# Electronic Supplementary Information

## A surfactant-assisted strategy to tailor Li-ion charge transfer interfacial resistance for scalable all-solid-state Li batteries

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## Experimental Section

### Electrolyte preparation and characterization

Garnet-type cubic $Li_{6.5}La_{2.9}Ba_{0.1}Zr_{1.4}Ta_{0.6}O_{12}$ (LLBZT) was synthesized by conventional solid-state reaction. Stoichiometric amounts of $LiNO_3$ (Alfa Aesar, 99.0%), $La_2O_3$ (Alfa Aesar, 99.9% pre-dried at 900 °C for 12 h), $Ba(NO_3)_2$ (Alfa Aesar, ≥ 99.0%), $ZrO_2$ (Aldrich, 99.0%), and $Ta_2O_5$ (99.0%, Alfa Aesar) were thoroughly mixed for 6 h using a planetary ball mill (Pulverisette, Fritsch, Germany) in isopropanol. 10 wt% excess $LiNO_3$ was added to compensate for lithium loss during the calcination and sintering processes. The well-mixed precursors were calcined at 700 °C for 6 h to decompose nitrate. The as-calcined powders were ball-milled and pressed into pellets and calcined at 900 °C for an additional 20 h, resulting pellets were crushed into powders and ball-milled for a final time in isopropanol for 6 h. The dried powders were uniaxially pressed in a 10-mm diameter die at 30 MPa and finally isostatically pressed at 150 MPa. The pellets were covered by the mother powder and sintered at 1150 °C for 6 h in clean alumina crucibles. The obtained pellets (thickness ~ 0.9 mm) were polished on both sides thoroughly with 80, 320 and 1500 grit sand papers using an isopropanol media and stored in an argon filled glovebox until time of use.

Powder X-ray diffraction (Powder X-ray Diffractometer, Model: Bruker D8 Advance) (Cu Kα, 40 kV, 40 mA) confirms the formation of garnet-type LLBZT. Typical measurements were performed from 2θ range 10° to 80° at a count rate of 4 s per step of 0.025° at room temperature. Ionic conductivity was measured between 20-150 $^{o}$C using a Solartron 1260; the applied voltage is 100 mV with a frequency range of 1 MHz to 0.1 Hz. Scanning electron microscopy imaging was doing using a Zeiss Sigma VP.

**Symmetric cell preparation**

The solution coating consisted of 0.3 M $Zn(NO_3)_2$ dissolved in isopropanol along with 10 wt% P123. Using a micropipette, solution was dropped onto the pellet surface at a loading of 25 μL $cm^{-2}$, process was repeated two time per side. The sample was then placed in a preheated oven at 350 °C for 20 minutes to decompose zinc nitrate and partially burn off P123. Pellets were gently polished on the edges with 1500 grit polish papers to remove any possible ZnO, once polished sample was transferred back to argon filled glovebox. Lithium granules were rolled into a foil and a disc (0.28 $cm^2$) was punched. Garnet samples were sandwiched between two lithium discs and heated on a hotplate at 250 °C for 1 h. A stainless-steel disc was placed on top of the garnet sandwich while heating to encourage uniform, adhesion.

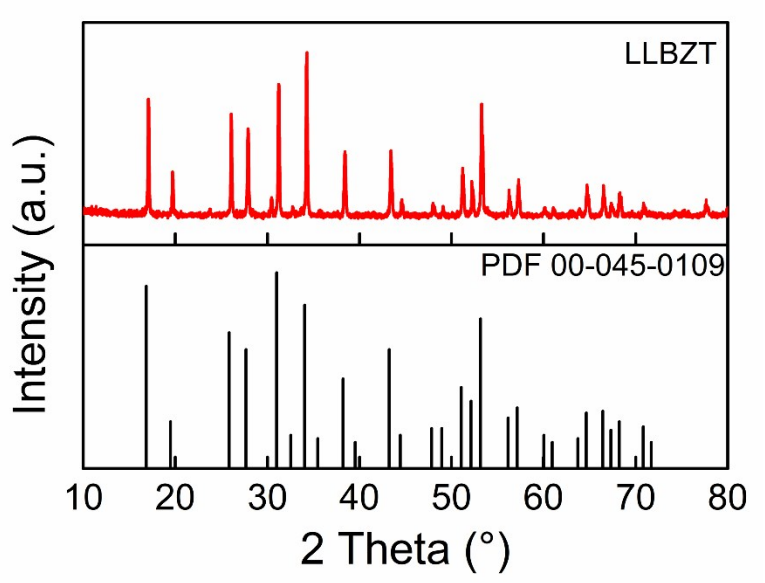


**Figure S1.** X-Ray diffraction (XRD) pattern of as prepared $Li_{6.5}La_{2.9}Ba_{0.1}Zr_{1.4}Ta_{0.6}O_{12}$ (LLBZT) compared with $Li_5La_3Nb_2O_{12}$ reference cubic garnet phase

