Supporting information

Table S1. Benchmark of LLZO with different dopant

Composition	**Syntheses Process**	**Sintering Parameter**	**Ionic conductivity** $\times 10^{-4}$ **(S/cm)**	**Activation energy (eV)**	**Ref.**
$Li_7La_3Zr_2O_{12}$	Solid phase sintering	1473 K for 12 h	0.17	0.47	[1]
$Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$	Solid phase sintering	1413 K for 12 h	10	0.35	[2]
$Li_{6.4}La_3Zr_{1.6}Nb_{0.4}O_{12}$	Solid phase sintering	1423 K for 1 h	3.49	0.32	[3]
$Li_{6.76}La_3Zr_{1.875}Te_{0.125}O_{12}$	Solid phase sintering	1373 K for 15 h	3.3	0.25	[4]
$Li_{6.3}La_3Zr_{1.65}W_{0.35}O_{12}$	Solid phase sintering	1473 K for 12 h	6.4	0.43	[1]
$Li_7La_3Zr_1Nb_{0.5}Y_{0.5}O_{12}$	Solid phase sintering	1503 K for 15 h	8.29	0.31	[5]
$Li_{6.925}La_{2.95}Y_{0.05}Zr_{1.925}Sb_{0.075}O_{12}$	Solid phase sintering	1463 K for 6 h	3.2	0.30	[6]
$Li_7La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$	Solid phase sintering	1373 K for 20 h	4.67	0.25	[7]
$Li_{6.4}La_3Zr_{0.4}Ta_{0.4}Nb_{0.4}Y_{0.6}W_{0.2}O_{12}$	Solid-state	1323 K for 36 h	1.16	0.23	[8]

Construction of computing crystal structure

The pure LLZO cubic bulk structure was constructed with a space group of $Ia\bar{3}d$ and a primitive unit cell formula $Li_{28}La_{12}Zr_8O_{48}$. Transition metal (TM) ions Ta^{5+}, Nb^{5+} and Y^{3+} were equally 2 cation occupied at the Zr sites based on EXAFS data that show these cations share the same environment, which indicating the original 8 Zr^{4+} cations were partially substituted by these cations. A primitive cell with 94 atoms and a stochiometric formula of $Li_{26}La_{12}Zr_2Ta_2Nb_2Y_2O_{48}$ was constructed. Li ions were distributed to minimize Li+/Li+ repulsion forces, following the rule proposed by O'Callaghan *et al.* [9] , generating the most stable garnet structure. We select 2 different lithium ion by-rule distribution scenario, and random distribution of TM ions at the Zr sites was examined, totally 12 different distributed TM ions structures were conducted (**Figure S1)**, and the most stable structure was selected for further calculations. The maximum energy variation in $Li_{26}La_{12}Zr_2Ta_2Nb_2Y_2O_{48}$ lattice among these distributions was 0.957 eV as shown in **Figure S2**. The lattice constant after optimization differed by less than 1% from experimental values, demonstrating the model is reliable (**Table S2**).

Hydration reactions were observed in the LLZO system in the presence of water molecules. Hydrogen from water tends to react with lithium ions in the material, forming LiOH in previous literature. [10] According to calculations, both pure LLZO and doped LLZTNYO, hydrogen preferably occupied the 96h site over the 24d site, where 96h and 24d sites indicated the lithium-ion Wyckoff position of the lattice (**Figure S3**). Various Li ion occupation scenarios were tested to determine the most stable configuration for further calculations.

The Kroger-Vink notation equation:

Increase lithium vacancies concentration

$$\mathbf{Ta(Nb)} \overset{LLZO}{\rightarrow} \mathbf{Ta(Nb)}_{Zr}^{\cdot} + \mathbf{V}_{Li}^{'}$$

Increase lithium-ion concentration

$$\mathbf{Y} \overset{LLZO}{\rightarrow} \mathbf{Y}_{Zr}^{'} + \mathbf{Li}_{Li}^{\cdot}$$

