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

Supplementary Information

Elucidating the Role of Dopants on the Critical Current Density for Dendrites Formation in Garnet Electrolytes

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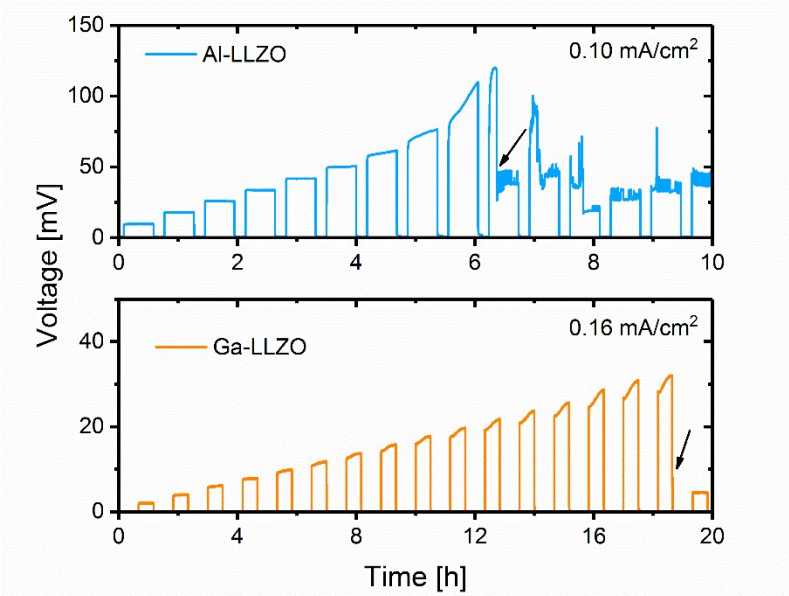
S1. ICP results

Table S1: ICP results for Al- and Ga-doped LLZO showing Li, Al and Ga concentrations. The Zr concentration was fixed to 2 whereas the La concentration could not be detected due to ppm values greater than the ICP limits. The numbers in brackets represent the standard deviation of the six measurements recorded for each element. It is also important to note that the higher content of aluminium is due to Al contaminations as a result of sintering in Al_2O_3 crucibles.

	Li	*Al*	*Ga*	*Zr*
Al-LLZO	*6.53 (0.05)*	*0.276 (0.008)*	*-*	*2.000*
Ga-LLZO	*6.4 (0.2)*	*0.09 (0.02)*	*0.160 (0.005)*	*2.000*

S2. Repeated electrochemical measurements



Al-LLZO Sample ID	Time at 0.10 mA/cm² before short circuit	Ga-LLZO Sample ID	Time at 0.16 mA/cm² before short circuit
Al-LLZO-07-A (1.02 mm)	23 minutes	Ga-LLZO-02-B (1.01 mm)	28 minutes
Al-LLZO-07-D (0.89 mm)	11 minutes	Ga-LLZO-02-D (0.98 mm)	18 minutes
Al-LLZO-08-B (0.98 mm)	22 minutes	Ga-LLZO-04-A (1.0 mm)	21 minutes
Al-LLZO-08-E (0.91 mm)	16 minutes	Ga-LLZO-04-C (0.98 mm)	17 minutes
Al-LLZO-11-B (0.96 mm)	20 minutes		

Figure S1: Li plating graph for Al-LLZO (blue line) and Ga-LLZO (orange line). The arrow in the figure indicate the moment in which short circuit occurs. Times at which short circuit occurs for different cells are reported in the table.

S3. XRD of post-cycling samples

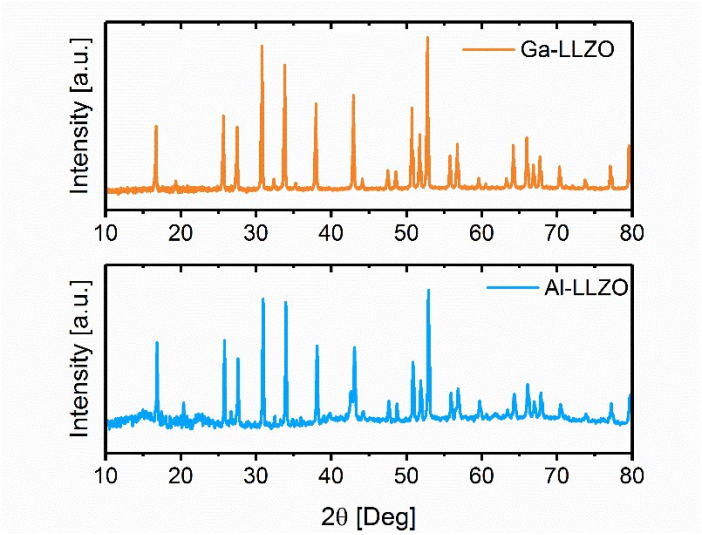


Figure S2: Post-cycling XRD patterns of Ga-LLZO (orange line) and Al-LLZO (blue line).

