Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

The Origin of Chemical Inhomogeneity in Garnet Electrolytes and its Impact on the Electrochemical Performance

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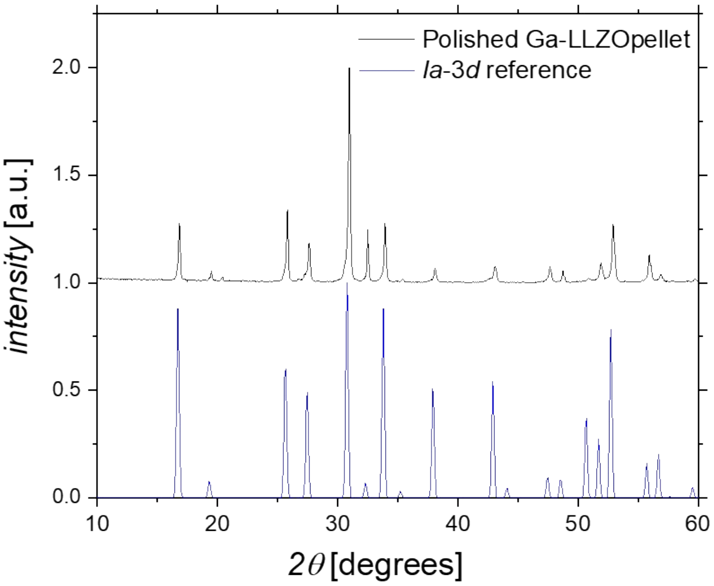

Figure S1. X-ray diffraction pattern (black line) of Ga-LLZO pellet and reference pattern (blue line) with the cubic $Ia\bar{3}d$ space group.

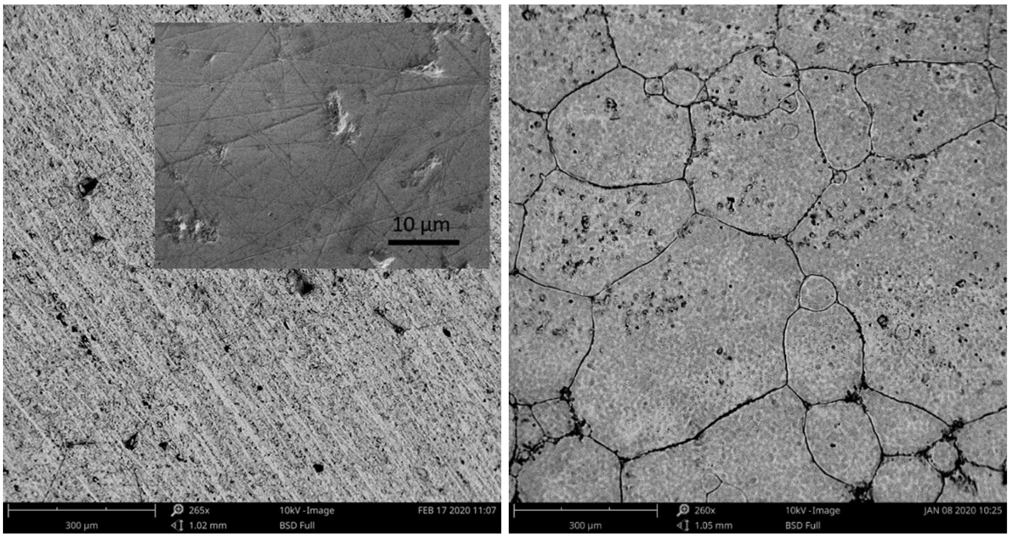

Figure S2. SEM micrographs of Ga-LLZO pellet following polishing with 4000-grit SiC (left), with inset at higher magnification and thermal etching at 900 °C (right).