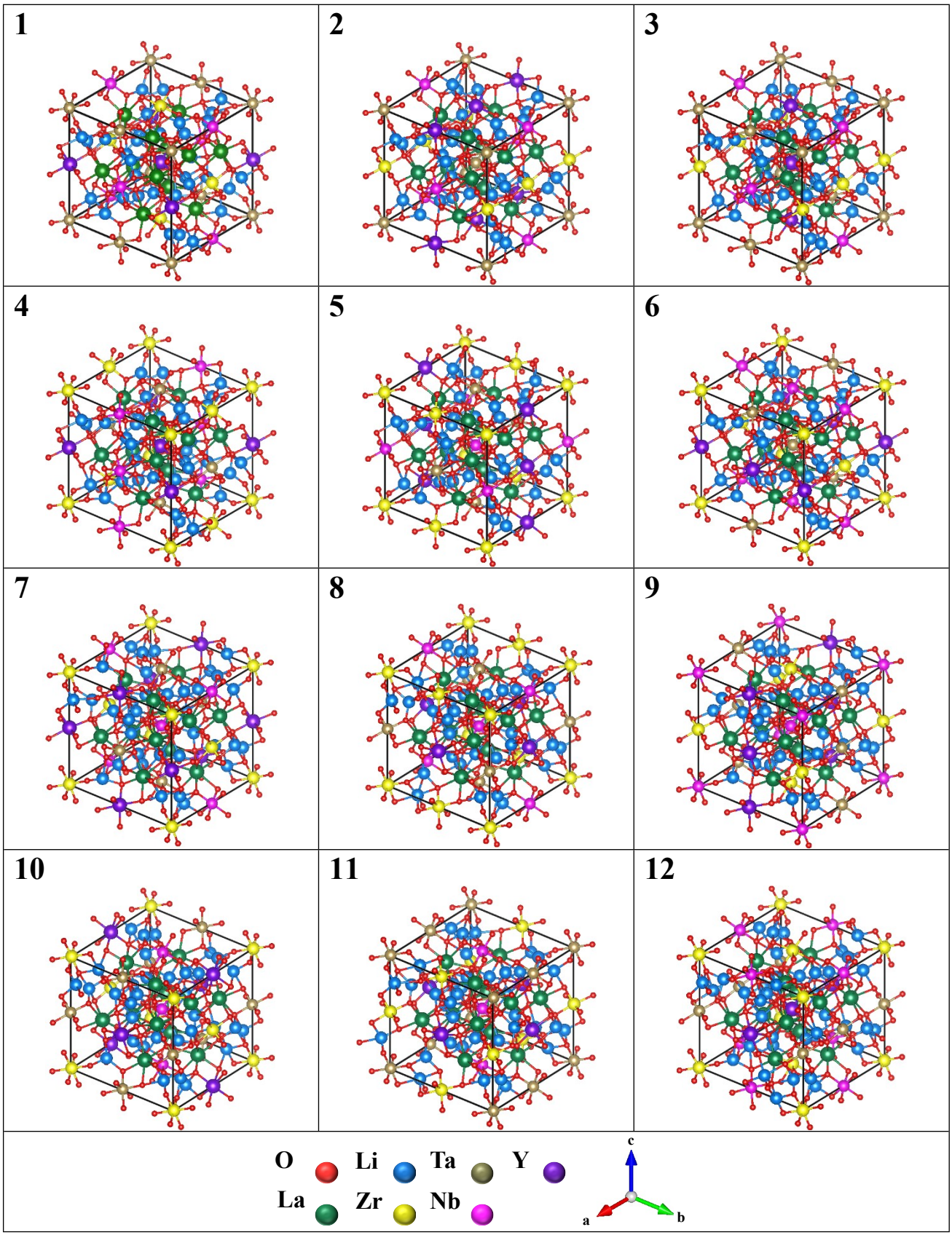
1
2
3
4
5
6
7
8
9
10
11
12
O
Li
Ta
Y
La
Zr
Nb
c
a
b

