Electronic supplementary information

Co-sintering a cathode material and garnet electrolyte to develop a bulk-type solid-state Li metal battery with wide electrochemical windows

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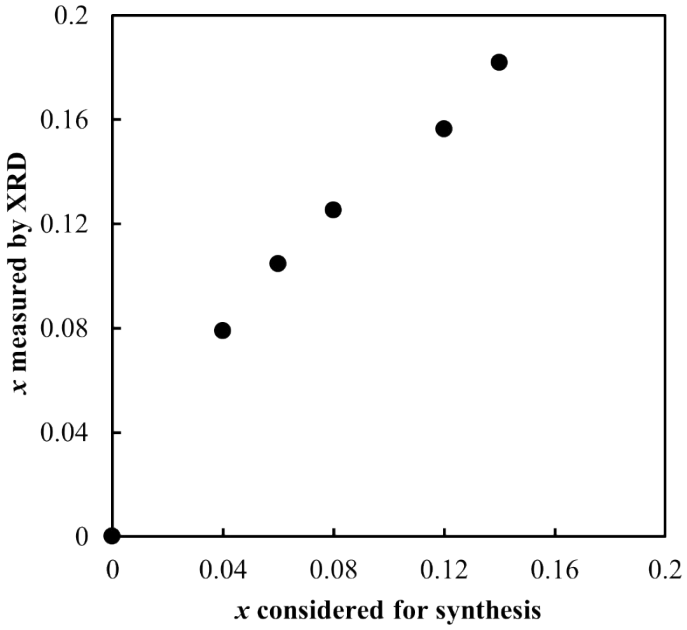

Fig. S1 Relationship between the *x* values considered for synthesis and those estimated by XRD.