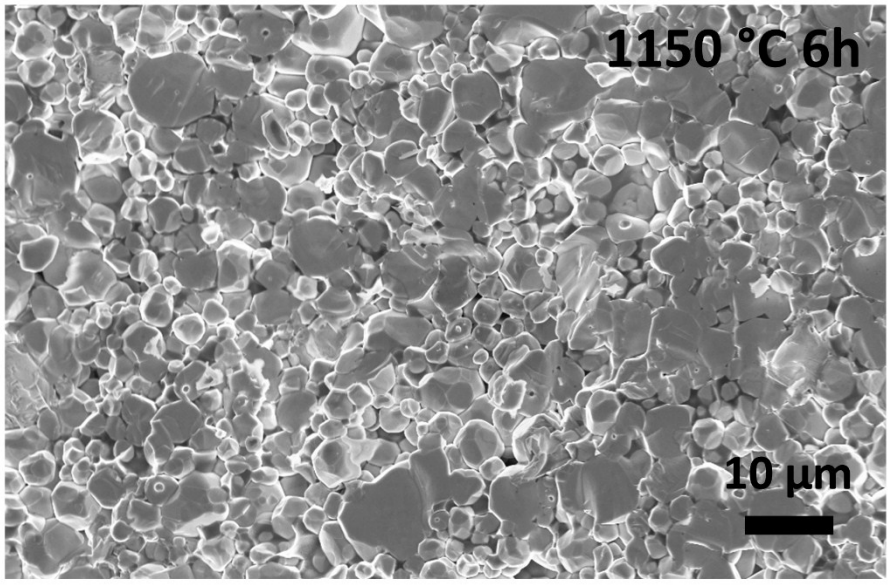


**Figure S2.** Scanning electron microscopy (SEM) image of a fracture cross-section of LLBZT.

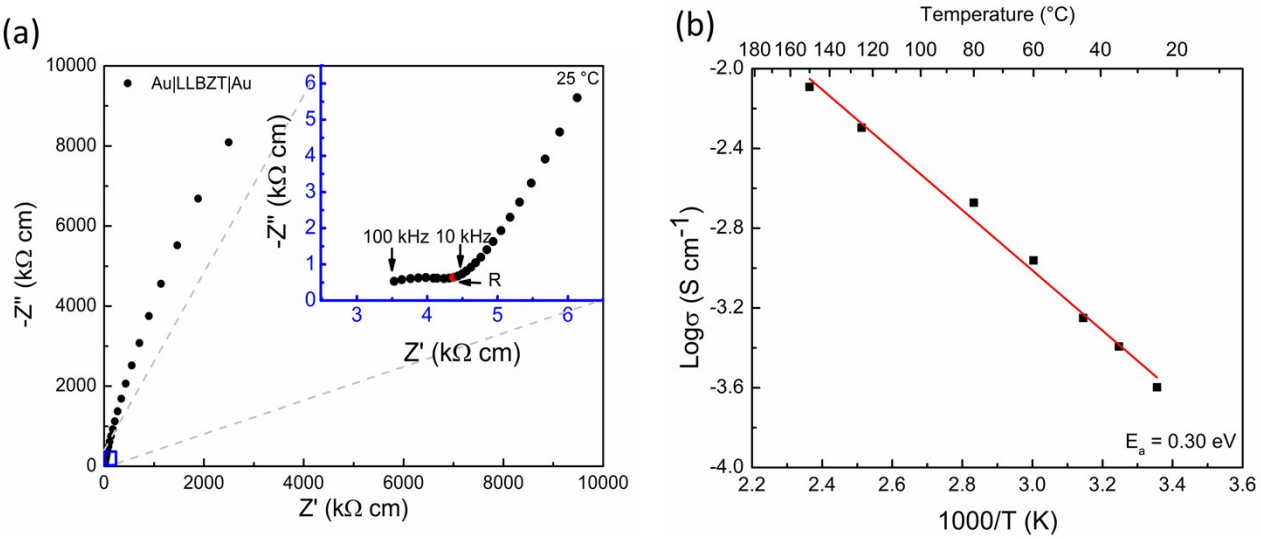


**Figure S3.** (a) Nyquist plot of LLBZT with gold lithium blocking electrodes at 25 °C. Applied voltage is 100 mV with a frequency range of 1 MHz to 0.1 Hz in the temperature range of 20 – 150 °C (b) Arrhenius of LLBZT total ionic conductivity. Conductivity calculated from $\sigma = (1/R)(l/A)$, where l is the thickness of the pellet, a is the surface area, and R is