Figure S1. Different LLZTNYO model with different ion distribution

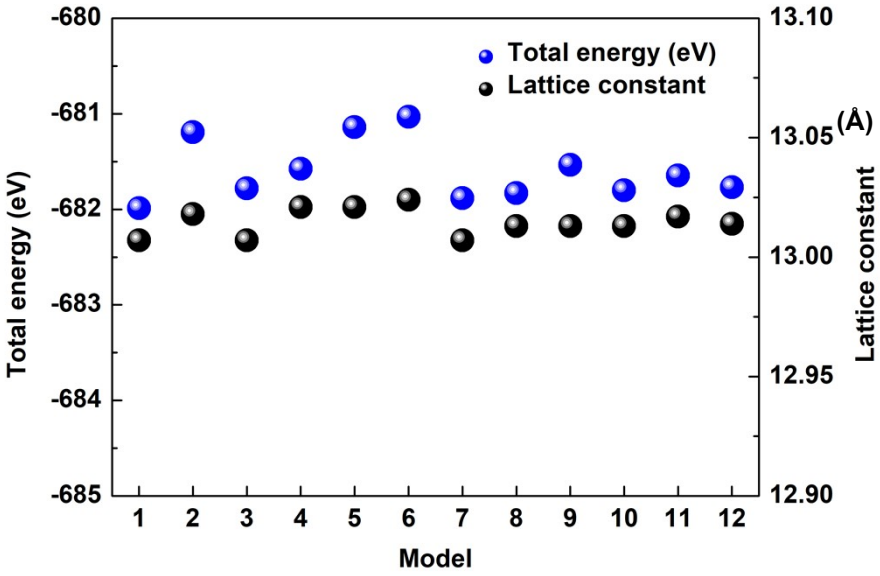

Figure S2. Different TM distribution sample's total energy and their lattice constant

Table S2. Lattice constant of our model compared to previous literature and experiment result.

	$Li_7La_3Zr_2O_{12}$		$Li_{6.5}La_3Zr_{0.5}Ta_{0.5}Nb_{0.5}Y_{0.5}O_{12}$	
	Exp	DFT	Exp	DFT
Lattice constant (Å)	13.004	12.988	12.934	13.013
△L (%)	0	0.123	0	-0.611
Ref	Ref [11]	DFT work	Exp work	DFT work