S4. Cross sectional SEM micrographs of Ga-LLZO

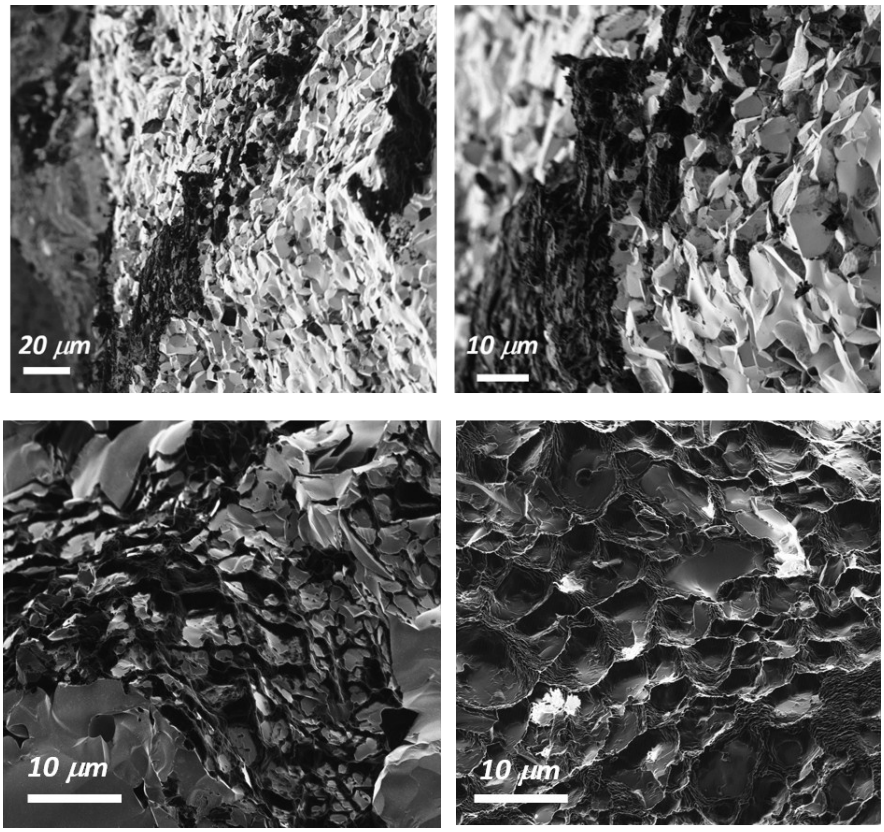


Figure S3: (Top) Cross sectional SEM micrographs of a cycled Ga-LLZO pellet showing a web-like dendritic feature across the pellet and (bottom) higher magnification micrographs of the dendritic feature reported in figure 7f.

S5. Extended cycling at lower currents

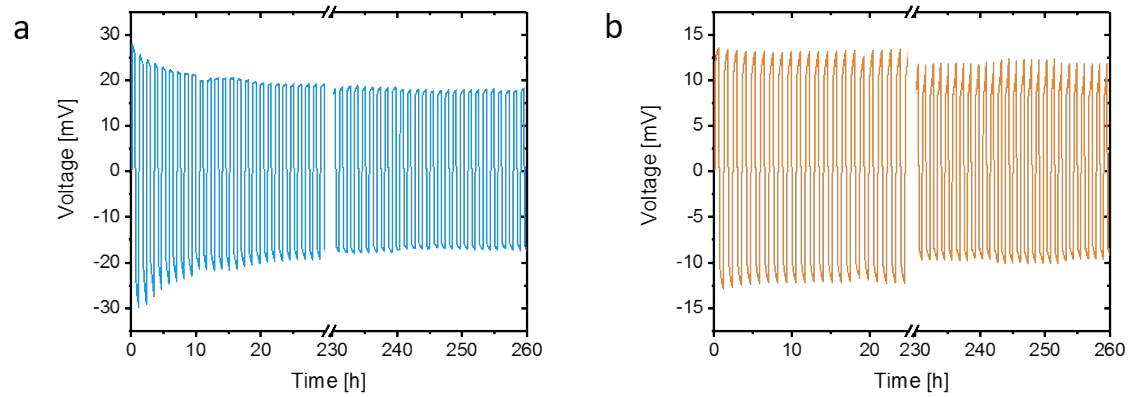


Figure S4. Extended electrochemical cycling carried out on (a) Al-LLZO and (b) Ga-LLZO at a current density of 0.08mA/cm^2 and 0.14mA/cm^2, respectively.

