Electronic Supplementary Information

for

A solid-state route to stabilize cubic $Li_7La_3Zr_2O_{12}$ at low temperature for all-solid-state-battery applications

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Methods

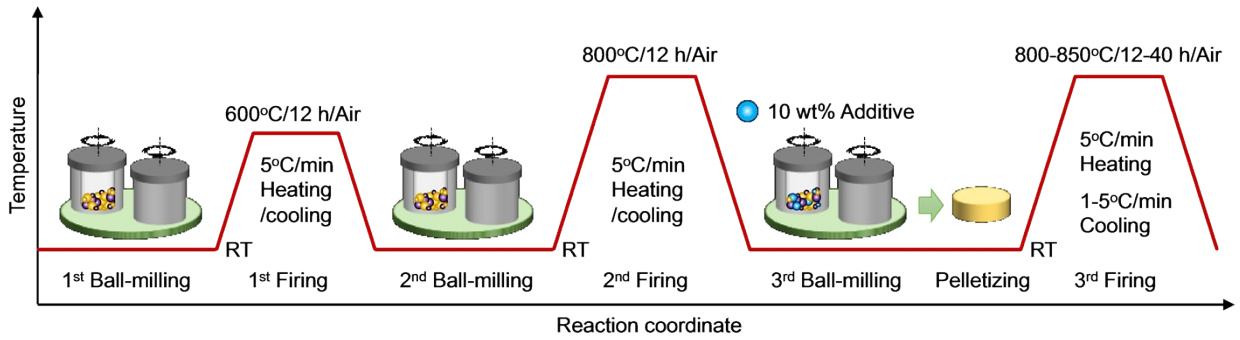

Figure S1. Schematic illustration of the LLZO preparation procedure in this work.

Preparation of $Li_7La_3Zr_2O_{12}$ (LLZO): The synthesis procedure of LLZO and Al-doped LLZO (Al-LLZO) is illustrated in Figure S1. We used a solid-state route consisting of three high-energy ball-milling steps and three firing stages. The 10 wt% excess amount of Li_2CO_3 (≥ 99%, Sigma Aldrich) and the stoichiometric amount of La_2O_3 (99.99%, Sigma Aldrich) and ZrO_2 (99%, Sigma Aldrich) were dispersed in acetone (99%, Alfa Aesar) and mixed using a planetary ball-mill (Retsch, PM200) at 300 or 450 rpm for 9 h. The excess amount of Li was to compensate Li evaporation during heat treatment. As-received La_2O_3 was heated at 900°C for 12 h before use. For Al-LLZO, 2.4 at% Al_2O_3 (99.99%, Sigma Aldrich) was added to the precursor mixture. After drying, the mixture was heated up at a 5°C/min rate, fired at 600°C for 12 h in air, and cooled down to room temperature at a 5°C/min rate. The powder samples were ball-milled again using the same setup at 300 or 450 rpm for 6 h and fired at 800°C for 12 h in air using the same heating and cooling rates as the first firing. To promote densification, 10 wt% Li_3BO_3, Li_3PO_4, or $AlPO_4$ were added to the product as a sintering aid after the second firing and ball-milled together at 450 rpm for 6 h. Disc-shaped pellets (6 mm diameter, 0.5 – 1 mm thickness) were formed by a hydraulic press (Carver). With 5°C/min heating, the pelletized samples were sintered at 800°C or 850°C for 12 h or 40 h in air and cooled down to room temperature (RT) at a 5°C/min or 1°C/min rate. Li_3BO_3 was prepared in-house, and the synthesis method can be found elsewhere.[1] Li_3PO_4 and $AlPO_4$ were used as received (Sigma-Aldrich).

Characterization: X-ray diffraction (XRD, Rigaku Ultima Ⅳ and Bruker D8 Discover) with Cu Kα radiation was used to analyze the phase composition of materials. The symmetry, lattice

