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Improvement of Li-ion conductivity and air stability of Ta-doped $Li_7La_3Zr_2O_{12}$ electrolyte via Ga co-doping and its application in Li-S battery

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Table S 1 Elemental analysis of Ga*x*-LLZT ($0 \le x \le 0.2$)

Ga*x*-LLZT	Molar ratio of the elements				
	Li	Ga	La	Zr	Ta
LLZT	6.834	-	3	1.592	0.425
Ga0.05-LLZT	6.619	0.045	3	1.613	0.397
Ga0.1-LLZT	6.462	0.118	3	1.624	0.391
Ga0.15-LLZT	6.242	0.159	3	1.591	0.419
Ga0.2-LLZT	6.134	0.222	3	1.625	0.391

Table S 2 Rietveld refinement results for Gax-LLZT ($0 \le x \le 0.2$)

	$x = 0$	$x = 0.05$	$x = 0.1$	$x = 0.15$	$x = 0.2$
La (24c) occupancy	1	1	1	1	1
x	1/8	1/8	1/8	1/8	1/8
y	0	0	0	0	0
z	1/4	1/4	1/4	1/4	1/4
U_{eq}	0.004(5)	0.012(2)	0.014(2)	0.008(2)	0.0115(18)
Zr/Ta (16a) occupancy	0.8/0.2	0.8/0.2	0.8/0.2	0.8/0.2	0.8/0.2
x	0	0	0	0	0
y	0	0	0	0	0
z	0	0	0	0	0
U_{eq}	0.0014(5)	0.0082(15)	0.0124(15)	0.0070(14)	0.0084(13)
Li1/Ga (24d) occupancy	0.42(10)/0	0.37(6)/0.017	0.3(4)/0.033	0.15(7)/0.05	0.08(2)/0.067
x	3/8	3/8	3/8	3/8	3/8
y	0	0	0	0	0
z	1/4	1/4	1/4	1/4	1/4
U_{eq}	0.0003(4)	0.083(10)	0.02(3)	0.052(6)	0.027(11)
Li2 (96h) occupancy	0.44(2)	0.444(16)	0.46(10)	0.474(17)	0.483(6)
x	0.665(7)	0.686(12)	0.683(6)	0.662(6)	0.688(4)
y	0.612(12)	0.583(2)	0.50(2)	0.649(5)	0.545(8)
z	0.090(4)	0.137(9)	0.140(15)	0.087(3)	0.102(5)
U_{eq}	0.019(4)	0.019(10)	0.050(13)	0.076(5)	0.03(6)
O (96h) occupancy	1	1	1	1	1
x	0.1014(7)	0.1014(7)	0.1023(12)	0.1007(7)	0.1038(8)
y	0.1954(7)	0.1948(6)	0.1938(7)	0.1960(6)	0.1960(6)
z	0.2809(6)	0.2807(5)	0.2782(8)	0.2796(5)	0.2805(6)
U_{eq}	0.0031(5)	0.022(10)	0.029(12)	0.015(14)	0.009(9)
a (Å)	12.9489(5)	12.9475(4)	12.9471(6)	12.9468(4)	12.9464(7)
ρ_{calc} (g·cm^{-3})	5.341	5.361	5.368	5.382	5.404
R_p (%)	5.44	6.09	6.66	6.47	5.98
R_{wp} (%)	7.08	8.03	8.85	8.53	7.69
χ^2	1.51	2.01	2.07	2.09	1.77