S6. EDX analysis on Al-LLZO Dendritic Features

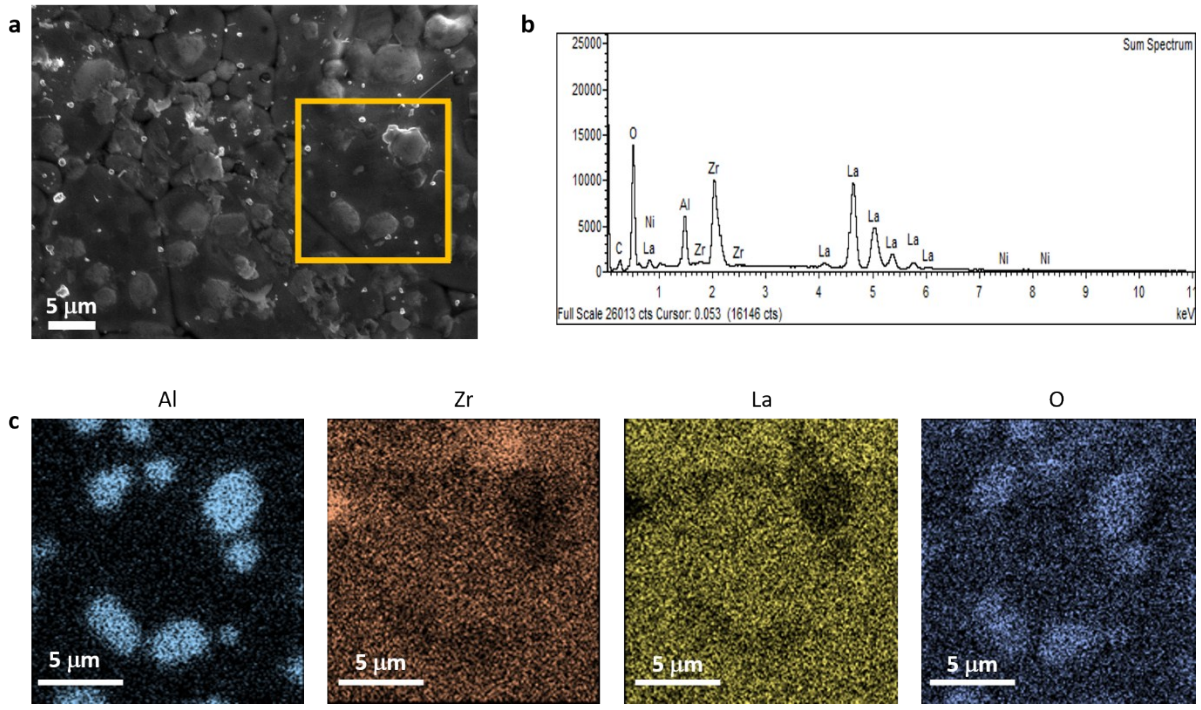


Figure S5: EDX analysis on Al-LLZO dendritic features. a) SEM micrograph of a cycled Al-LLZO, b) EDX spectrum and c) EDX elemental maps for Al, Zr, La and O.

S7. Stability of Li/Al-LLZO/Li prior to electrochemical cycling

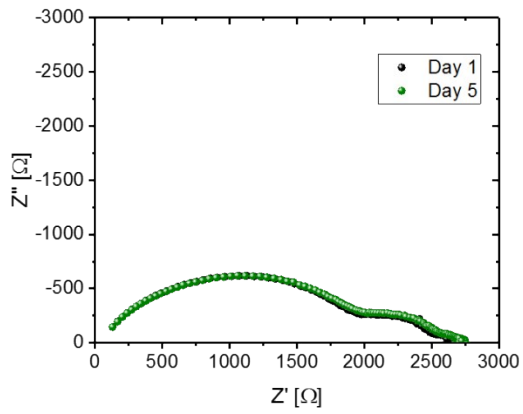


Figure S6: EIS spectra recorded for Al-doped LLZO at an interval of five days