parameter, and microstrain of synthesized LLZO were identified using a HighscorePlus software. Field-emission scanning electron microscopy (FE-SEM, Zeiss Auriga) and high-resolution transmission electron microscopy (HR-TEM, FEI Tecnai G2 spirit TWIN) were used to reveal particle morphologies. Electrochemical impedance spectroscopy (EIS) was used to estimate ionic conductivity of Al-LLZO. Silver as a blocking electrode was pasted onto both sides of as-sintered Al-LLZO pellets. Using a spring-loaded, customized Swagelok cell or a noise-shielding sample holder (Biologic, CESH), AC impedance was measured on a frequency response analyzer (Biologic SP-300) in a frequency range 7 MHz – 100 mHz (10 mV AC amplitude). For a variable temperature test, a dedicated thermoelectric temperature chamber (Biologic ITS) was used. The activation barrier (E_a) for Li conductivity was estimated by plotting the Arrhenius-type equation: $\sigma T = A\exp(-E_a/k_B T)$, where σ is the total ionic conductivity measured by EIS, A is conductivity pre-factor, k_B is the Boltzmann constant, and T is temperature. Obtained EIS data were fitted using a ZView software. A custom Swagelok union made of polytetrafluoroethylene with spring-loaded stainless-steel current collectors was used to assemble a Li symmetric cell. We used a 10 wt% Li_3BO_3-added LLZO pellet fired at 850°C for 40 h with 1°C /min cooling (4.97 mm diameter, 1.12 mm thickness) sandwiched in between two Li metal foils (4.76 mm diameter, 100 μm thickness) using a hydraulic press. Cu foils (6 mm diameter, 10 μm thickness) were used as a current collector. The cell was cycled galvanostatically at ±0.05 mA/cm^2 on a potentiostat (Biologic SP-300). The current polarity was switched every 20 min. The critical current density (CCD) was tested by applying various current densities from 2 μA/cm^2 to 5 mA/cm^2 through the Li symmetric cell.

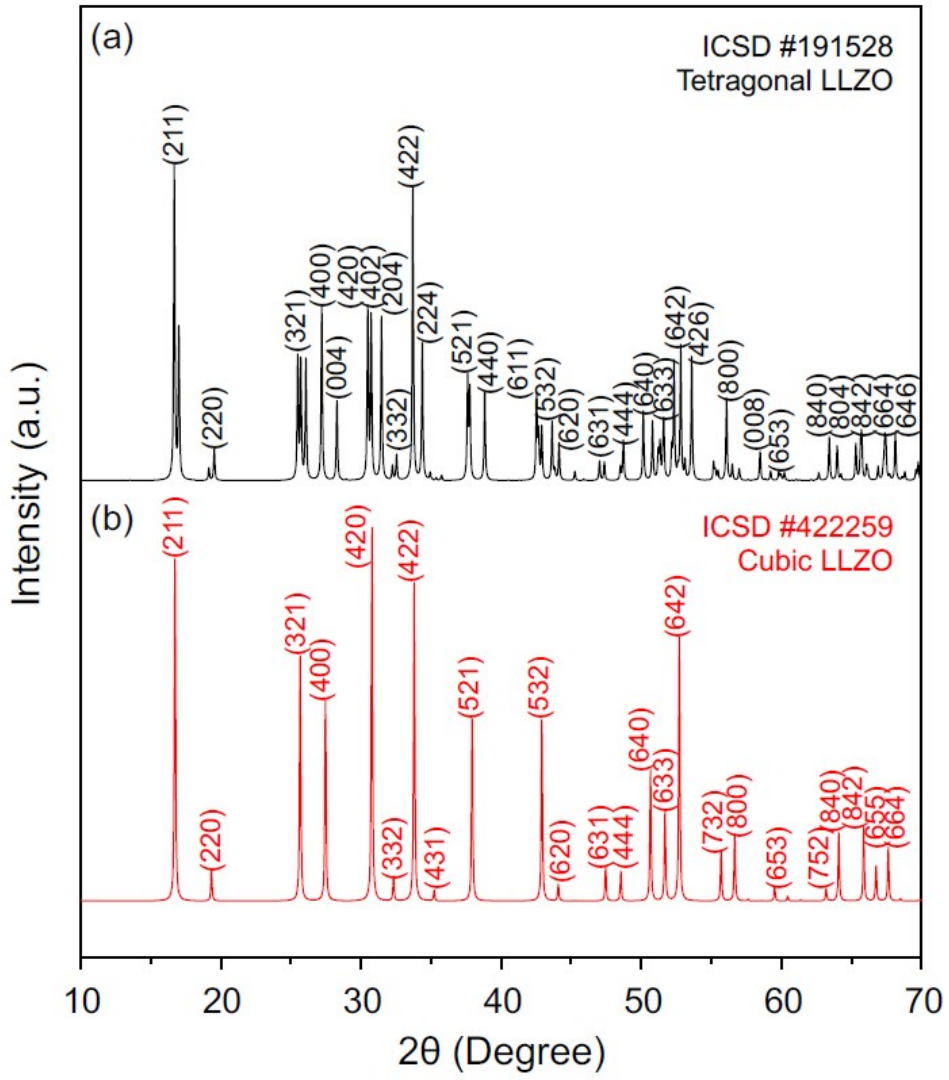

Figure S2. XRD patterns with indexing the planes of (a) tetragonal and (b) cubic phase LLZO.