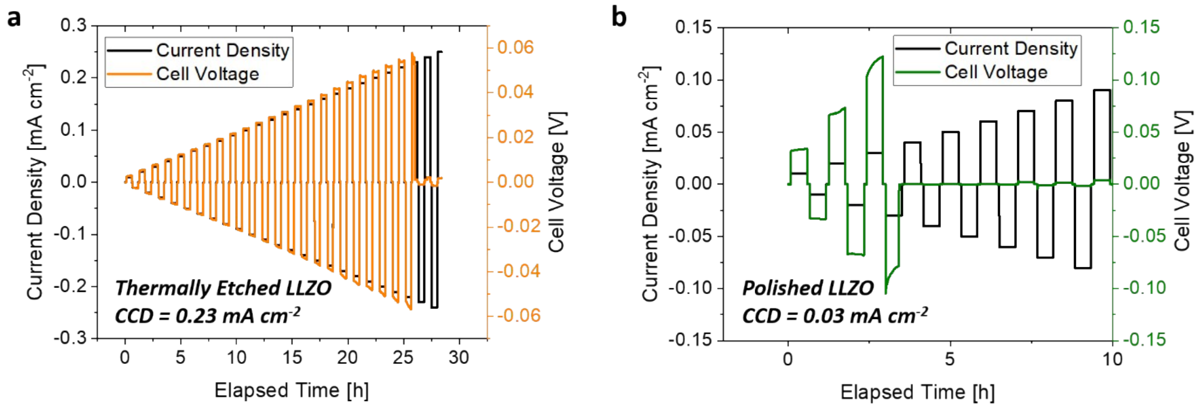

Figure S3. Galvanostatic charge-discharge plots for thermally etched (a) and polished (b) Ga-LLZO with the same microstructure and thickness.