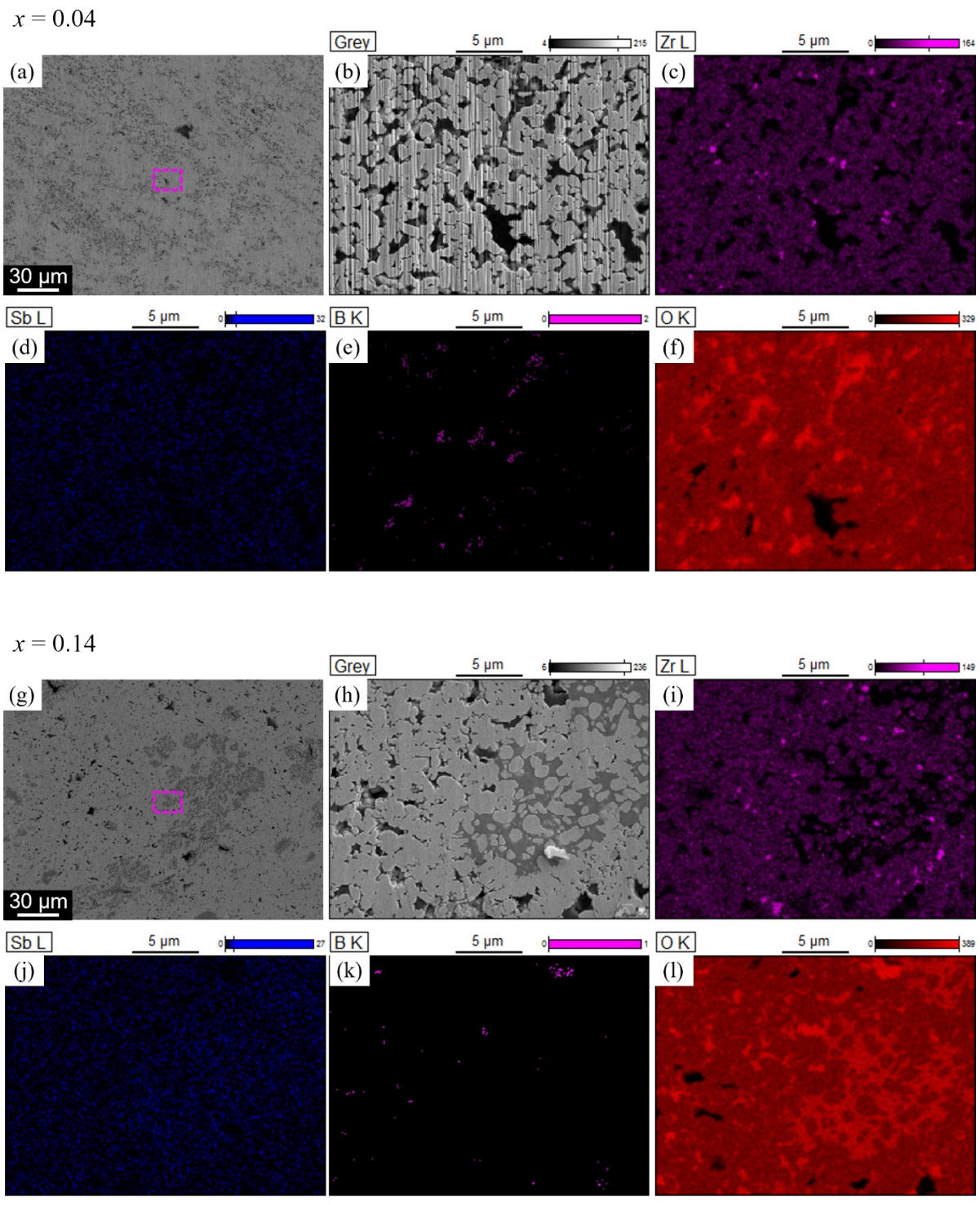

Fig. S2 (a, b, g, h) SEM images and (c–f, i–l) EDS-derived elemental maps of the LZ-CaSb + $x$$Li_7SbO_6$ + Li_3BO_3 composite electrolyte sintered at 750 °C for x values of (a–f) 0.04 and (g–l) 0.14. The SEM and EDS images in (b–f) and (h–l) correspond to the pink square shown in (a) and (g).