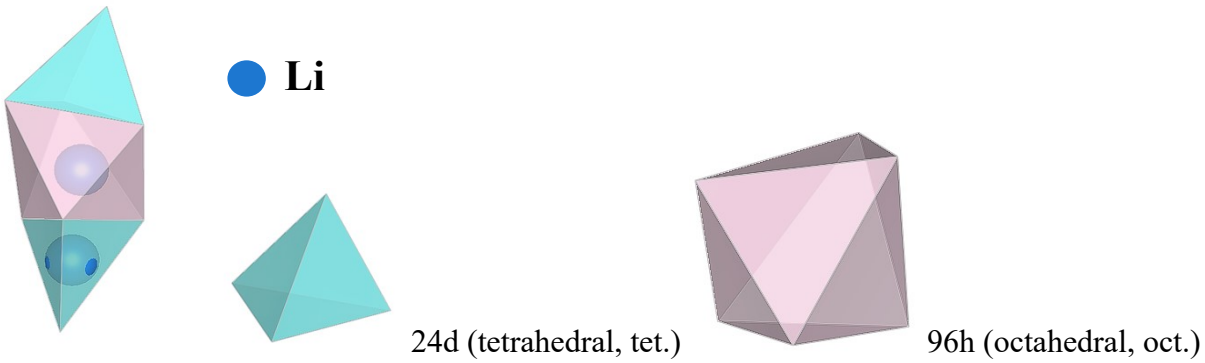

Figure S3. Structure of 24d and 96h Wyckoff positions

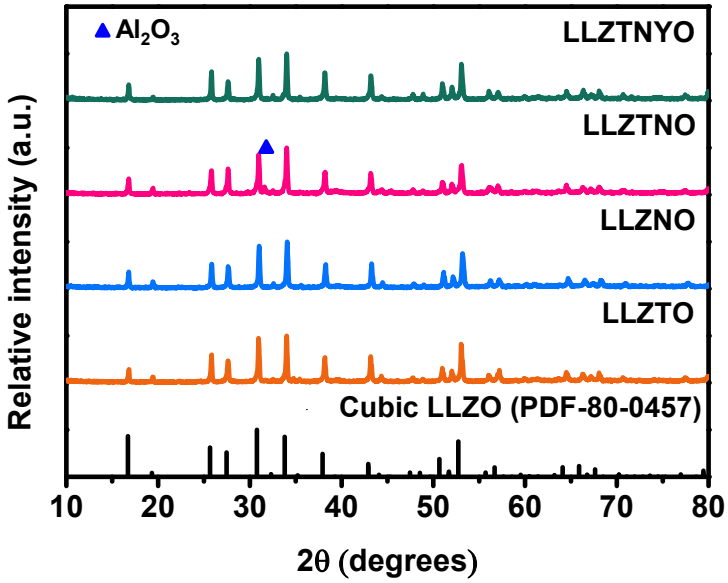

Figure S4. XRD patterns of Cubic LLZO, $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLZTO), $Li_{6.5}La_3Zr_{1.5}Nb_{0.5}O_{12}$ (LLZNO), $Li_{6.5}La_3Zr_1Ta_{0.5}Nb_{0.5}O_{12}$ (LLZTNO), and $Li_{6.5}La_3Zr_{0.5}Ta_{0.5}Nb_{0.5}Y_{0.5}O_{12}$ (LLZTNYWO)

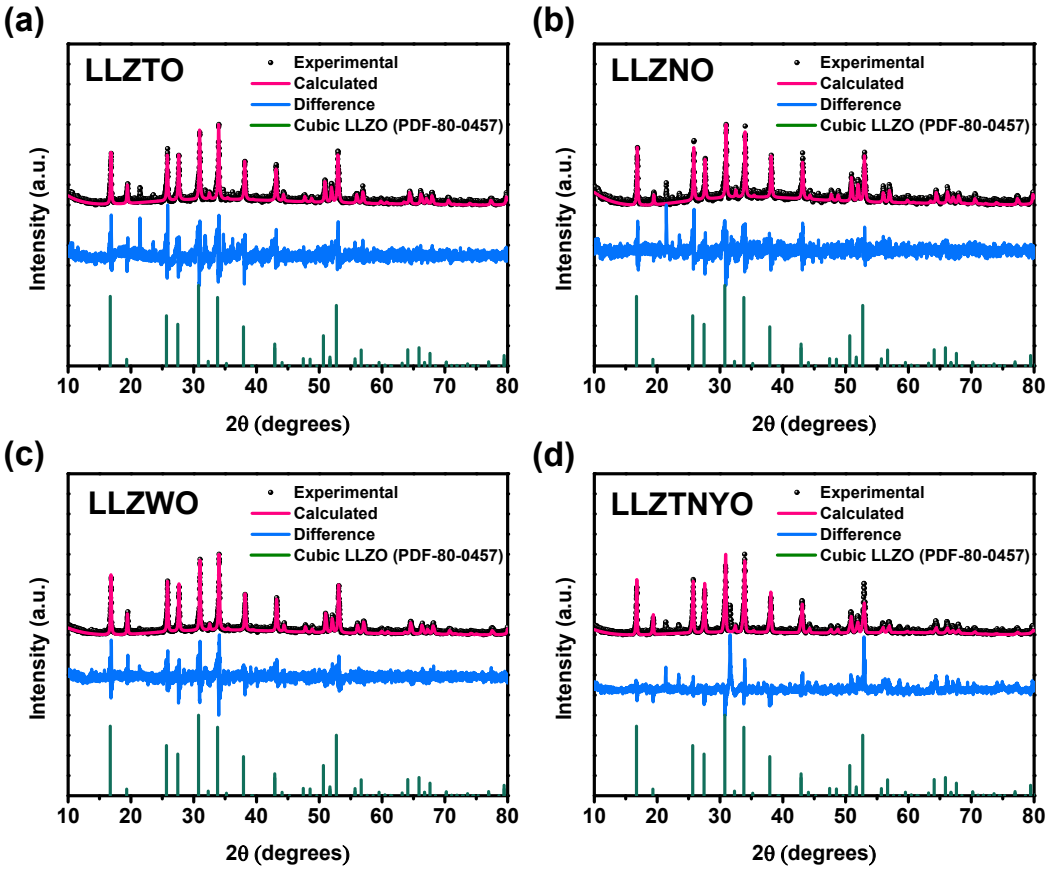

Figure S5. Refinement data of Cubic LLZO, (a) $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLZTO), (b) $Li_{6.5}La_3Zr_{1.5}Nb_{0.5}O_{12}$ (LLZNO), (c) $Li_6La_3ZrTa_{0.5}Nb_{0.5}O_{12}$ (LLZTNO), and (d) $Li_{6.5}La_3Zr_{0.5}Ta_{0.5}Nb_{0.5}Y_{0.5}O_{12}$ (LLZTNYO)