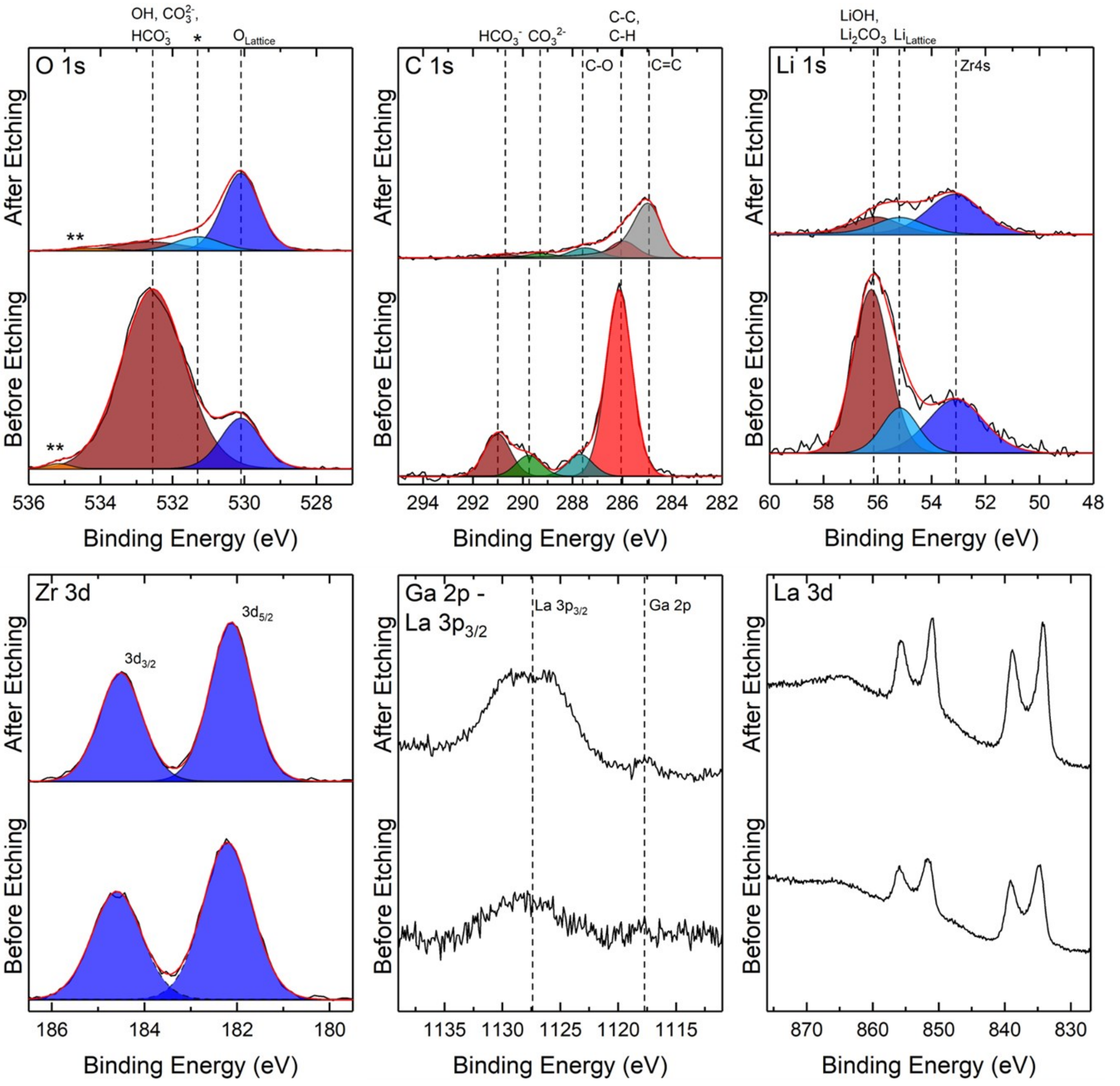

Figure S4. X-ray photoelectron spectra of a Ga-LLZO pellet, before (bottom row) and after (top row) heating to 800 °C under vacuum, on a polished sample. C 1*s*, O 1*s*, Li 1*s*, and Zr 3*d* spectra are fitted using Voigt line shapes for each component and Shirley backgrounds. Peaks indicated by * and ** in the O 1*s* region are attributed to charging artefacts (differential charging of species); with * also potentially relating to the presence of Li_2O but a corresponding peak in the Li 1*s* region is not apparent. These charging peaks were allowed to relax up to 2eV higher than main peak with no FWHM restriction.

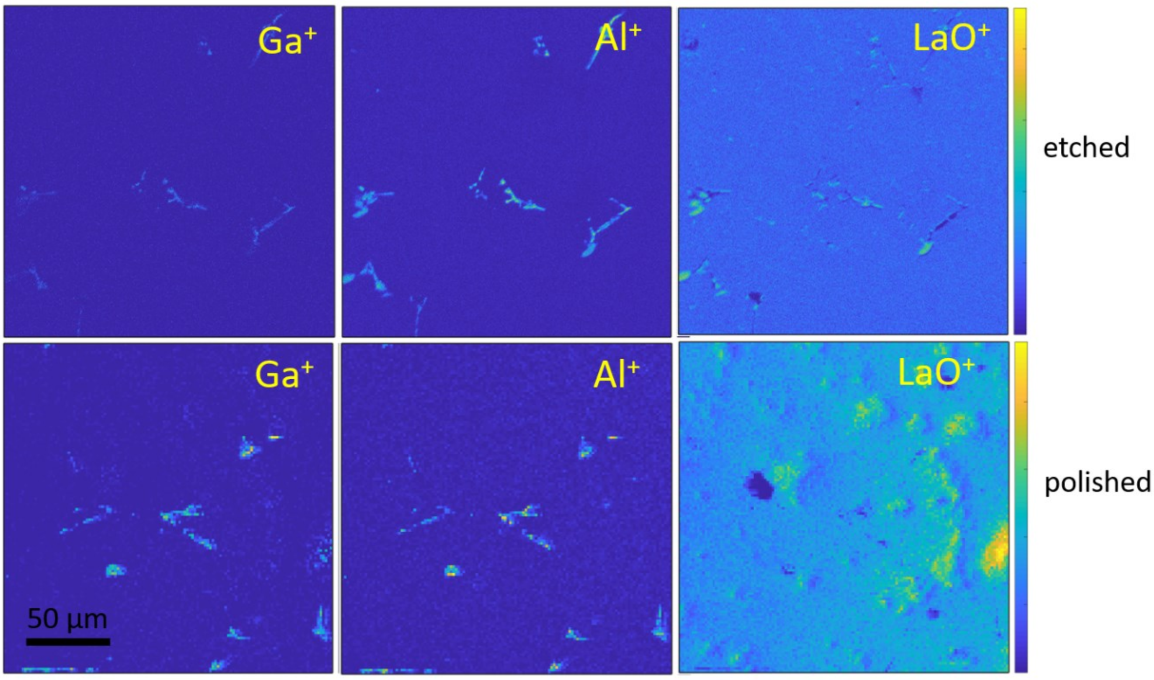

Figure S5. ToF-SIMS positive secondary ion maps of etched and polished samples, corresponding to the depth profiles in Figure 3. The analysis was performed using 25 keV Bi^+ primary ions as the analytical beam and the sputtering was performed by Ar_n^+ (13.5 nA) (burst mode).