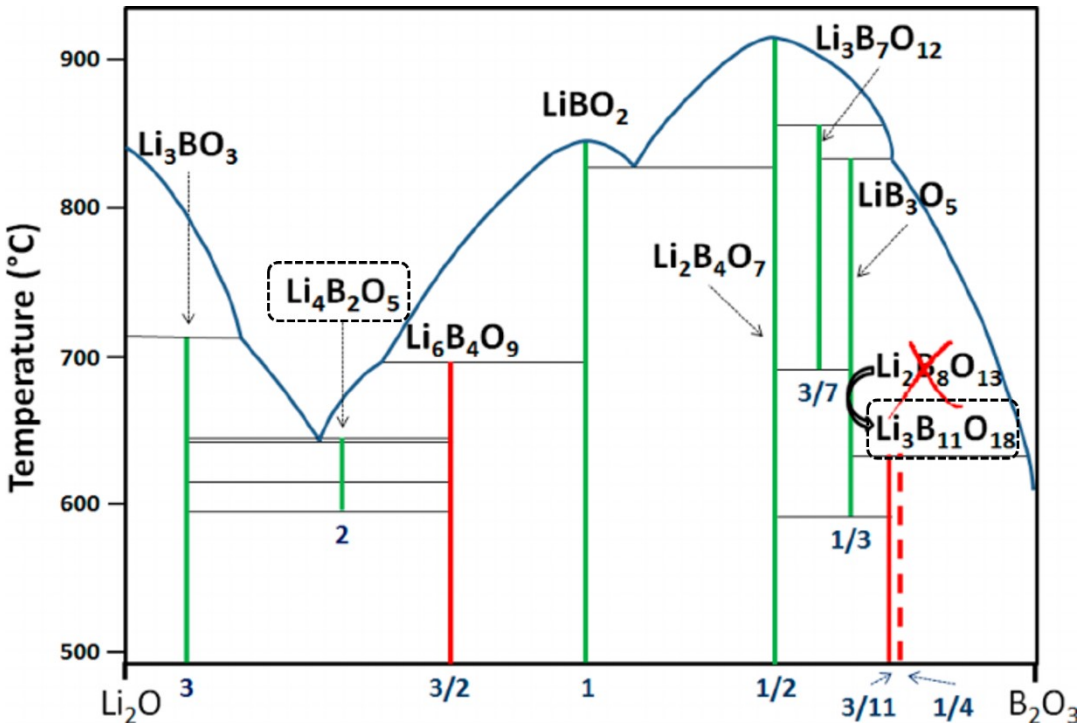

Fig. S3 The L_2O–B_2O_3 phase diagram reported by Rousse *et al*.[37]

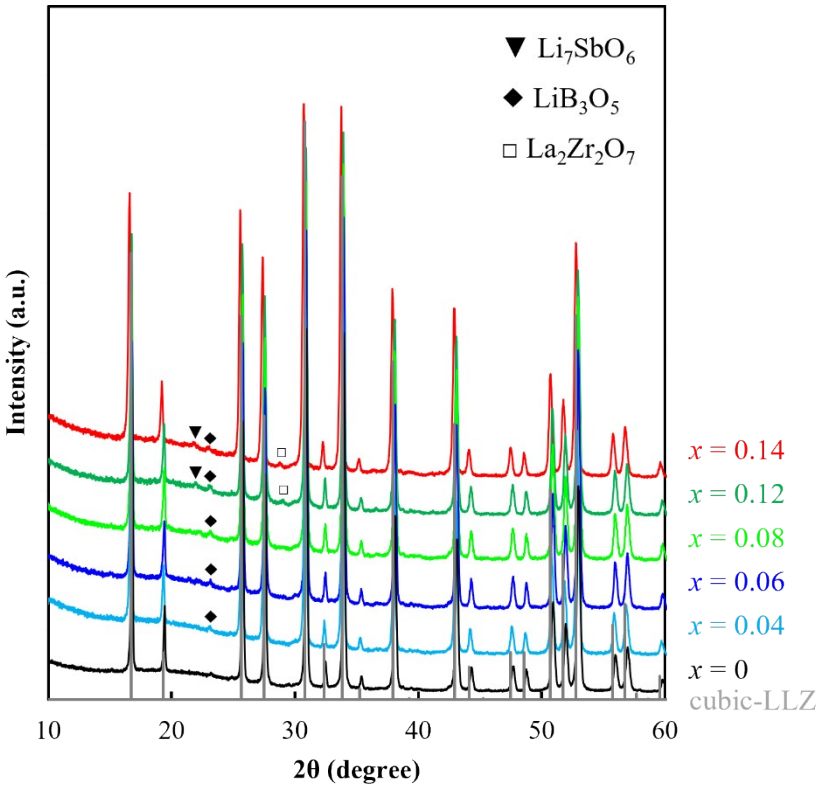

Fig. S4 XRD patterns of the LLZ-CaSb + $x$$Li_7SbO_6$ + Li_3BO_3 composite electrolytes sintered at 750 °C.