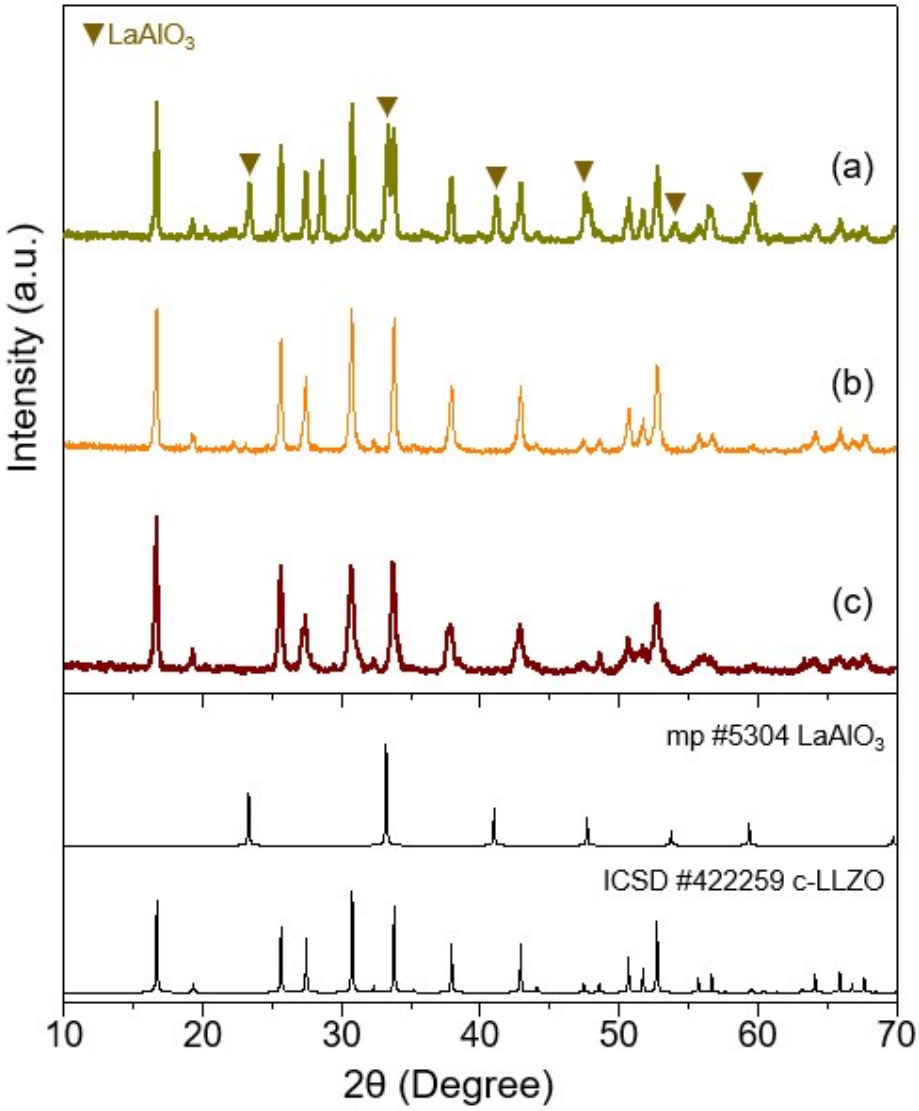

Figure S3. XRD patterns of Al-doped LLZO with (a) $AlPO_4$ 10 wt%, (b) Li_3PO_4 10 wt% and (c) Li_3BO_3 10 wt% obtained by first and second heat treatment at 600°C and 800°C for 12 h and subsequently heat treated at 800°C for 12 h at high cooling rate (5°C/min)

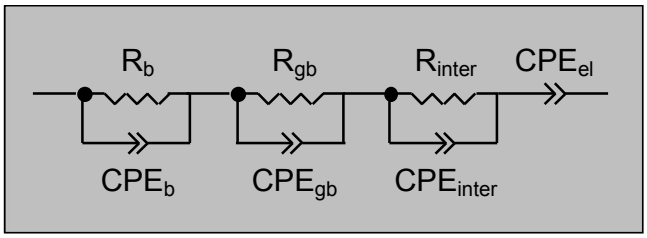

Figure S4. Equivalent circuit to model impedance of bulk (b), grain boundary (gb), and interphase (inter).