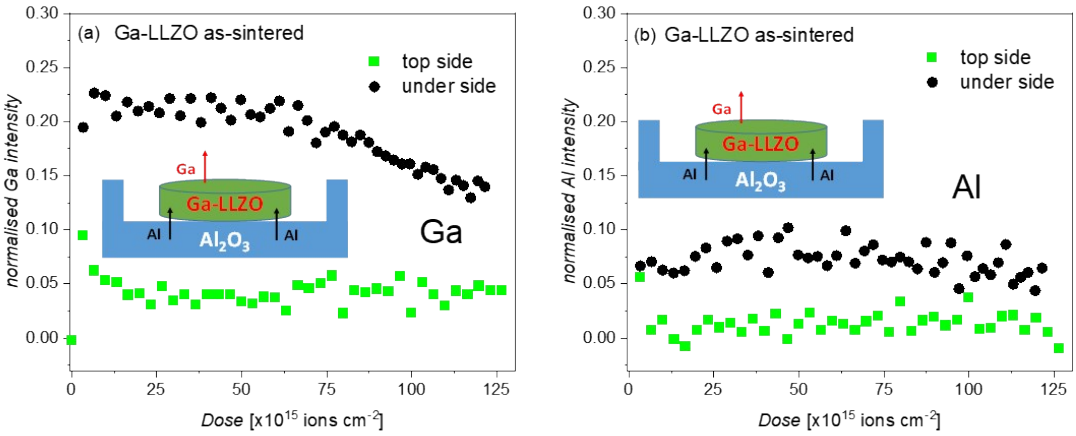

Figure S6. ^{4}He LEIS depth profiles with a 0.5 keV Ar sputter gun showing normalized Ga (a) and Al (b) intensities (with respect to the sum of all surface species) for a Ga-LLZO pellet sintered in an alumina crucible, measured on both sides of the pellet. The sputter area is 1500 by 1500 µm and the analysis area is 750 by 750 µm.