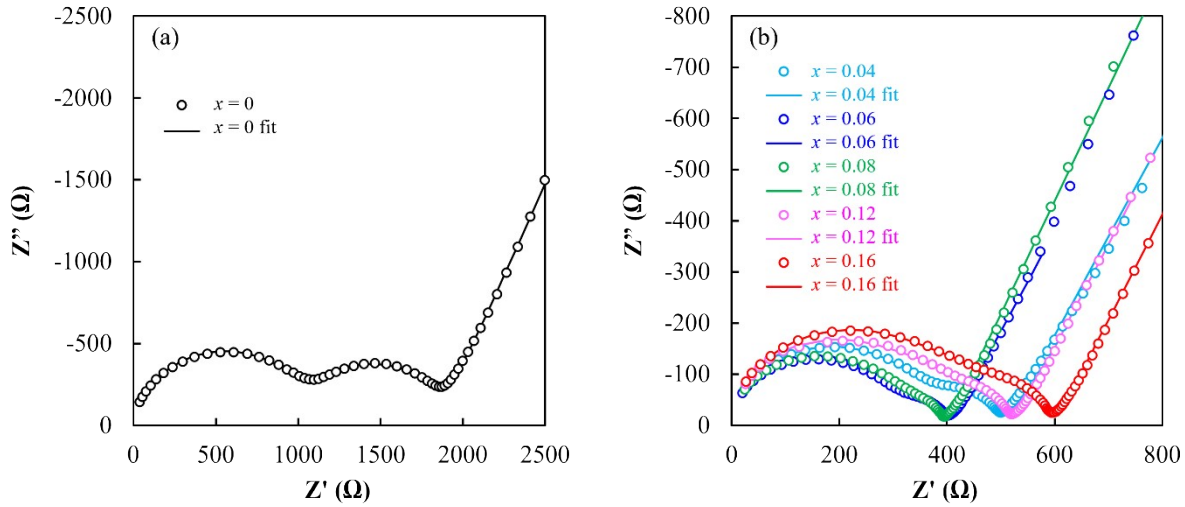

Fig. S5 Nyquist plots acquired at 298 K for the LLZ-CaSb + $x$$Li_7SbO_6$ (x = 0–0.16) + Li_3BO_3 composite electrolytes sintered at 750 °C.

