of the ceramics was tested using X-ray diffraction (XRD, Rigaku Ultima IV), and the structural properties of the fumed silica was obtained by using fourier transform infrared spectroscopy (FTIR, Nicolet 6700). The morphological information of the materials was collected by using scanning

electron microscopy (SEM, Phenom Pro X), atomic force microscope (AFM, Bruker Dension Icon) and transmission electron microscopy (TEM, JEM-2100HR). The surface composition of the ceramics was obtained by using X-ray photoelectron spectroscopy (XPS, AXIS SUPRA). The conductivities of the pellets and cells were measured on an electrochemical working station (Autolab) in a frequency range between 1 MHz~1 Hz. The energy storage properties of the cells were performed on Neware charge/discharge equipment.

References

1 W. Lan, H. Fan, V. W.-h. Lau, J. Zhang, J. Zhang, R. Zhao and H. Chen, *Sustainable Energy & Fuels,* 2020, 4, 1812-1821.