the resistance obtained from bulk + grain boundary contributions in the impedance arc.

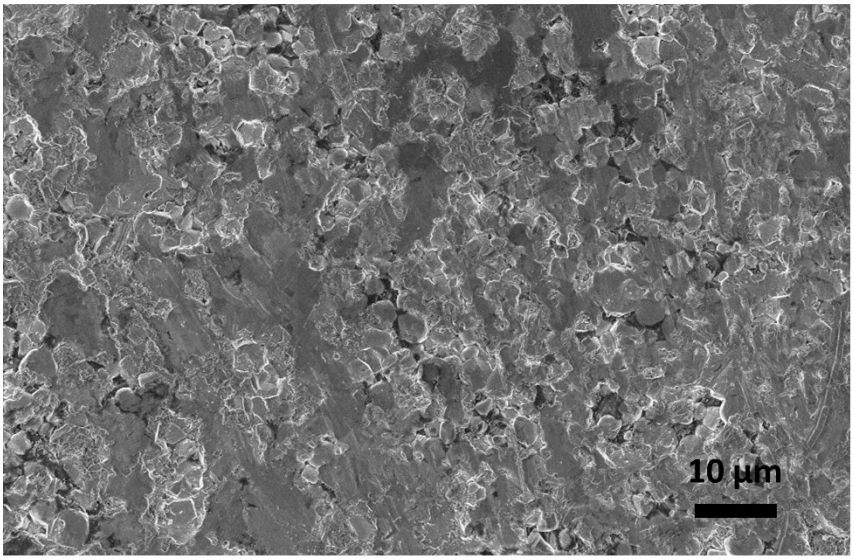


**Figure S4.** SEM image of the LLBZT after polishing with 1500 grit sand paper.

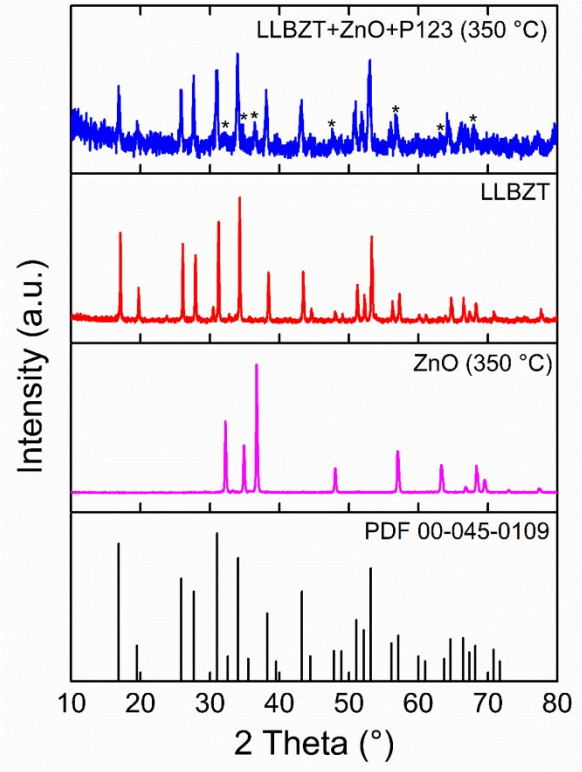


**Figure S5.** XRD pattern of LLBZT after mixing with ZnO+P123 solution and heating to 350 °C showing no other impurity phase has formed when compared to the XRD patterns of only LLBZT and ZnO. XRD pattern of garnet cubic phase reference $Li_5La_3Nb_2O_{12}$ (PDF 00-045-0109) is also shown.