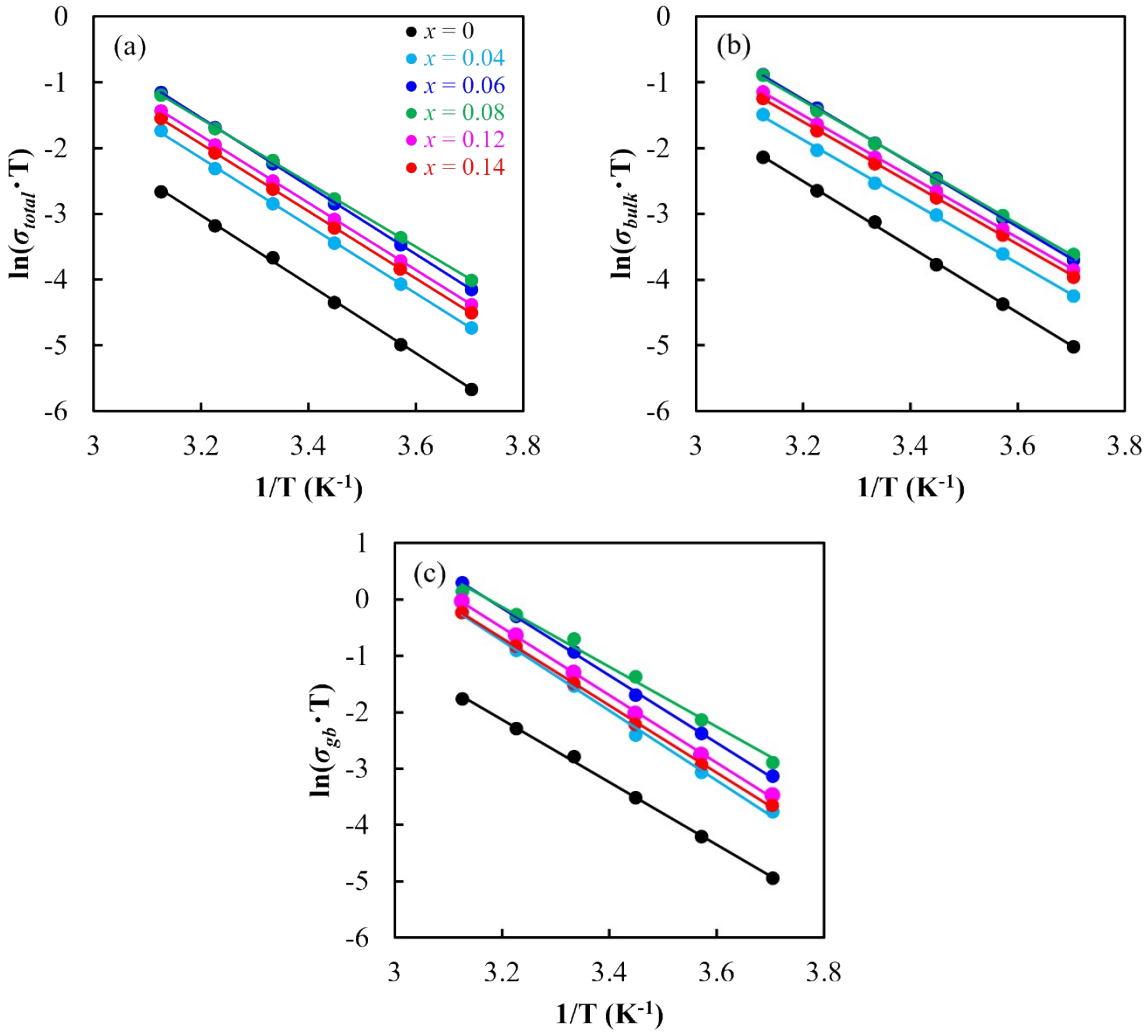

Fig. S6 Arrhenius plots of (a) total ionic conductivity, (b) bulk ionic conductivity, (c) and grain-boundary ionic conductivity measured at 240–320 K.

