Probing into the Origin of Electronic Conductivity Surge in Garnet Solid-State Electrolyte

Supporting Information

Methods

$Li_7La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$ (LLCZN) powder and ceramics preparation: Stoichiometric amount of Li_2CO_3 (99.99 %, Alfa, with 10% excess to compensate the Li loss during sintering), La_2O_3 (99.99 %, Alfa), $CaCO_3$ (99.99 %, Alfa), ZrO_2 (99.99 %, Alfa), Nb_2O_5 (99.99 %, Alfa) precursors were mixed by ball milling for 10 h and calcined at 900 ℃ in an alumina crucible for 10 h to obtain LLCZN powder.The LLCZN powder were pressed into pellets with a diameter of 1/2 inches, the white pellets were covered with mother powders and sintered in alumina crucible at 1100 ℃ for 10 h. The resulting pellets were polished to suitable thickness with sand papers and stored in Ar-filled glovebox to prevent reaction with humidity and CO_2.

Characterization and electrochemical measurement: The structural characterization was performed by X-ray diffraction (XRD, Bruker D8 Advance powder X-ray diffractometer) with 2θ in the range of 10-80° with a step size of 0.05°. Morphology study was performed using a scanning electron microscopy (SEM, Zeiss SUPRA-55). The impedance spectroscopy and electronic conductivity of solid electrolytes various temperature were measured by an electrochemical workstation (1400 cell test system, Solartron). A symmetric cell was assembled by stacking LLCZN between two Li foils in a Swagelok cell. The lithium plating/stripping test was carried out by galvanostatic cycling with an automatic galvanostatic charge–discharge unit (Maccor, MC-16 Battery Test System).

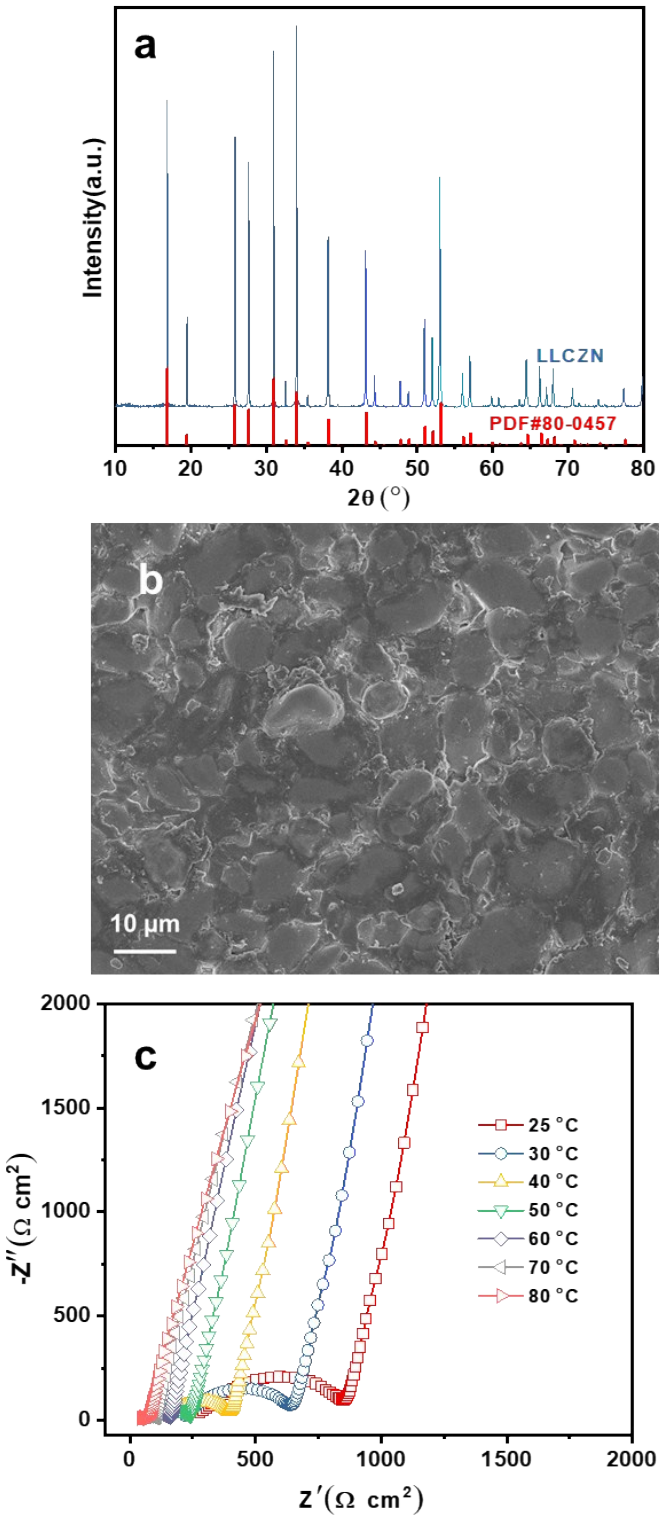

Figure S1. (a) XRD pattern (b) SEM image and (c) electrochemical impedance spectra at different temperatures of the as-prepared LLCZN.