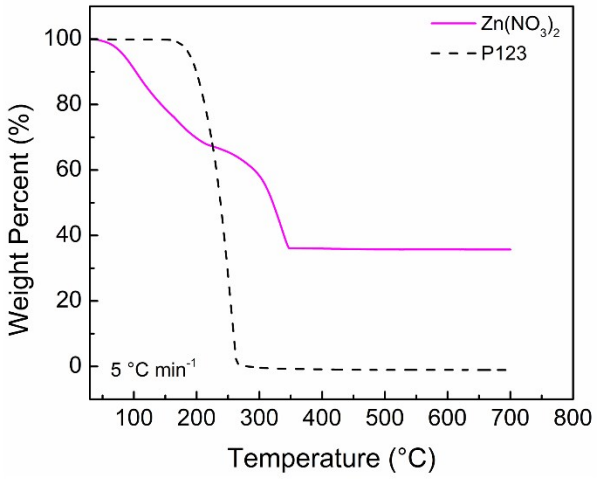


**Figure S6.** Thermogravimetric analysis of $Zn(NO_3)_2 \cdot 6H_2O$ (solid pink) and P123 (dashed black) at a heating rate of 5 °C $min^{-1}$ under 50:50 Ar:$O_2$. The first weight decrease (50-200 °C) for zinc nitrate is associated with dehydration, while the second weight decrease (225-350 °C) is the decomposition of $Zn(NO_3)_2$: $2\ Zn(NO_3)_2 \rightarrow 2\ ZnO + 4\ NO_2 + O_2$

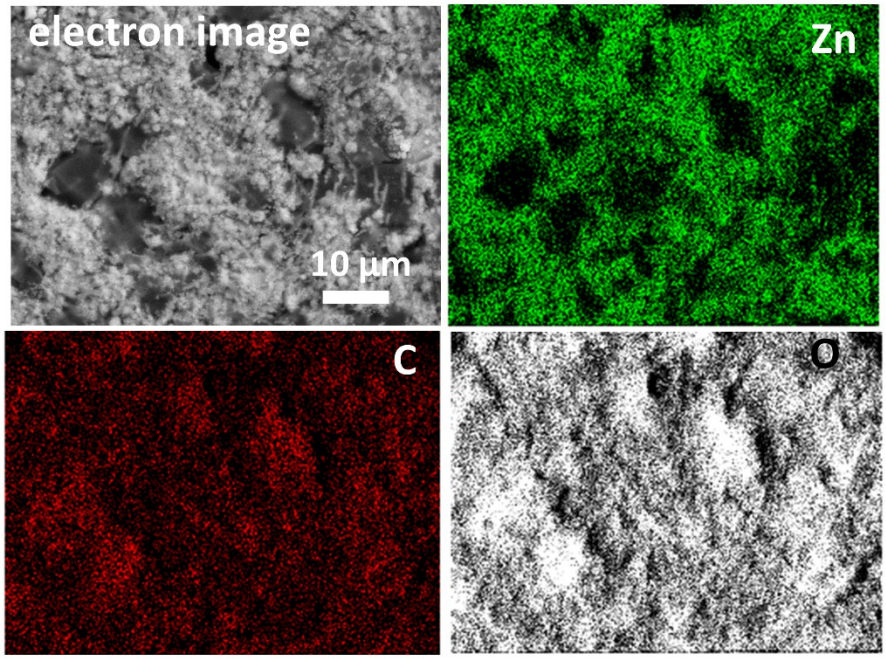


**Figure S7.** (a) SEM image of the top surface of LLBZT after heating a solution 0.3 M $Zn(NO_3)_2$ without P123 (b)-(d) EDX mapping of Zn, C, and O, respectively.