Table S1. Summary of electrochemical impedance spectroscopy results: bulk, grain boundary, and interphase resistances and bulk and total Li conductivities of B-Al-LLZO sintered at various conditions.

Sintering conditions (Temperature-Time-Cooling rate)	R_{bulk} (Ω)	$R_{grain\ boundary}$ (Ω)	$R_{interphase}$ (Ω)	σ_{bulk} (S/cm)	σ_{total} (S/cm)
800°C-12h-5°C/min	3596	23963	1516	9.8×10^{-5}	1.2×10^{-5}
800°C-40h-5°C/min	3188	17960	1488	1.9×10^{-4}	2.6×10^{-5}
800°C-40h-1°C/min	1039	1844	570	3.4×10^{-4}	1.0×10^{-4}
850°C-40h-1°C/min	1012	1213	425	3.6×10^{-4}	1.4×10^{-4}

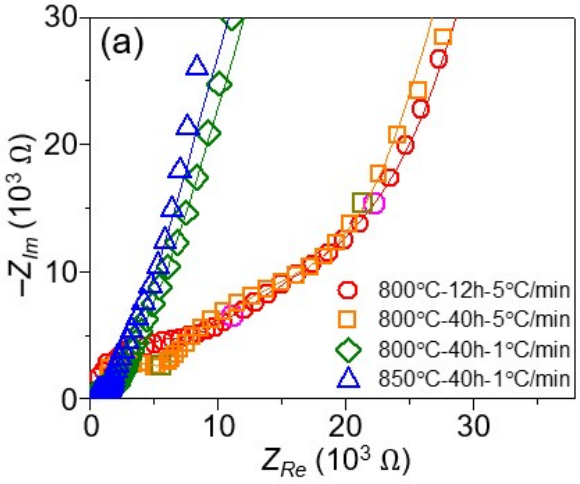

Figure S5. A Nyquist plot of the B-Al-LLZO samples with different heating conditions. EIS was measured in 7 MHz – 3 kHz at room temperature.

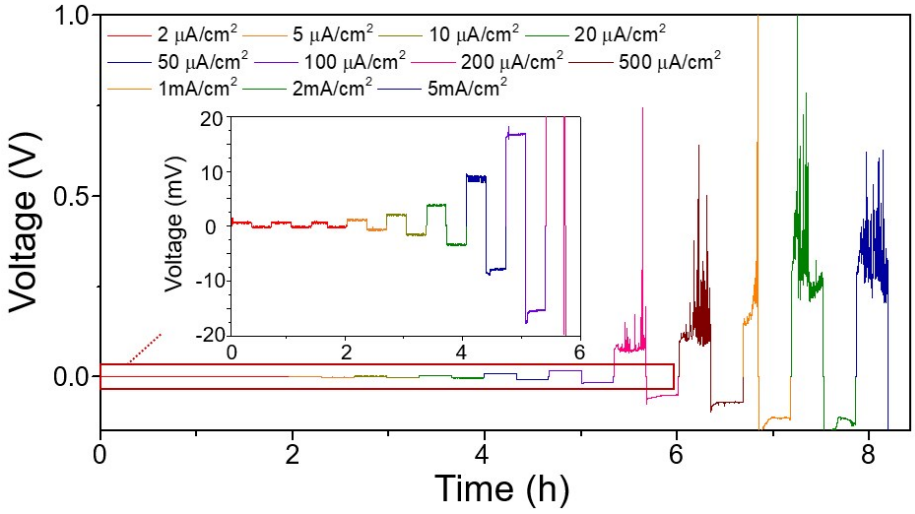

Figure S6. The voltage polarization profile of the Li symmetric cell of B-Al-LLZO sintered at 850°C for 40 h with 1°C/min cooling at room temperature as a function of applied current density ranging from 2 μA/cm^2 to 5 mA/cm^2.

Reference

1. M. Tatsumisago, R. Takano, M. Nose, K. Nagao, A. Kato, A. Sakuda, K. Tadanaga and A. Hayashi, *J. Ceram. Soc. Jpn.*, 2017, **125**, 433-437.