Electronic Supplementary Information

Green water-based fabrication of garnet-based solid electrolyte separators for solid-state lithium batteries

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This ESI file includes:

Supplementary Text: Calculation of conductivity; Calculation of the degree of Li^+/H^+-exchange and pH of slurry;

Supplementary Figures S1, S2 and S3;

Supplementary Table S1, S2.

Supplementary Text:

Calculation of conductivity

The ionic conductivity (σ) is calculated based on

$$\sigma = \frac{L}{A \times Z}$$

where *L* is the thickness and area of solid electrolyte separator, *A* is the area of lithium foil electrode, and *Z* is the impedance for real axis of the high-frequency semicircle in Nyquist plot (**Fig. 6a**).

In our case:

$$\sigma = \frac{150\ [\mu m]}{\pi \times (\frac{7\ [mm]}{2})^2 \times 256.7\ [\Omega]} = 0.15\ [mS\ cm^{-1}]$$

Calculation of the degree of Li^+/H^+-exchange and pH of slurry

We assume here all Li-loss in sample "LLZ-slurry" (**Table S1**) is caused by Li^+/H^+-exchange and thus calculate the amount of Li^+ diffusing into the dispersion medium (n_{Li^+}) as

$$n_{Li^+} = \left(1 - \frac{Li_{LLZ-slurry}}{Li_{LLZ-AlTa}}\right) \times \frac{m_{LLZ-AlTa}}{M_{LLZ-AlTa}} = (1 - \frac{4.42}{6.45}) \times \frac{52.40\ [g]}{873.02\ [g\ mol^{-1}]} = 0.0189\ [mol]$$

where $Li_{LLZ-slurry}$ and $Li_{LLZ-AlTa}$ is the number of Li per formula in sample "LLZ-slurry" and stoichiometric Al- and Ta-substituted LLZ (LLZ-Al-Ta), respectively, and $m_{LLZ-AlTa}$ is the weight of LLZ powder in slurry and $M_{LLZ-AlTa}$ is molar mass of LLZ-AlTa.

To balance the electric neutrality in slurry, we assume the concentration of OH^- (c_{OH^-}) equals to the concentration of exchanged Li^+ (c_{Li^+}):

$$c_{OH^-} = c_{Li^+} = \frac{n_{Li^+}}{m_{water}/\rho_{water}} = \frac{0.0189\ [mol]}{43.66\ [g]/1.00\ [g\ mL^{-1}]} = 0.433\ [mol\ L^{-1}]$$

where m_{water} is the weight of water in slurry and ρ_{water} is the density of water. We here ignore the volume expansion due to the presence of polymers in slurry and make here a rough estimation of the volume of dispersion medium by simply applying the volume of water.

Thus the pH value of the slurry can be obtained as

$$pH = 14 - pOH = 14 + log_{10}\ c_{OH^-}) = 14 + log_{10}(0.433\ [mol\ L^{-1}]) = 13.6$$

We can find that the calculated pH value is higher than the measured one (12.5). Therefore, we assume that a large amount of OH^- is not in the bulk but is adsorbed on the surface of solid particles, providing electrostatic repulsive force to stabilize the suspension.

Supplementary Figures:

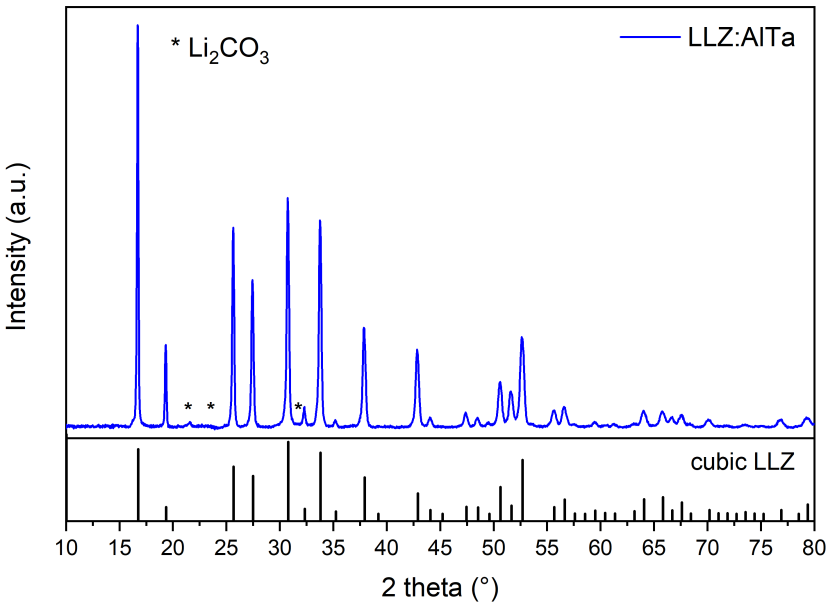

Figure S1: XRD pattern of as-synthesized LLZ:AlTa powder.

