Electronic Supplementary Information (ESI)

Understanding the Role of Microstructure and Grain Boundary in Governing the Ionic Conductivity of NASICON-Type Solid-State Electrolytes

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Experimental Section

Preparation of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) Ceramic Pellets

The LATP powder (Shenzhen Kejing Star Technology Co., Ltd., 99.9%, 300 nm) was weighed 200 mg, placed into a 10 mm diameter cylindrical tablet press mold, and pressed into round tablets under a uniaxial pressure of 3 tons (≈ 400 MPa) for 5 mins. The tablets were sintered in a muffle furnace (KSL-1100X, Hefei Kejing Materials Technology Co., Ltd., China) for 12 h at 850 °C, 900 °C, 950 °C, 1000 °C, and 1050 °C, respectively. To prevent the formation of byproducts on the surface of LATP ceramic pellets at high temperatures, a small amount of pristine powder was applied to cover the surface of the pellets during sintering.[1] After sintering, the surfaces of the LATP were polished, cleaned with anhydrous ethanol, and dried in an oven to yield final LATP ceramic pellets.

Materials Characterization

X-ray diffraction (XRD) patterns of LATP powder and pellets were obtained to characterize the crystal structures and analyze the crystallinity. XRD patterns were performed on an Empyrean diffractometer from Malvern Panalytical using Cu Kα (λ = 1.5406 Å) at 45 kV and 40 mA in the range of 10° to 60°. The morphology and energy disperse spectrum mapping were obtained using SEM (JSM-7610Fplus, JEOL Ltd., Japan). Grain size analysis of sintered LATP was performed using Nano Measurer software. X-ray computed tomography (XCT, nanoVoxel-3000, Sanying Precision Instruments Co., Ltd, China) was employed to analyze the three-dimensional morphology of the sintered LATP ceramic pellets. The reconstructed XCT data were imported into Volume Graphics software, for 3D visualization and porosity analysis.

Electrochemical Tests and Analysis

Ionic conductivity was measured by Electrochemical impedance spectroscopy (EIS) tests. 10 mV AC voltage (0.1 Hz to 7 MHz) was applied at room temperature using a BioLogic SP-300 potentiostat workstation. The top and bottom surfaces of the LATP ceramic pellets were sputter coated with Au as blocking electrode layers. Moreover, the Nyquist curves were fitted by equivalent circuit to obtain the resistance of LATP ceramic pellets. The EIS data were mathematically processed to generate Distribution of relaxation time (DRT) spectra using DRTtools on MATLAB 2018a.2-4 The Gaussian process was applied for DRT deconvolution, with the analysis based on the combined real and imaginary components of the EIS data.

Supporting Figures

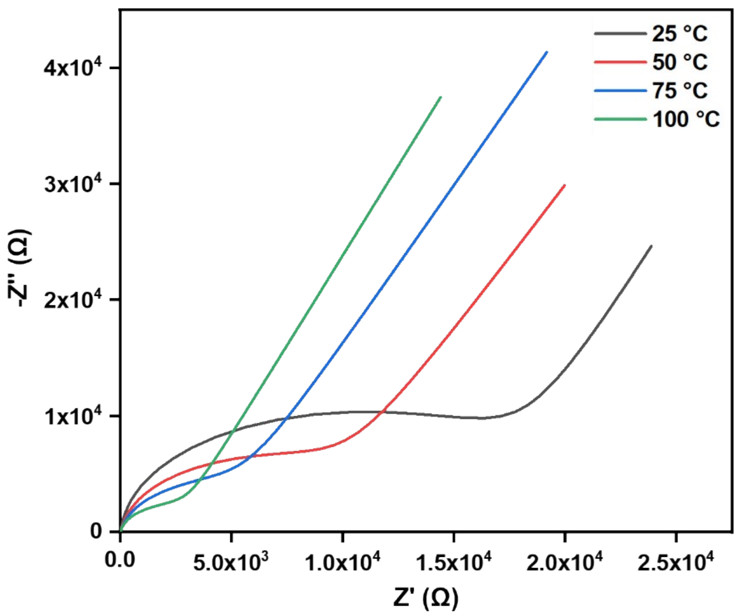

Fig. S1 Nyquist plots of the LATP ceramic pellets sintered at 850 °C. The EIS curves were collected at 25 °C, 50 °C, 75 °C and 100 °C.

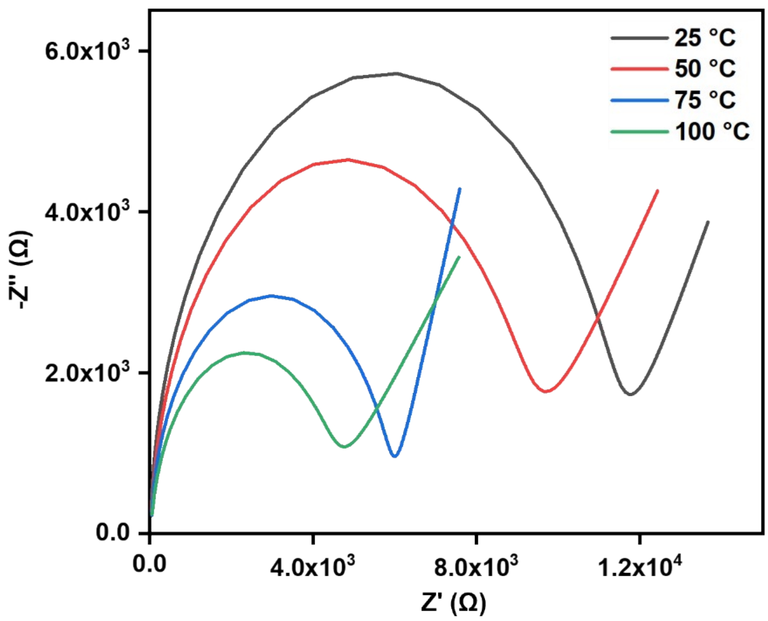

Fig. S2 Nyquist plots of the LATP ceramic pellets sintered at 900 °C. The EIS curves were collected at 25 °C, 50 °C, 75 °C and 100 °C.