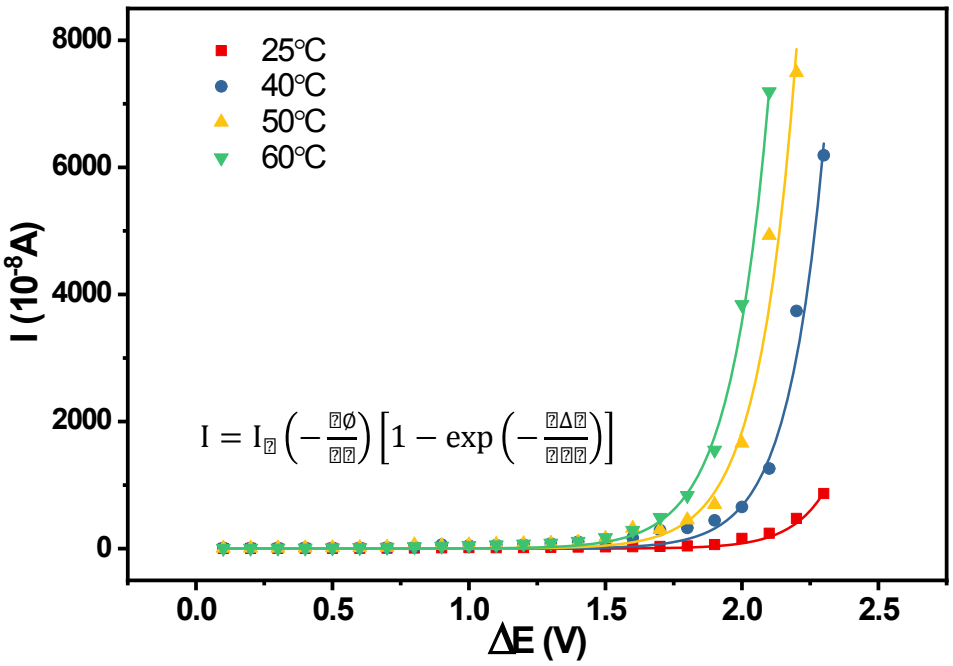

Figure S2. Fitting curves of I-V data for LLCZN at different temperatures.

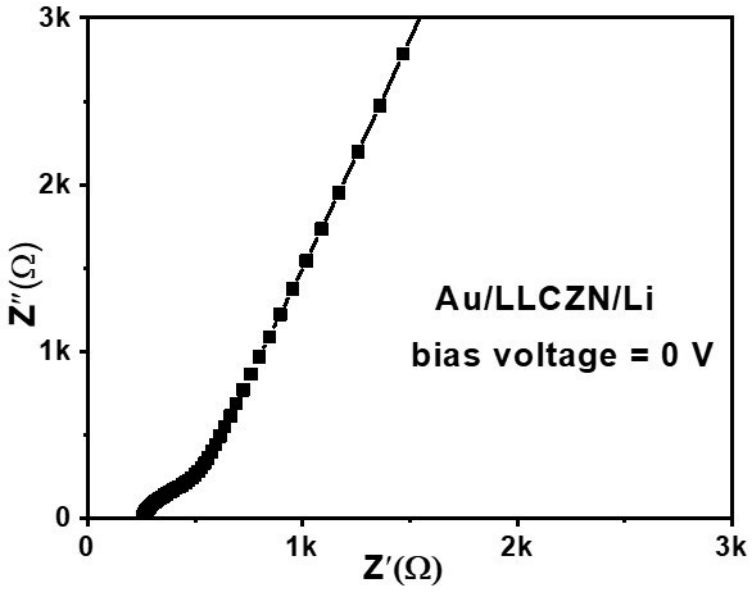

Figure S3. Electrochemical impedance spectrum of Au/LLCZN/Li cell without external voltage bias.