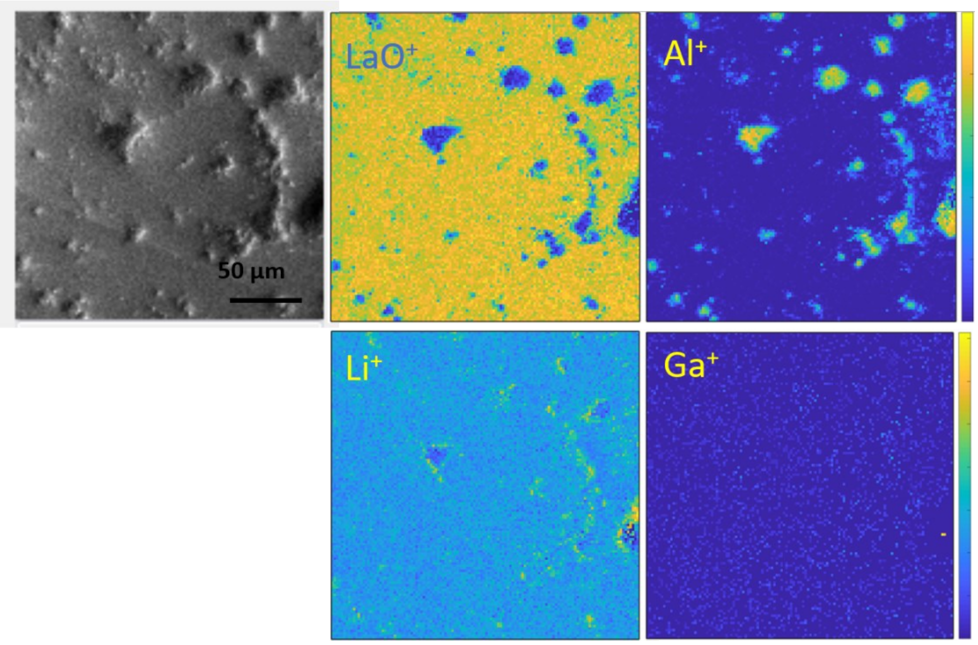

Figure S7. ToF-SIMS positive secondary ion maps and optical images (greyscale) of polished sample, corresponding to the depth profiles in Figure 4b and 5b. The analysis was performed using 25 keV Bi^+ primary ions as the analytical beam and the sputtering was performed by 1 keV O_2^+ beam (burst mode).

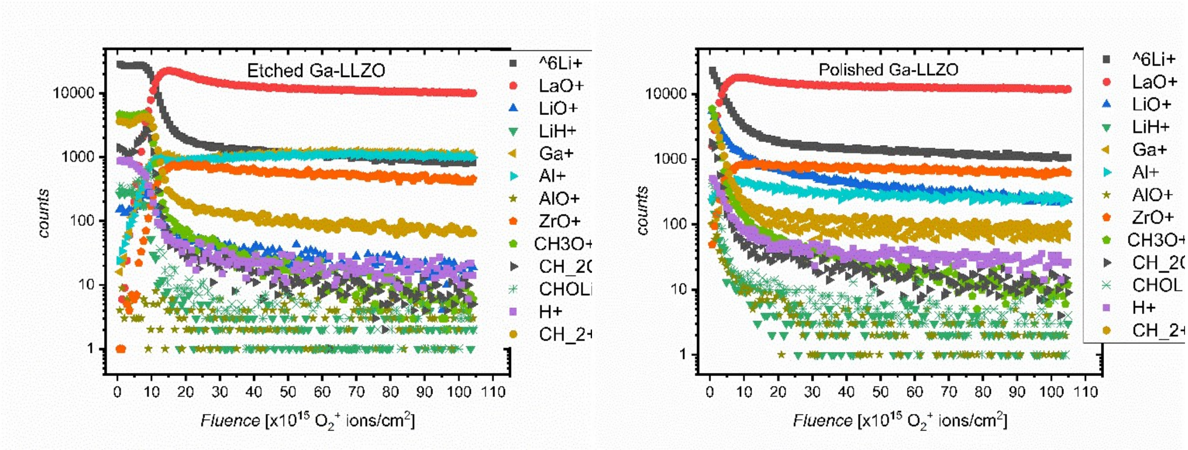

Figure S8. ToF-SIMS depth profiles of etched (left) and polished (right) LLZO pellets. The analysis was performed using 25 keV Bi^+ primary ions as the analytical beam and the sputtering was performed by 1 keV 280 nA O_2^+ beam (burst mode).

Table S1. Quantification of *ex situ* RT photoelectron spectroscopy spectra on two Ga-LLZO pellets, polished and etched at 900 C in the glove box, and both samples left in the glove box for several hours.

Peak identity	Atomic %	
	Polished	Etched
C 1*s* C-C	5.89	9.12
C 1*s* CO_3^{2-}	0.86	1.17
C 1*s* H-CO_3^-	1.96	3.65
C 1*s* C-O	0.49	0.90