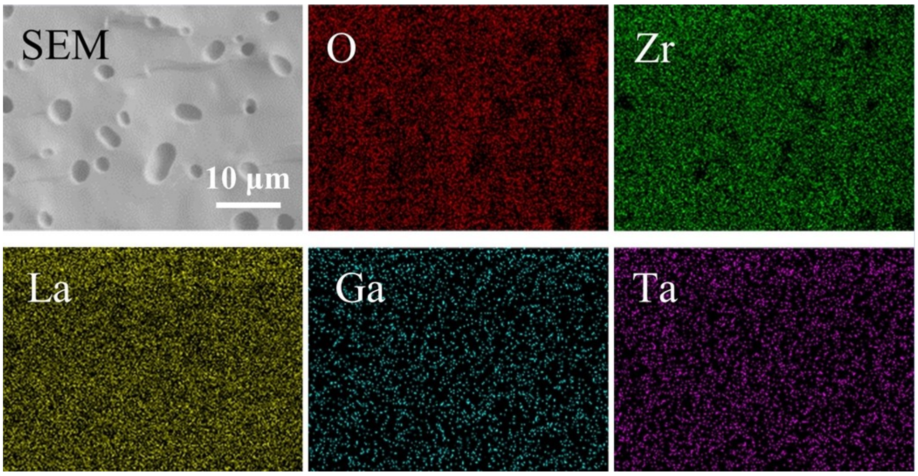

Fig. S 1 EDS element mappings of Ga0.1-LLZT sample

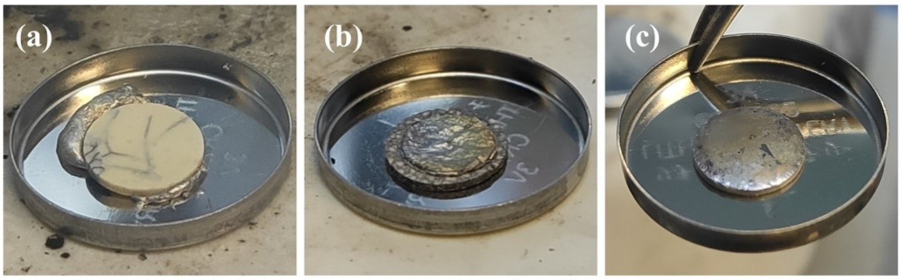

Fig. S 2 Photos of the (a) Ga0.1-LLZT and (b) Ga0.2-LLZT ceramics sintered at 1150 °C) after contact with molten Li. (c) Photo of Ga0.1-LLZT ceramic sintered at 1050 °C well bonded to molten Li.

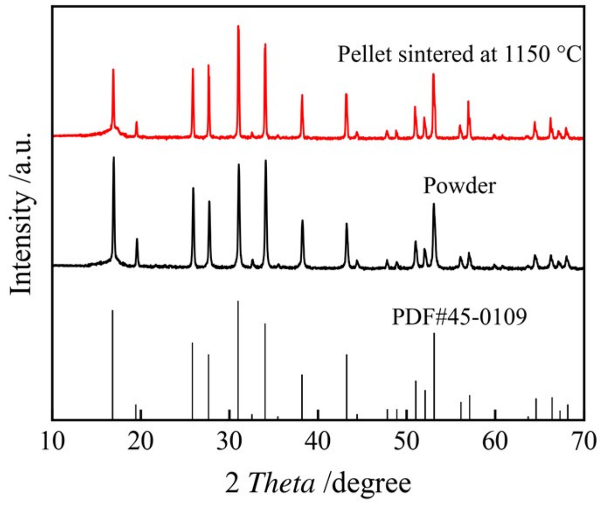

Fig. S 3 XRD patterns of Ga0.2-LLZT powder and pellet sintered at 1150 °C.

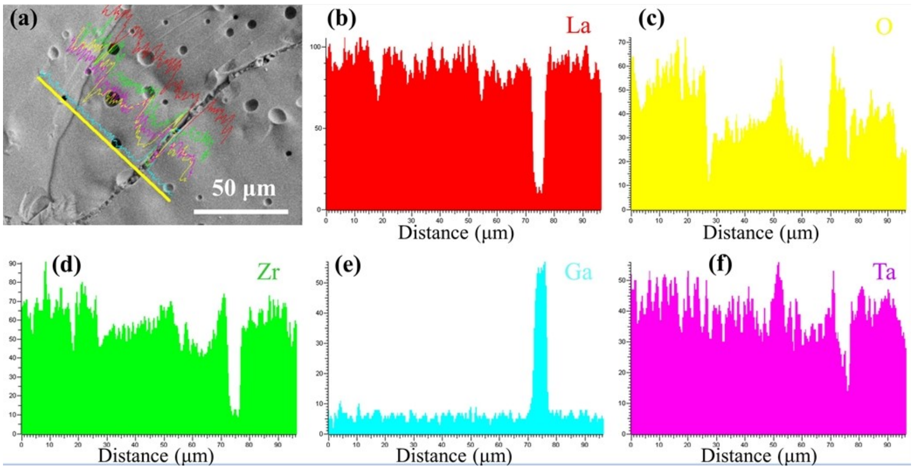

Fig. S 4 SEM image and (b-f) elements line distribution near grain boundary of Ga0.1-LLZT ceramic sintered at 1150 °C.