Table S3. XRD Rietveld refinement parameters of LLZTO, LLZNO, LLZTNO, and LLZTNYO

Composition	Lattice parameter (Å)	Rwp	GOF
LLZTO	12.925	13.78	1.33
LLZNO	12.922	13.34	1.24
LLZTNO	12.905	11.29	1.18
LLZTNYO	12.934	16.39	1.7

Table S4. Structural solution of LLZTNYO from Rietveld refinement on neutron diffraction data.

Space group: "I a -3 d", a = 13.02796 Å, α = 90°, V = 2211.208 Å^3, Rwp = 5.298%						
Atom	multiplicity	x	y	z	fraction	Uiso (Å^2)
La	24	0.125	0	0.25	1	0.0165
Nb	16	0	0	0	0.25	0.0161
Ta	16	0	0	0	0.25	0.0161
Y	16	0	0	0	0.25	0.0161
Zr	16	0	0	0	0.25	0.0161
Li	24	0.375	0	0.25	0.53	0.027
Li	96	0.098858	0.188941	0.42926	0.41	0.027
O	96	0.10228	0.19745	0.27925	1	0.0226

Table S5. Structural solution of LLZTNYO from neutron PDF fitting.

Space group = P1, a = b =c 12.957 Å, α = β = γ = 90°, Rwp = 25.82%				
Atom	Positions			Occupancy
La	0.125	0	0.25	1
La	0.25	0.875	0.5	1
La	0.375	0	0.75	1
La	0.25	0.125	0	1
La	0.5	0.25	0.875	1
La	0.75	0.375	0	1
La	0	0.25	0.125	1
La	0.875	0.5	0.25	1
La	0	0.75	0.375	1
La	0.875	0	0.75	1
La	0.75	0.125	0.5	1
La	0.625	0	0.25	1
La	0.75	0.875	0	1
La	0.5	0.75	0.125	1
La	0.25	0.625	0	1
La	0	0.75	0.875	1
La	0.125	0.5	0.75	1
La	0	0.25	0.625	1
La	0.625	0.5	0.75	1
La	0.75	0.625	0.5	1
La	0.5	0.75	0.625	1
La	0.375	0.5	0.25	1
La	0.25	0.375	0.5	1
La	0.5	0.25	0.375	1
Li	0.375	0	0.25	0.53
Li	0.25	0.125	0.5	0.53
Li	0.125	0	0.75	0.53
Li	0.25	0.875	0	0.53
Li	0.25	0.375	0	0.53
Li	0.5	0.25	0.125	0.53
Li	0.75	0.125	0	0.53
Li	0	0.25	0.875	0.53
Li	0.875	0	0.25	0.53
Li	0	0.25	0.375	0.53
Li	0.125	0.5	0.25	0.53
Li	0	0.75	0.125	0.53
Li	0.625	0	0.75	0.53
Li	0.75	0.875	0.5	0.53
Li	0.75	0.625	0	0.53
Li	0.5	0.75	0.875	0.53
Li	0	0.75	0.625	0.53
Li	0.875	0.5	0.75	0.53