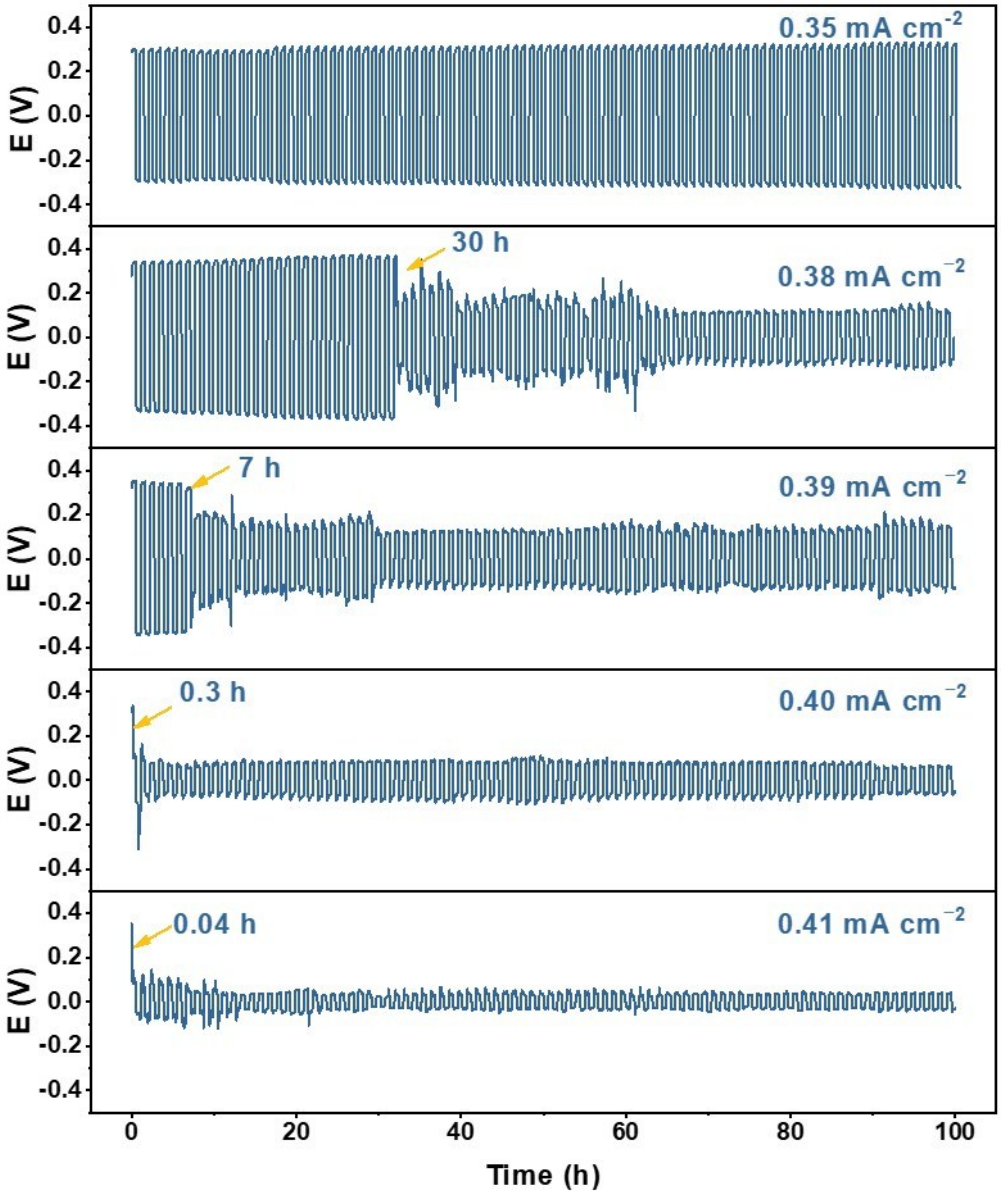

Figure S4. Lithium platting/stripping performance of Li/LLCZN/Li symmetric cells at 25 ℃ under different current densities..