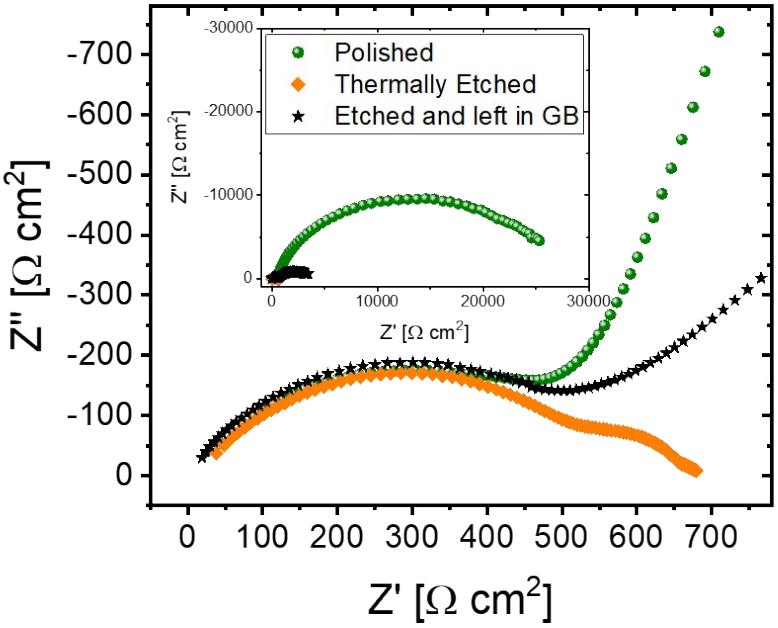

Figure S9. Electrochemical impedance Nyquist plots of etched (orange squares) and polished (green circles) Ga-LLZO and Ga-LLZO left in glove box after etching for ~16 hours (black stars) in a symmetric Li|LLZO|Li coin cell, measured at 298 K across the frequency range 13MHz to 1 Hz. The inset shows the low frequency data points.

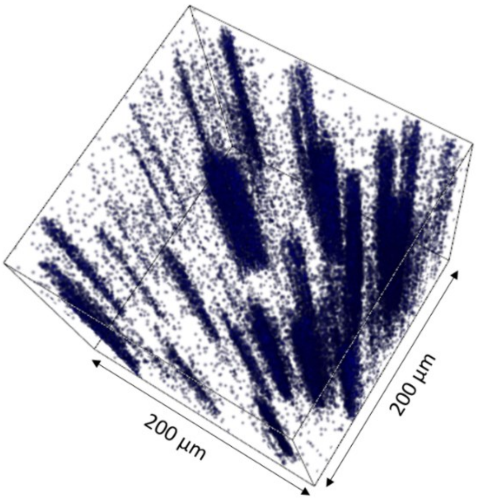

Figure S10. Three-dimensional reconstruction of the polished Ga-LLZO sample, showing Al^+ ions in the pores.

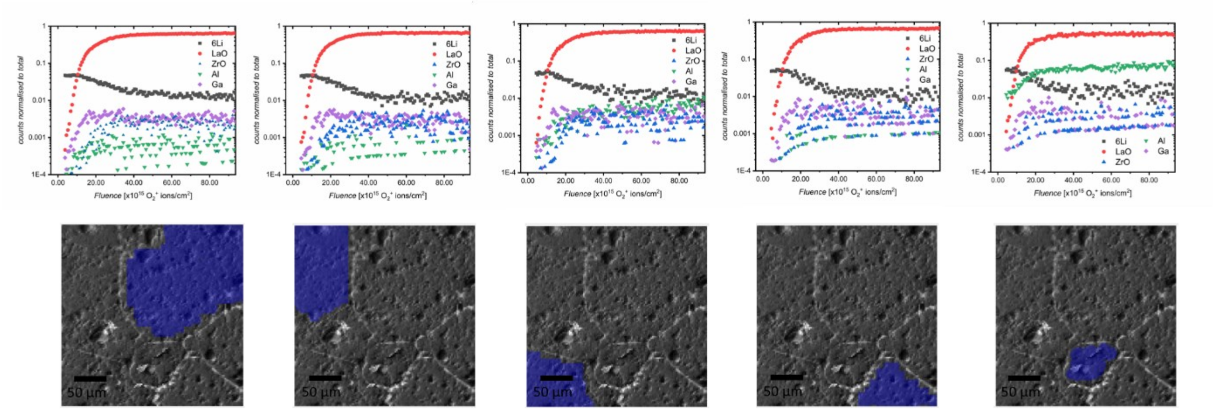

Figure S11 – ToF-SIMS positive secondary ion depth profiles and corresponding region of interest highlighted on optical images (greyscale) of an etched LLZO sample. The analysis was performed using 25 keV Bi^+ primary ions as the analytical beam and the sputtering was performed by 1 keV O_2^+ beam (burst mode).