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Supplemental Information for

The effects of aluminum concentration on the microstructural and electrochemical properties of lithium lanthanum zirconium oxide

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Supplementary Methods

To obtain information about the phase purity and structure of the calcined powders, characterizations were performed using X-ray diffraction (XRD). The instrument was a D4 Endeavour instrument (Bruker GmbH, Mannheim, Germany) using Cu Kα radiation and equipped with a 1D detector LYNXEY and a DIFFRACplus BASIC package, which was released in 2009. All samples were measured from 10 to 90° 2Θ with 0.02° steps. For the measurements the powders were mortared to fine powder to ensure good statistics.

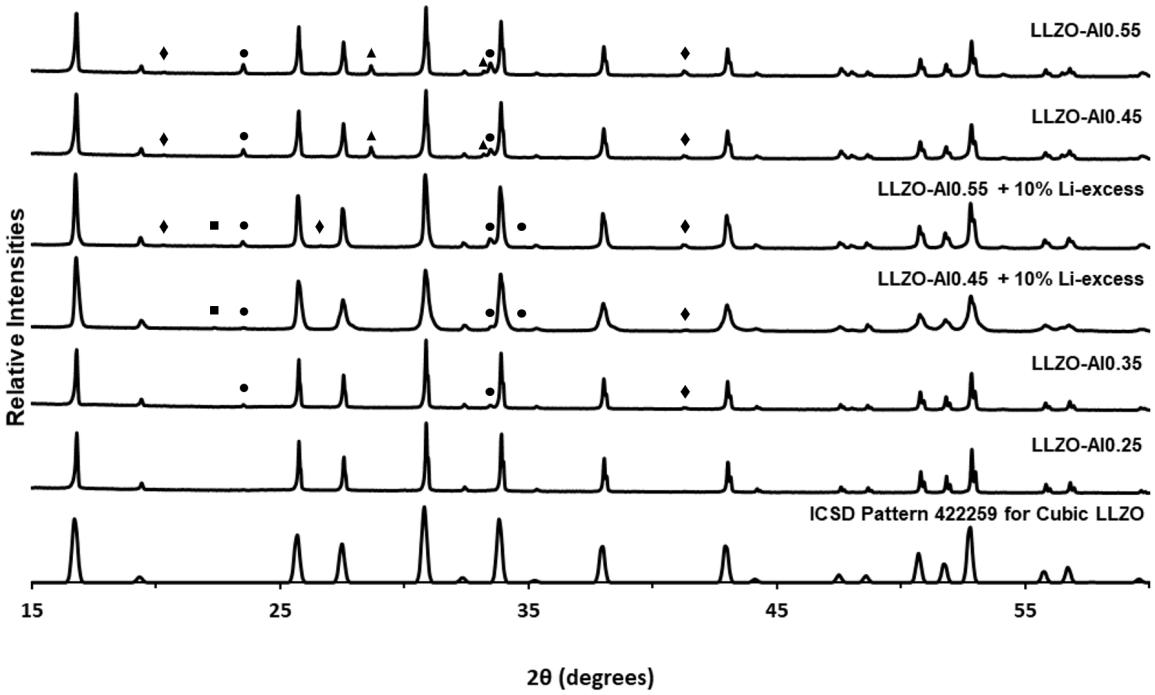

Figure S1: XRD patterns of calcined powders before hot pressing. ICSD Pattern 422259 was used for cubic LLZO. Impurity phases are indicated by: ▲ $La_2Zr_2O_7$, ● $LaAlO_3$, ♦ Li_2ZrO_3, and ■ $LiAlO_2$.

Table S1: ICP-OES of the calcined powders before hot-pressing

	Li	Al	La*	Zr	Li excess
LLZO-Al0.25	6.531	0.254	3.226	1.98	0%
LLZO-Al0.35	6.304	0.348	3.175	1.98	0%
LLZO-Al0.45	6.958	0.476	3.115	1.98	10%
LLZO-Al0.55	6.506	0.567	3.073	1.98	10%

* The technique used is overestimating La, so Zr was used for normalization. More details can be found here.[1] The remaining 0.02 of Zr is accounted for with Hf impurities in the starting powders.