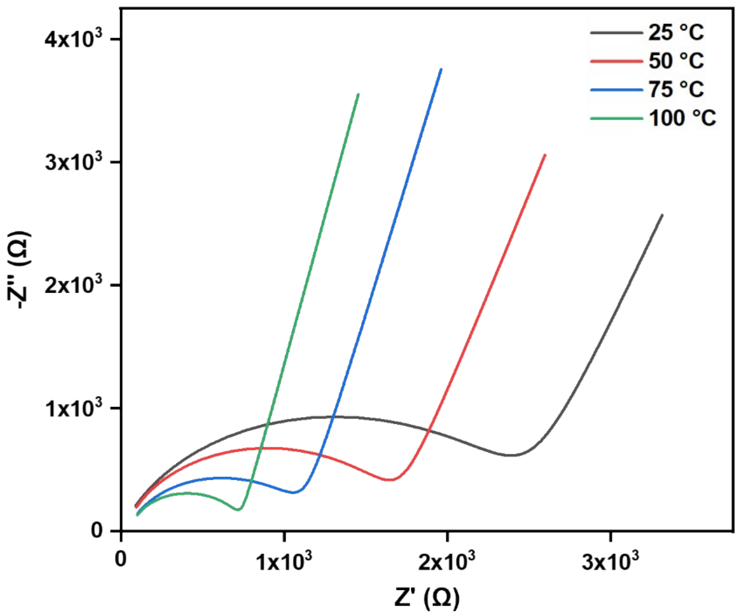

Fig. S3 Nyquist plots of the LATP ceramic pellets sintered at 950 °C. The EIS curves were collected at 25 °C, 50 °C, 75 °C and 100 °C.

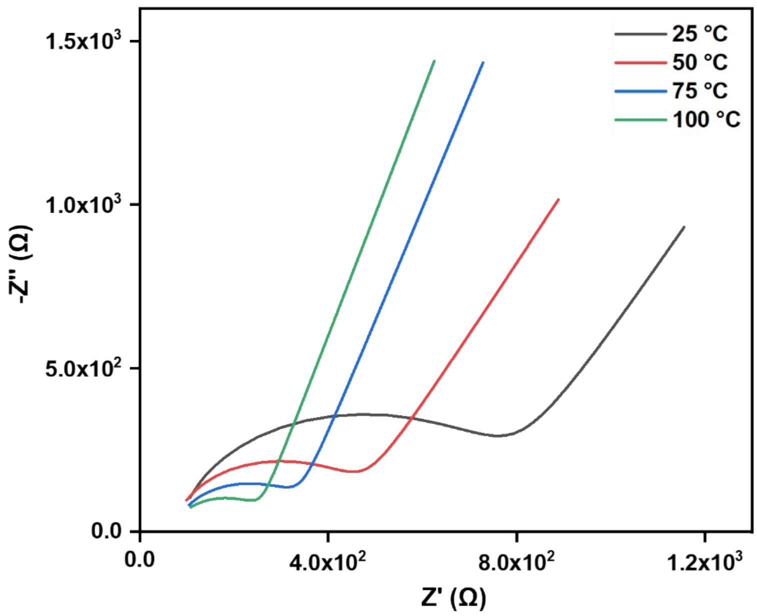

Fig. S4 Nyquist plots of the LATP ceramic pellets sintered at 1000 °C. The EIS curves were collected at 25 °C, 50 °C, 75 °C and 100 °C.

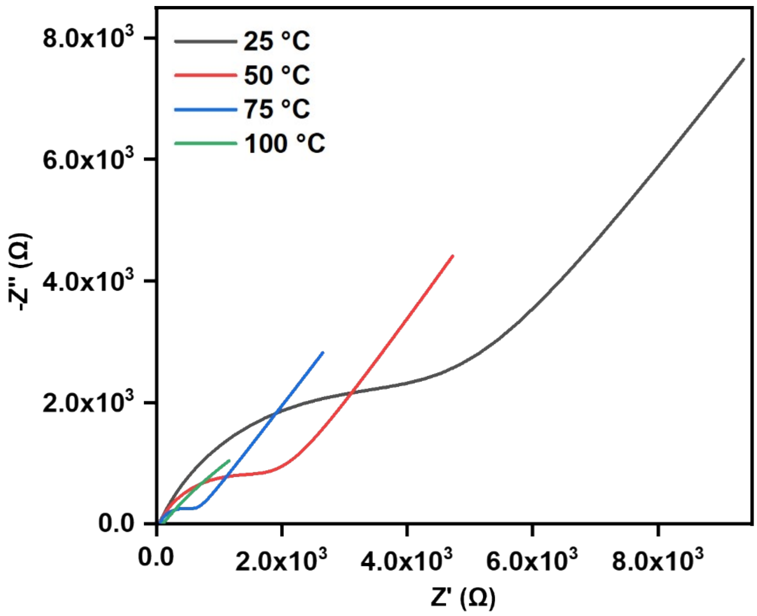

Fig. S5 Nyquist plots of the LATP ceramic pellets sintered at 1050 °C. The EIS curves were collected at 25 °C, 50 °C, 75 °C and 100 °C.

References

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