

Supplementary Information

Synergistic multi-doping effects on the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid electrolyte for fast lithium ion conduction

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Figure S1. XRD patterns of the single Ta-doped ($\text{Li}_{7-3x-y}\text{Al}_x\text{La}_3\text{Zr}_{2-y}\text{Ta}_y\text{O}_{12}$; $x = 0, y = 0.4$) and single Al-doped ($\text{Li}_{7-3x-y}\text{Al}_x\text{La}_3\text{Zr}_{2-y}\text{Ta}_y\text{O}_{12}$; $x = 0.4, y = 0$) LLZO. Although dominant XRD patterns of both structures indicate cubic phase, impurity phases ($\blacktriangledown\text{La}_2\text{Zr}_2\text{O}_7$ for Ta-doped LLZO, ∇LaAlO_3 for Al-doped LLZO) also arise.

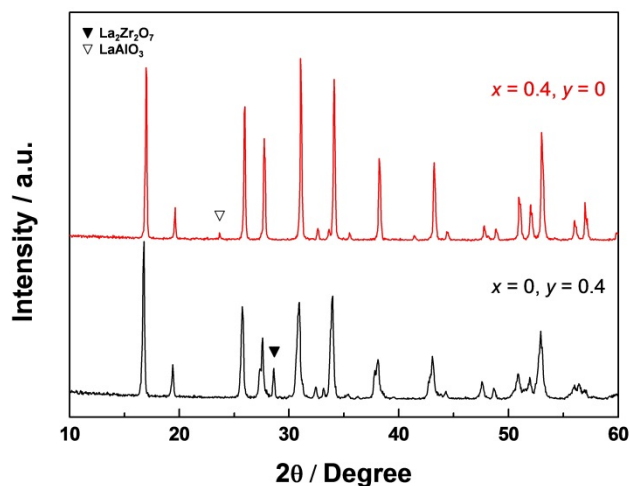


Figure S2. XRD patterns of the (a) single Al-doped ($\text{Li}_{7-3x-y}\text{Al}_x\text{La}_3\text{Zr}_{2-y}\text{Ta}_y\text{O}_{12}$; $x = 0.2$, $y = 0$) and (b) multi-doped ($\text{Li}_{7-3x-y}\text{Al}_x\text{La}_3\text{Zr}_{2-y}\text{Ta}_y\text{O}_{12}$; $x = 0.2$, $y = 0.2$) LLZO as a function of sintering time. Impurity phases are denoted as ▼ and ▽ for $\text{La}_2\text{Zr}_2\text{O}_7$ and LaAlO_3 , respectively.

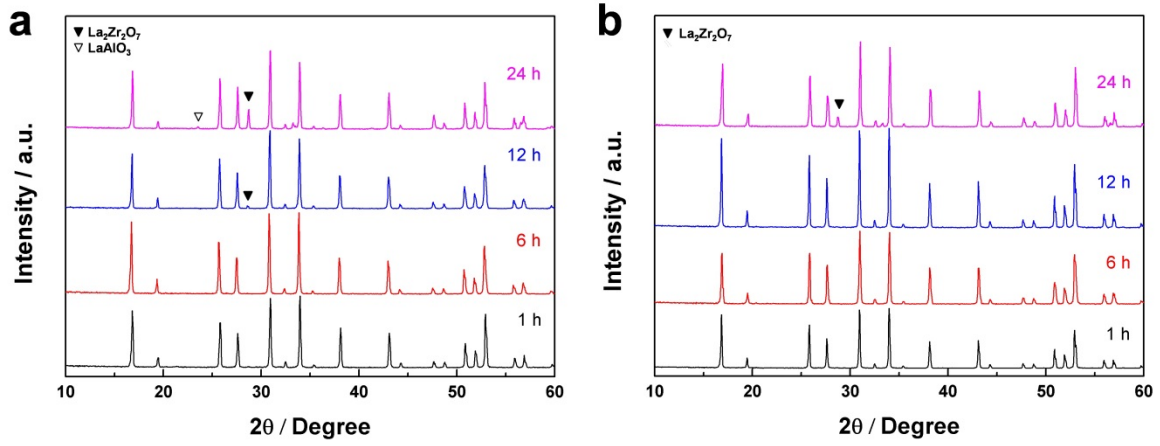


Figure S3. Room temperature AC impedance plots of the (a) single Al-doped ($\text{Li}_{7-3x-y}\text{Al}_x\text{La}_3\text{Zr}_{2-y}\text{Ta}_y\text{O}_{12}$; $x = 0.2, y = 0$) and (b) multi-doped ($\text{Li}_{7-3x-y}\text{Al}_x\text{La}_3\text{Zr}_{2-y}\text{Ta}_y\text{O}_{12}$; $x = 0.2, y = 0.2$) LLZO sintered for various time at 1200 °C.