Li	0.625	0.5	0.25	0.53
Li	0.75	0.375	0.5	0.53
Li	0.25	0.625	0.5	0.53
Li	0.5	0.75	0.375	0.53
Li	0.375	0.5	0.75	0.53
Li	0.5	0.25	0.625	0.53
Li	0.125	0.17849	0.42849	0.414
Li	0.07152	0.875	0.67849	0.414
Li	0.375	0.82151	0.92849	0.414
Li	0.42849	0.125	0.17849	0.414
Li	0.125	0.82151	0.07152	0.414
Li	0.07152	0.125	0.82151	0.414
Li	0.375	0.17849	0.57151	0.414
Li	0.42849	0.875	0.32152	0.414
Li	0.67849	0.07152	0.875	0.414
Li	0.92849	0.375	0.82151	0.414
Li	0.17849	0.42849	0.125	0.414
Li	0.82151	0.07152	0.125	0.414
Li	0.57151	0.375	0.17849	0.414
Li	0.32152	0.42849	0.875	0.414
Li	0.875	0.67849	0.07152	0.414
Li	0.82151	0.92849	0.375	0.414
Li	0.17849	0.57151	0.375	0.414
Li	0.875	0.32152	0.42849	0.414
Li	0.875	0.82151	0.57151	0.414
Li	0.92849	0.125	0.32152	0.414
Li	0.625	0.17849	0.07152	0.414
Li	0.57151	0.875	0.82151	0.414
Li	0.875	0.17849	0.92849	0.414
Li	0.92849	0.875	0.17849	0.414
Li	0.625	0.82151	0.42849	0.414
Li	0.57151	0.125	0.67849	0.414
Li	0.32152	0.92849	0.125	0.414
Li	0.07152	0.625	0.17849	0.414
Li	0.82151	0.57151	0.875	0.414
Li	0.17849	0.92849	0.875	0.414
Li	0.42849	0.625	0.82151	0.414
Li	0.67849	0.57151	0.125	0.414
Li	0.125	0.32152	0.92849	0.414
Li	0.17849	0.07152	0.625	0.414
Li	0.82151	0.42849	0.625	0.414
Li	0.125	0.67849	0.57151	0.414
Li	0.625	0.67849	0.92849	0.414
Li	0.92849	0.625	0.67849	0.414
Li	0.625	0.32152	0.57151	0.414
Li	0.57151	0.625	0.32152	0.414
Li	0.67849	0.92849	0.625	0.414

Li	0.32152	0.57151	0.625	0.414
Li	0.375	0.32152	0.07152	0.414
Li	0.07152	0.375	0.32152	0.414
Li	0.375	0.67849	0.42849	0.414
Li	0.42849	0.375	0.67849	0.414
Li	0.32152	0.07152	0.375	0.414
Li	0.67849	0.42849	0.375	0.414
Y	0	0	0	1
Nb	0.25	0.75	0.25	1
Y	0.5	0	0.5	1
Nb	0.25	0.25	0.75	1
Zr	0	0	0.5	1
Nb	0.25	0.25	0.25	1
Zr	0.5	0	0	1
Nb	0.25	0.75	0.75	1
Y	0.5	0.5	0	1
Nb	0.75	0.25	0.25	1
Zr	0	0.5	0	1
Nb	0.75	0.25	0.75	1
Y	0	0.5	0.5	1
Nb	0.75	0.75	0.25	1
Nb	0.75	0.75	0.75	1
Zr	0.5	0.5	0.5	1
O	0.10085	0.19759	0.28076	1
O	0.05241	0.85085	0.53076	1
O	0.39915	0.80241	0.78076	1
O	0.44759	0.14915	0.03076	1
O	0.10085	0.80241	0.21924	1
O	0.05241	0.14915	0.96924	1
O	0.39915	0.19759	0.71924	1
O	0.44759	0.85085	0.46924	1
O	0.28076	0.10085	0.19759	1
O	0.53076	0.05241	0.85085	1
O	0.78076	0.39915	0.80241	1
O	0.03076	0.44759	0.14915	1
O	0.21924	0.10085	0.80241	1
O	0.96924	0.05241	0.14915	1
O	0.71924	0.39915	0.19759	1
O	0.46924	0.44759	0.85085	1
O	0.14915	0.03076	0.44759	1
O	0.19759	0.28076	0.10085	1
O	0.85085	0.53076	0.05241	1
O	0.80241	0.78076	0.39915	1
O	0.14915	0.96924	0.05241	1
O	0.19759	0.71924	0.39915	1
O	0.85085	0.46924	0.44759	1
O	0.80241	0.21924	0.10085	1