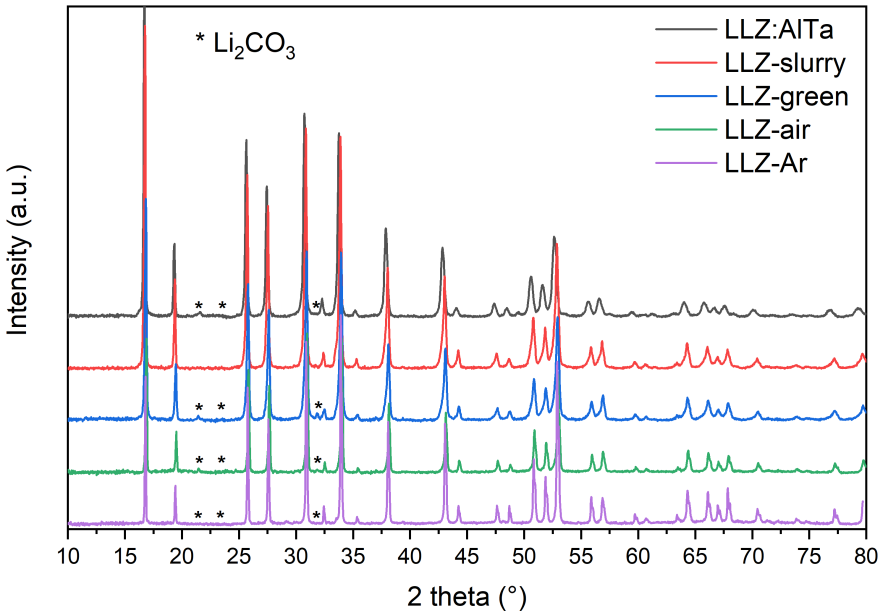

Figure S2: XRD patterns of LLZ samples from each step of fabrication procedure. The Rietveld refinements were conducted based on these XRD data.

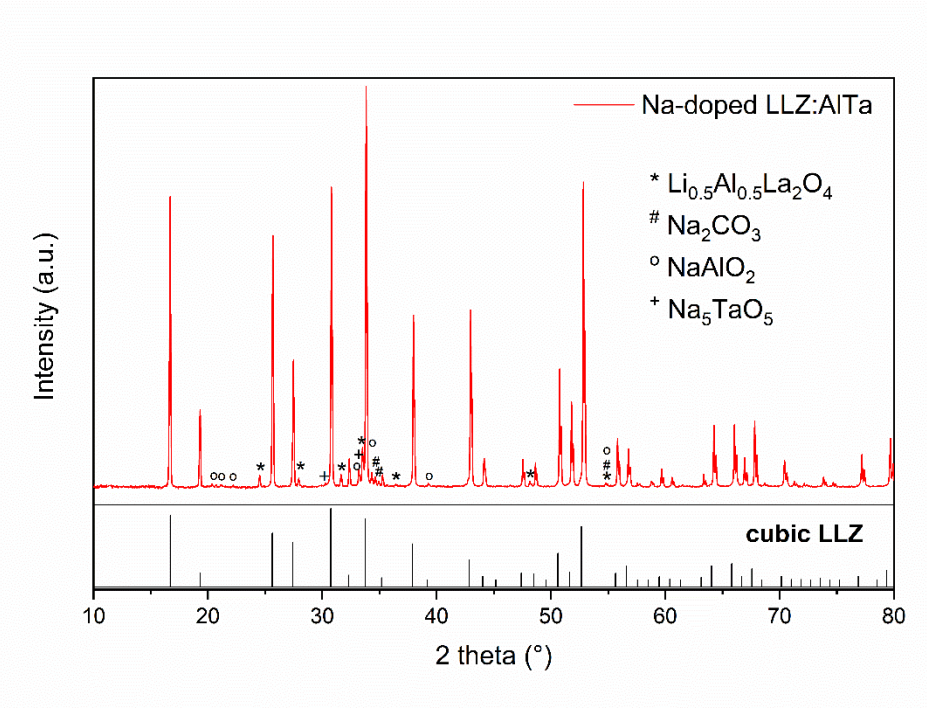

Figure S3: XRD pattern of sintered Na-doped LLZ pellet. A mixture of 0.5 g LLZ:AlTa powder and 0.05 g $Na_2CO_3 \cdot H_2O$ was pressed into pellet and sintered at 1175 °C for 4 hours. The XRD pattern afterwards shows clearly that Na_2CO_3 reacts with LLZ:AlTa to form several secondary phases.

Supplementary Table:

Table S1: Elemental analysis of LLZ samples from each step of fabrication procedure

	Elemental Content (normalized to La)[a]				
	Li	Al	La	Zr	Ta
LLZ:AlTa	7.56	0.07	3.00	1.53	0.37
LLZ-slurry	4.42	0.07	3.00	1.53	0.37
LLZ-green	7.56	0.08	3.00	1.53	0.37
LLZ-air	6.72	0.08	3.00	1.53	0.37
LLZ-Ar	6.40	0.08	3.00	1.52	0.40

[a] Target composition: $Li_{6.45}Al_{0.05}La_3Zr_{1.6}Ta_{0.4}O_{12}$

Table S2: Calculated values of the EIS data

Element	R1 [Ω]	L1	R2 [Ω]	CPE1 [F s^{n-1}]	n1	R3 [Ω]	CPE2 [F s^{n-1}]	n2
Value	143.5	2.43E-6	113.2	1.45E-9	0.95	248.4	7.89E-4	0.35
Error [%]	4.22	4.56	5.60	13.28	1.35	0.75	1.76	0.93