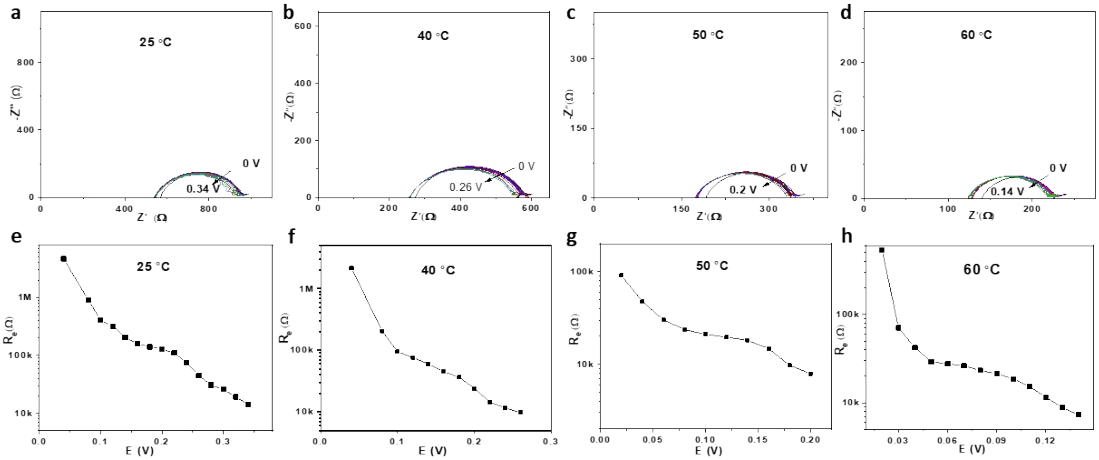

Figure S5. (a-d) Electrochemical impedance spectra of Li/LLCZN/Li cells under different voltage biases and temperatures and (e-h) calculated R_e.

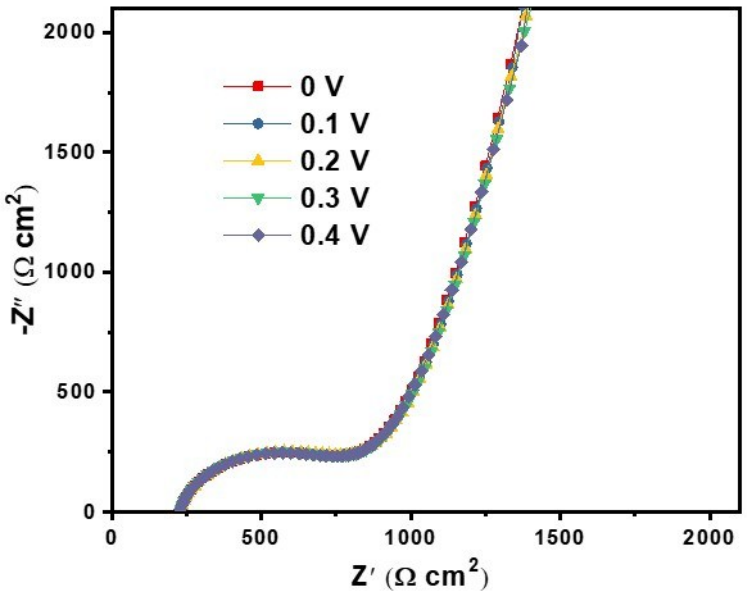

Figure S6. Electrochemical impedance spectra of Au/LLCZN/Au cell under different voltage biases at 25 ℃.

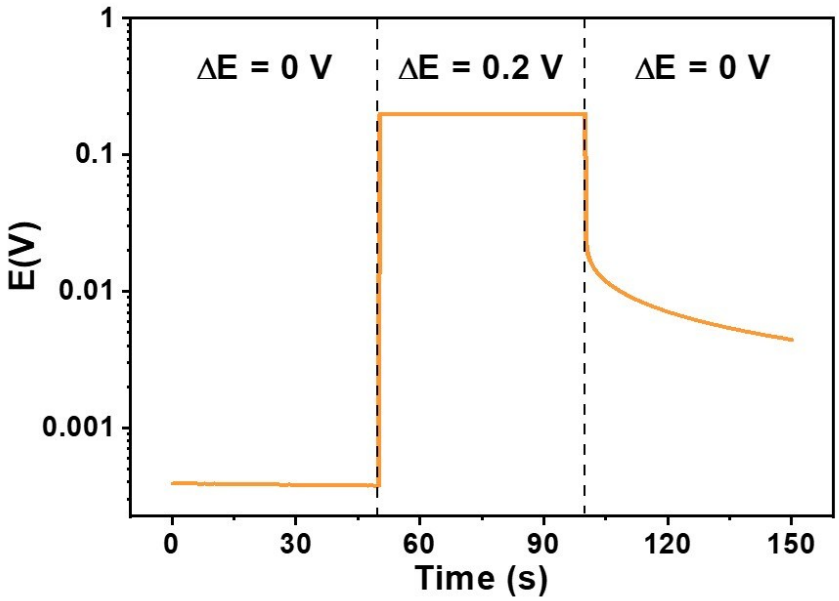

Figure S7. The change of open-circuit voltage with applied external voltages in a Li/LLCZN/Li cell.