O	0.89915	0.80241	0.71924	1
O	0.94759	0.14915	0.46924	1
O	0.60085	0.19759	0.21924	1
O	0.55241	0.85085	0.96924	1
O	0.89915	0.19759	0.78076	1
O	0.94759	0.85085	0.03076	1
O	0.60085	0.80241	0.28076	1
O	0.55241	0.14915	0.53076	1
O	0.71924	0.89915	0.80241	1
O	0.46924	0.94759	0.14915	1
O	0.21924	0.60085	0.19759	1
O	0.96924	0.55241	0.85085	1
O	0.78076	0.89915	0.19759	1
O	0.03076	0.94759	0.85085	1
O	0.28076	0.60085	0.80241	1
O	0.53076	0.55241	0.14915	1
O	0.85085	0.96924	0.55241	1
O	0.80241	0.71924	0.89915	1
O	0.14915	0.46924	0.94759	1
O	0.19759	0.21924	0.60085	1
O	0.85085	0.03076	0.94759	1
O	0.80241	0.28076	0.60085	1
O	0.14915	0.53076	0.55241	1
O	0.19759	0.78076	0.89915	1
O	0.60085	0.69759	0.78076	1
O	0.55241	0.35085	0.03076	1
O	0.89915	0.30241	0.28076	1
O	0.94759	0.64915	0.53076	1
O	0.60085	0.30241	0.71924	1
O	0.55241	0.64915	0.46924	1
O	0.89915	0.69759	0.21924	1
O	0.94759	0.35085	0.96924	1
O	0.78076	0.60085	0.69759	1
O	0.03076	0.55241	0.35085	1
O	0.28076	0.89915	0.30241	1
O	0.53076	0.94759	0.64915	1
O	0.71924	0.60085	0.30241	1
O	0.46924	0.55241	0.64915	1
O	0.21924	0.89915	0.69759	1
O	0.96924	0.94759	0.35085	1
O	0.64915	0.53076	0.94759	1
O	0.69759	0.78076	0.60085	1
O	0.35085	0.03076	0.55241	1
O	0.30241	0.28076	0.89915	1
O	0.64915	0.46924	0.55241	1
O	0.69759	0.21924	0.89915	1
O	0.35085	0.96924	0.94759	1

O	0.30241	0.71924	0.60085	1
O	0.39915	0.30241	0.21924	1
O	0.44759	0.64915	0.96924	1
O	0.10085	0.69759	0.71924	1
O	0.05241	0.35085	0.46924	1
O	0.39915	0.69759	0.28076	1
O	0.44759	0.35085	0.53076	1
O	0.10085	0.30241	0.78076	1
O	0.05241	0.64915	0.03076	1
O	0.21924	0.39915	0.30241	1
O	0.96924	0.44759	0.64915	1
O	0.71924	0.10085	0.69759	1
O	0.46924	0.05241	0.35085	1
O	0.28076	0.39915	0.69759	1
O	0.53076	0.44759	0.35085	1
O	0.78076	0.10085	0.30241	1
O	0.03076	0.05241	0.64915	1
O	0.35085	0.46924	0.05241	1
O	0.30241	0.21924	0.39915	1
O	0.64915	0.96924	0.44759	1
O	0.69759	0.71924	0.10085	1
O	0.35085	0.53076	0.44759	1
O	0.30241	0.78076	0.10085	1
O	0.64915	0.03076	0.05241	1
O	0.69759	0.28076	0.39915	1

Table S6. Fitting data of Nyquist plots under different measuring temperatures. R_g and R_{gb} represent the grain and grain boundary impedance, respectively.

Composition	Temperature	Diameter (cm)	Thickness (cm)	Area (cm^2)	R_b (Ω)	R_{gb} (Ω)	Conductivity (S/cm)
LLZTO	25	1.034	0.088	0.840	365.5	153.2	1.73×10^{-4}
	40				346.6	89.23	2.06×10^{-4}
	60				220.5	34.69	3.52×10^{-4}
	80				169.4	11.13	4.98×10^{-4}
LLZNO	25	1.043	0.077	0.854	257.7	173.9	2.09×10^{-4}
	40				185.6	102.6	3.13×10^{-4}
	60				128.7	41.54	5.30×10^{-4}
	80				70.81	5.58	1.18×10^{-3}
LLZTNO	25	1.050	0.073	0.866	338.6	88.47	1.97×10^{-4}
	40				236.8	22.04	3.26×10^{-4}
	60				141.3	10.94	5.54×10^{-4}
	80				76.53	6.399	1.02×10^{-3}
LLZTNYO	25	1.038	0.08	0.846	342.2	164.4	1.87×10^{-4}
	40				257.6	86.84	2.75×10^{-4}
	60				181	41.69	4.25×10^{-4}
	80				119.2	14.58	7.07×10^{-4}

Table S7. Fitting data of Nyquist plots from Day 1 to Day 30.