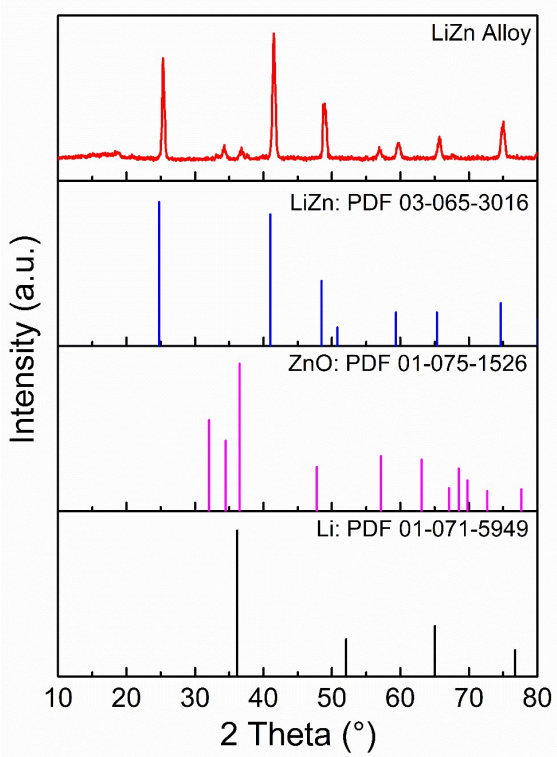


**Figure S8.** XRD pattern of ZnO powder mixed with lithium metal after heating at 250 °C. Lithium (PDF 01-071-5949), ZnO (PDF 01-075-1526) and LiZn (PDF 03-065-3016) added for reference.

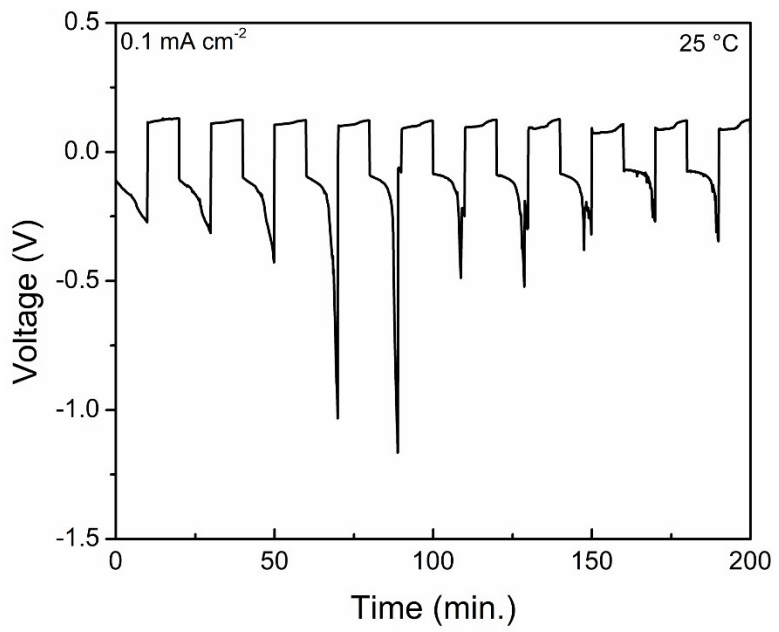


**Figure S9.** Li plating and stripping of untreated Li | LLBZT | Li sample under 0.1 mA $cm^{-2}$ at 25 °C. Large potential peaks are attributed to the high interfacial resistance between the lithium anode and garnet interface.

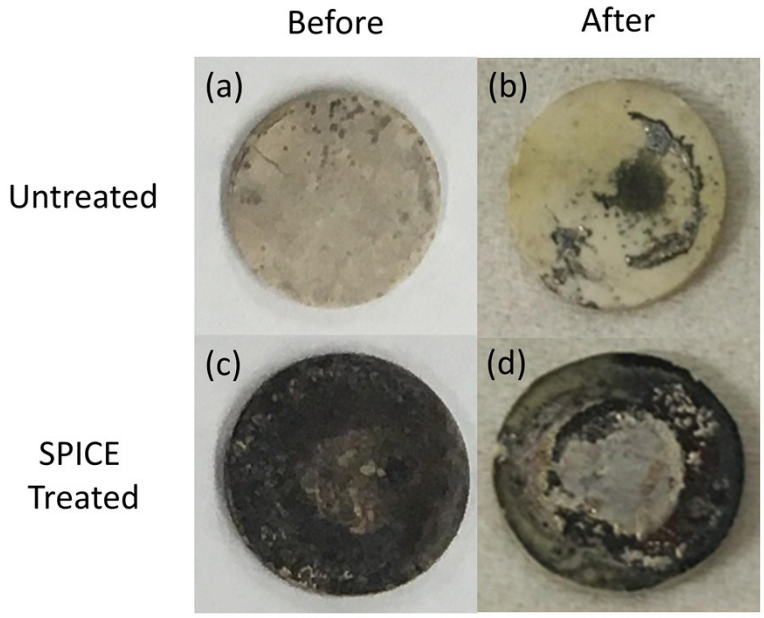


**Figure S10.** Pictures of (a) untreated pellet before lithium plating and striping (b) after plating and striping untreated pellet (c) SPICE-treated LLBZT pellets before Li plating and stripping measurements and (d) SPICE treated pellet after lithium plating and striping.