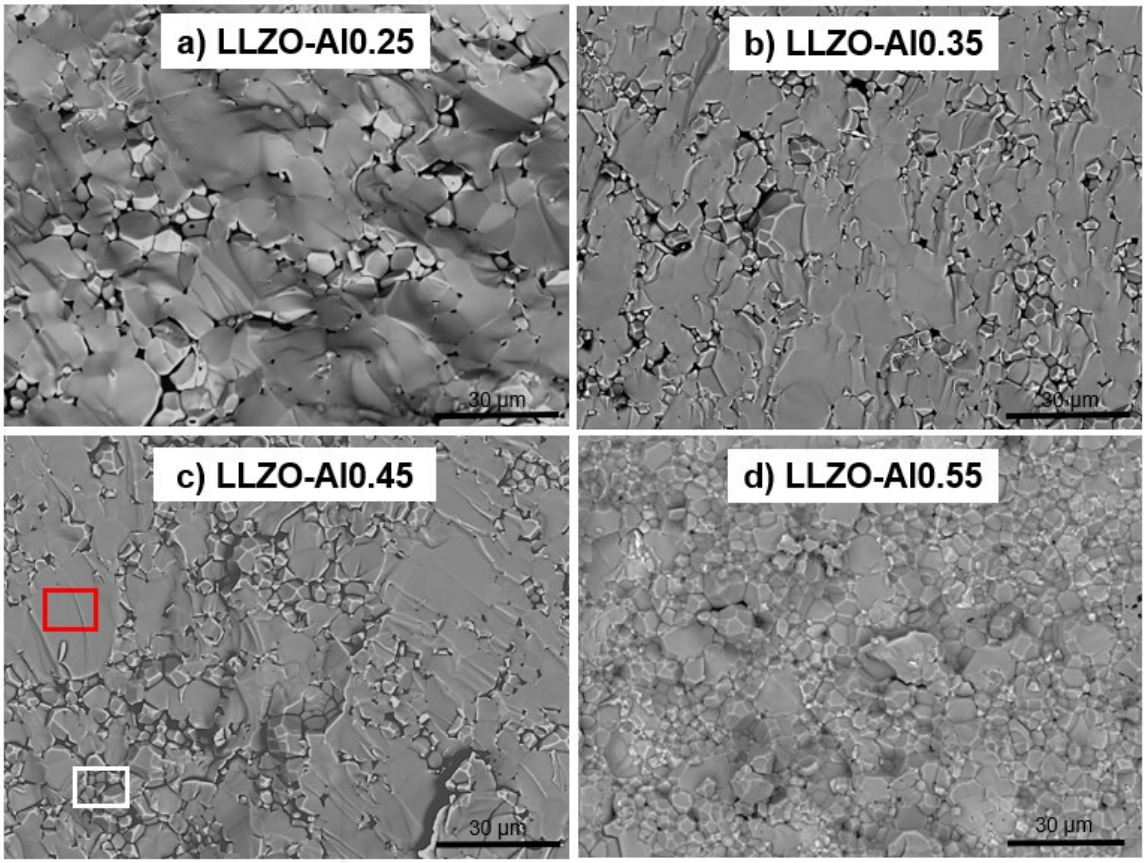

Figure S2: Fracture surface of hot-pressed a) LLZO-Al0.25, b) LLZO-Al0.35, c) LLZO-Al0.45, d) LLZO-Al0.55. The red box is an example of intragranular fracture and the white box is an example of intergranular fracture.

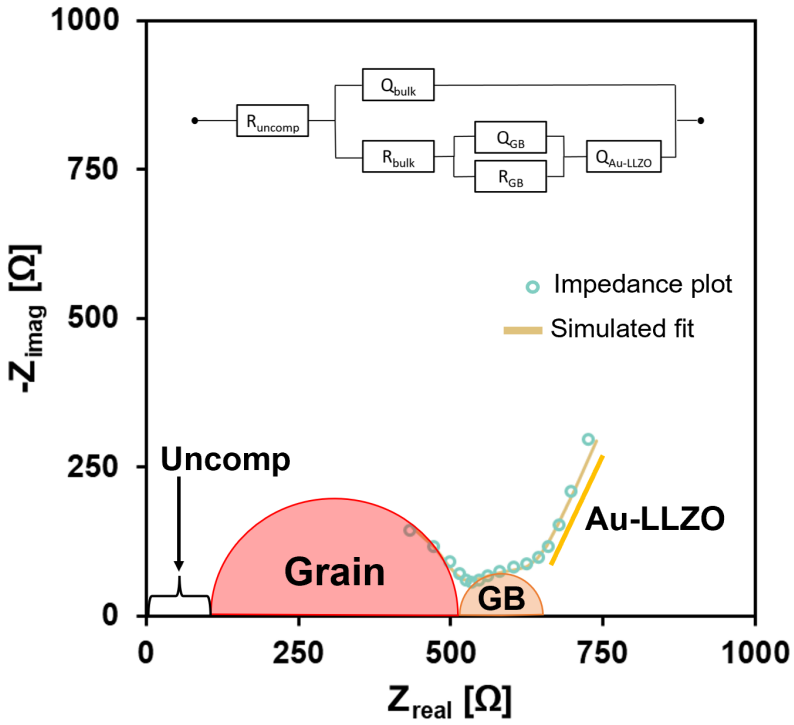

Figure S3: Representative Nyquist plot with modeled equivalent circuit fit. Blue circles are the data from the impedance plot and the tan line is the simulated fit based on the featured modified Huggins equivalent circuit.[2] R is resistance, Q is capacitance, Uncomp is uncompensated, GB is grain boundary, and Au-LLZO is the electrode-electrolyte interface. Grain and grain boundary contributions to the impedance are marked by semi-circles. Electrode-LLZO interface is marked by the yellow line. Uncompensated resistance is demarcated by the bracket.

References

1 T. F. Malkowski, E. D. Boeding, D. Fattakhova-Rohlfing, N. Wettengl, M. Finsterbusch and G. M. Veith, *Ionics*, , DOI:10.1007/s11581-022-04536-0.

2 R. A. Huggins, *Ionics*, 2002, **8**, 300–313.