Sample	Day	Diameter (cm)	Thickness (cm)	Area (cm^2)	R_b (Ω)	R_{gb} (Ω)	Conductivity (S/cm)
LLZTO	1	1.034	0.088	0.84	365.5	153.2	1.73×10^{-4}
	3				313.4	169.4	2.17×10^{-4}
	5				340.5	141.5	2.17×10^{-4}
	10				316.5	253	1.84×10^{-4}
	15				322.3	307.3	1.66×10^{-4}
	20				290.5	502.8	1.32×10^{-4}
	30				309.1	648.6	1.09×10^{-4}
LLZNO	1	1.043	0.077	0.854	257.7	173.9	2.09×10^{-4}
	3				257.1	311.6	1.59×10^{-4}
	5				256.5	365.6	1.45×10^{-4}
	10				302.8	486	1.14×10^{-4}
	15				280.5	646.7	9.72×10^{-5}
	20				288.9	847	7.93×10^{-5}
	30				288.9	847	7.93×10^{-5}
LLZTNO	1	1.05	0.073	0.866	338.6	88.47	1.97×10^{-4}
	3				340.2	123.8	1.82×10^{-4}
	5				236.5	189.4	1.98×10^{-4}
	10				439.1	82.92	1.63×10^{-4}
	15				451.9	145.6	1.41×10^{-4}
	20				456.8	191.8	1.30×10^{-4}
	30				453	214.3	1.26×10^{-4}
LLZTNYO	1	1.038	0.08	0.846	342.2	164.4	1.87×10^{-4}
	3				308	164.9	2×10^{-4}
	5				315.2	160.2	1.99×10^{-4}
	10				248	131.9	2.49×10^{-4}
	15				247.3	166.6	2.28×10^{-4}
	20				208.5	198.5	2.32×10^{-4}
	30				209.8	189.3	2.37×10^{-4}

Table S8 Reaction energy of different percentage of Lithium-Hydrogen exchange (LHX)

LLZO		LLZTNYO	
Reaction energy (eV)	Li^+/H^+ (%)	Reaction energy (eV)	Li^+/H^+ (%)
−1.957	1.786	−1.934	1.852
−9.840	8.929	−9.861	9.259
−23.508	21.429	−23.439	23.077
−39.434	35.714	−39.168	38.462
−55.280	50	−51.258	50

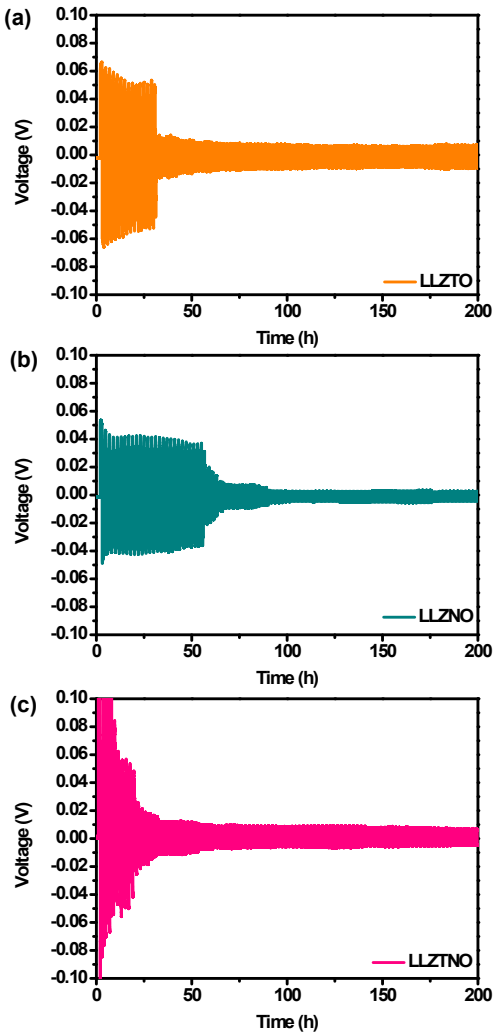

Figure S6 Galvanostatic cycling test of (a) LLZTO, (b) LLZNO, and (c) LLZTNO (lithium plating or stripping was set to 1 h).

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