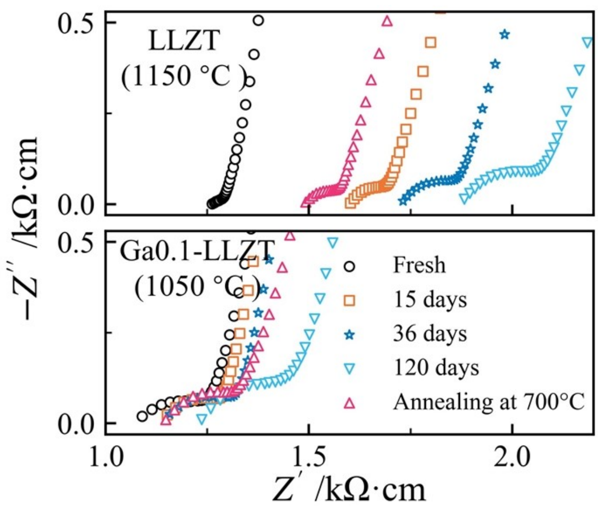

Fig. S 5 Nyquist plots of LLZT (1150 °C) and Ga0.1-LLZT (1050 °C) over atmospheric exposure time

Table S 3 Ionic conductivity of LLZT (1150 °C) and Ga0.1-LLZT (1050 °C) before and after the exposure to the ambient air

	Fresh (10^{-4} $S\cdot cm^{-1}$)	120 days (10^{-4} $S\cdot cm^{-1}$)	120 days + Annealing (10^{-4} $S\cdot cm^{-1}$)
LLZT (1150 °C)	7.75	4.74 (61%)	6.06 (78%)
Ga0.1-LLZT (1050 °C)	8.05	6.94 (86%)	7.60 (94%)

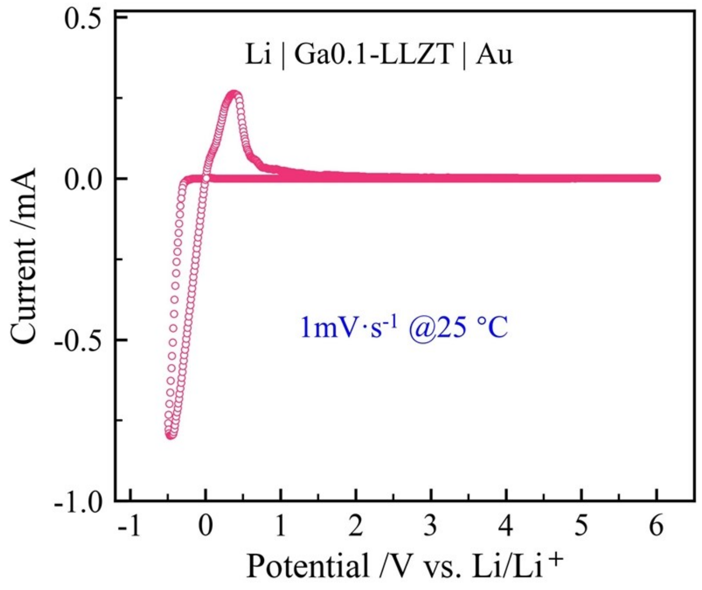

Fig. S 6 Cyclic voltammogram of Li|Ga0.1-LLZT (1150 ℃)|Au cell.

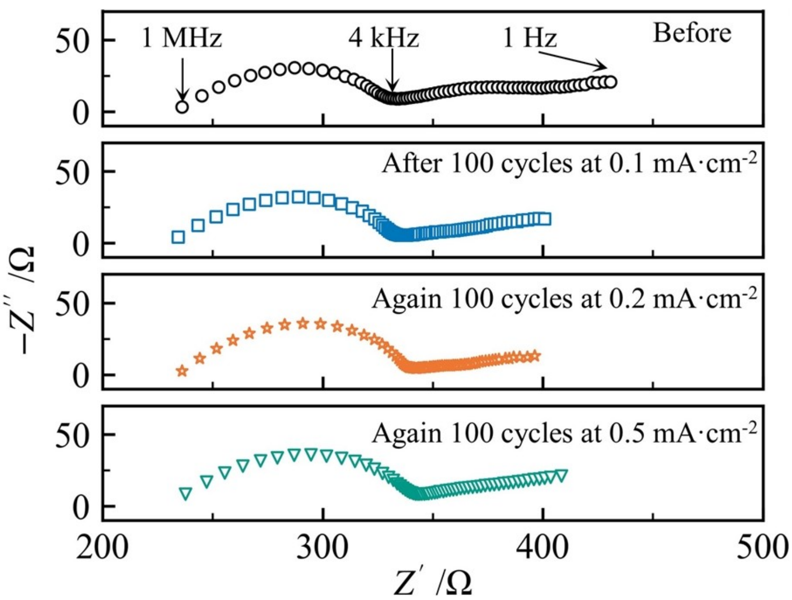

Fig. S 7 Electrochemical impedance plots of Li|Ga0.1-LLZT|Li symmetry cell