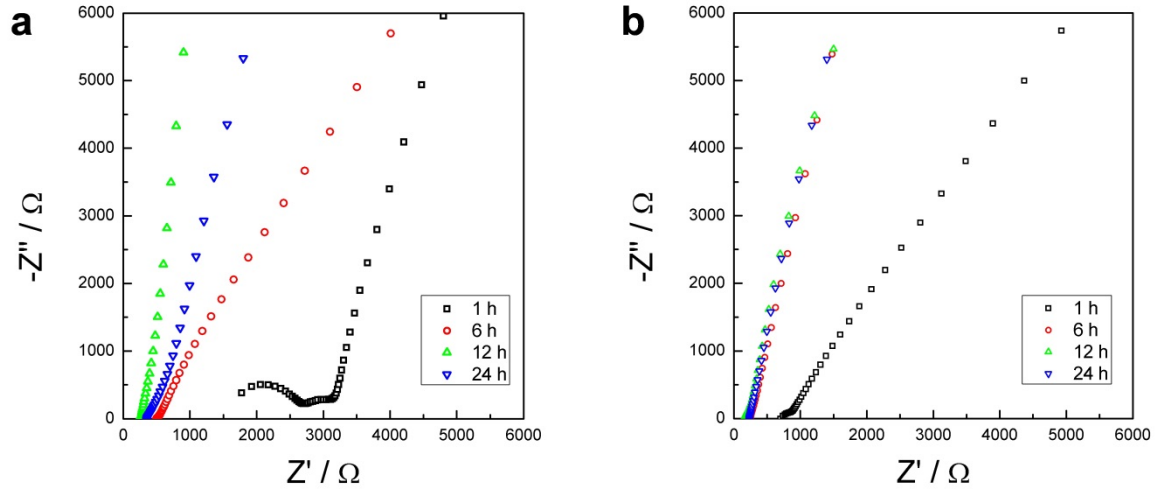


Figure S4. The temperature dependence of total ionic conductivity of the (a) single Al-doped ($\text{Li}_{7-3x-y}\text{Al}_x\text{La}_3\text{Zr}_{2-y}\text{Ta}_y\text{O}_{12}$; $x = 0.2, y = 0$) and (b) multi-doped ($\text{Li}_{7-3x-y}\text{Al}_x\text{La}_3\text{Zr}_{2-y}\text{Ta}_y\text{O}_{12}$; $x = 0.2, y = 0.2$) LLZO sintered for various time at 1200 °C.

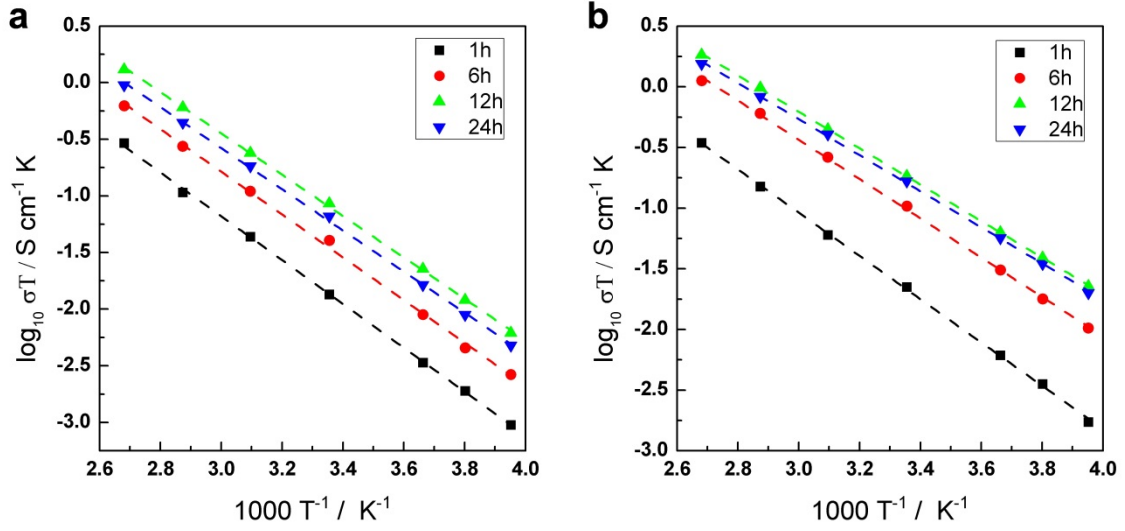


Table S1. Summary of experimental results of the single Al-doped ($\text{Li}_{7-3x-y}\text{Al}_x\text{La}_3\text{Zr}_{2-y}\text{Ta}_y\text{O}_{12}$; $x = 0.2, y = 0$) and multi-doped ($\text{Li}_{7-3x-y}\text{Al}_x\text{La}_3\text{Zr}_{2-y}\text{Ta}_y\text{O}_{12}$; $x = 0.2, y = 0.2$) LLZO.

Composition	Sintering time (h)	Relative density (%)	Conductivity at 25 °C (S cm^{-1})	Activation energy (eV)	Impurity phase
$\text{Li}_{6.4}\text{Al}_{0.2}\text{La}_3\text{Zr}_2\text{O}_{12}$	1	81.5	4.52×10^{-5}	0.40	-
	6	88.3	1.63×10^{-4}	0.38	-
	12	91.8	2.54×10^{-4}	0.36	$\text{La}_2\text{Zr}_2\text{O}_7$
	24	93.1	2.21×10^{-4}	0.37	$\text{La}_2\text{Zr}_2\text{O}_7, \text{LaAlO}_3$
$\text{Li}_{6.2}\text{Al}_{0.2}\text{La}_3\text{Zr}_{1.8}\text{Ta}_{0.2}\text{O}_{12}$	1	83.2	7.51×10^{-5}	0.36	-
	6	90.1	3.41×10^{-4}	0.32	-
	12	92.8	6.14×10^{-4}	0.29	-
	24	93.9	5.54×10^{-4}	0.30	$\text{La}_2\text{Zr}_2\text{O}_7$

Table S2. The comparison of the X-ray diffraction Rietveld refinement results of multi-doped LLZO ($\text{Li}_{7-3x-y}\text{Al}_x\text{La}_3\text{Zr}_{2-y}\text{Ta}_y\text{O}_{12}$; $x = 0.2$, $y = 0.2$) according to the two assumed conditions.

Condition	Al occ. In 24d	Al occ. In 96h	Bragg R-factor (%)	Rf-factor (%)	χ^2 (%)
No Al in the structure	0	0	6.59	5.16	5.00
Al in both 24d and 96h site	0.004 (2)	0.016 (2)	4.89	4.85	3.04