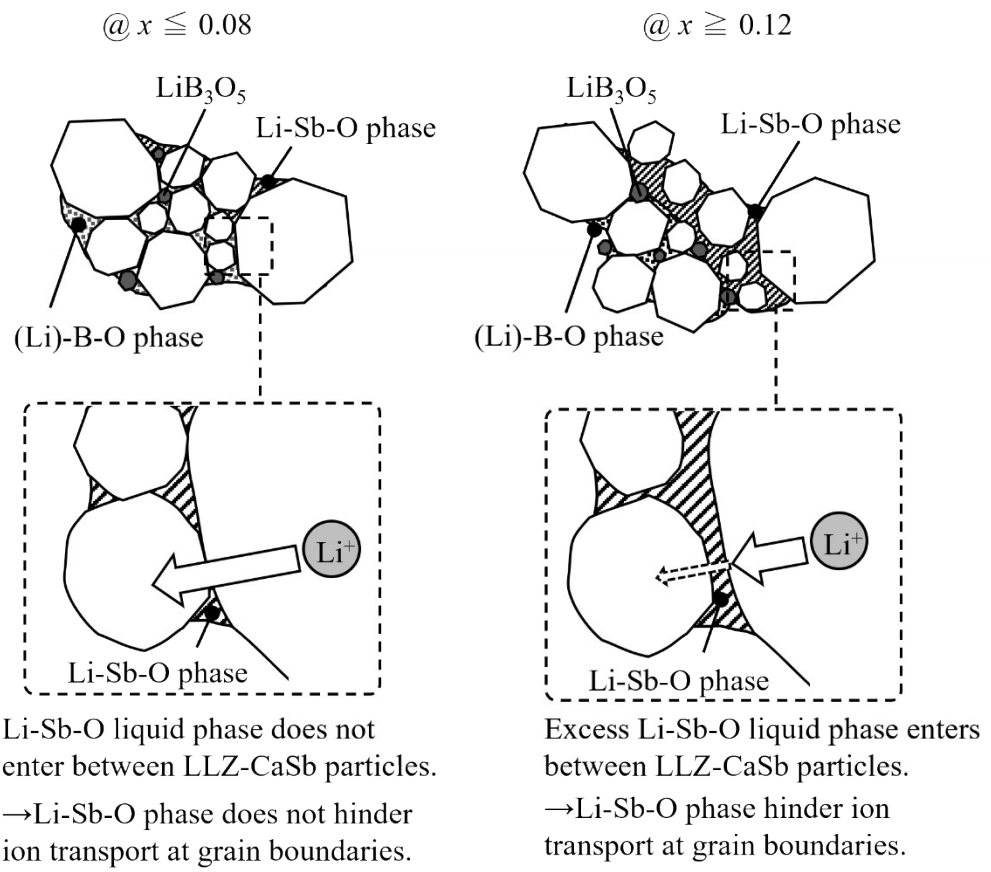

Fig. S7 Schematics illustrating the manner in which the amount of the Li–Sb–O phase depends on ion transport.

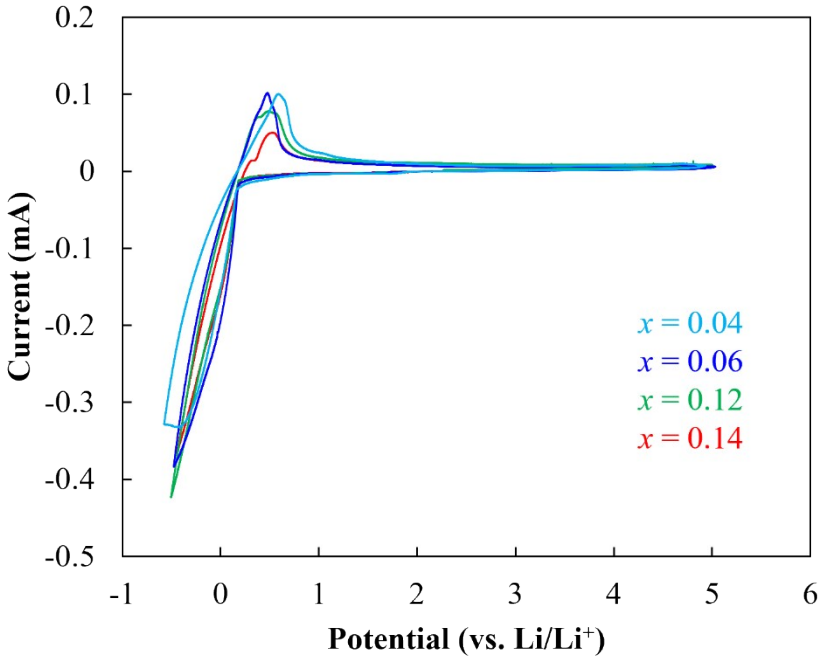

Fig. S8 Cyclic voltammetry profiles of the Au|LLZ-CaSb + $x$$Li_7SbO_6$ (x = 0.04, 0.06, 0.12, and 0.14) + Li_3BO_3|Li cell at a scan rate of 1 mV/s.

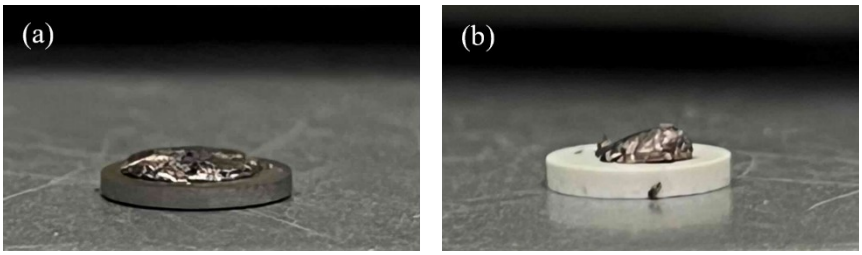

Fig. S9 Molten Li metal wetting behaviour of LLZ-CaSb + 0.08Li_7SbO_6 + Li_3BO_3 electrolyte specimens (a) with and (b) without Au surface coating.

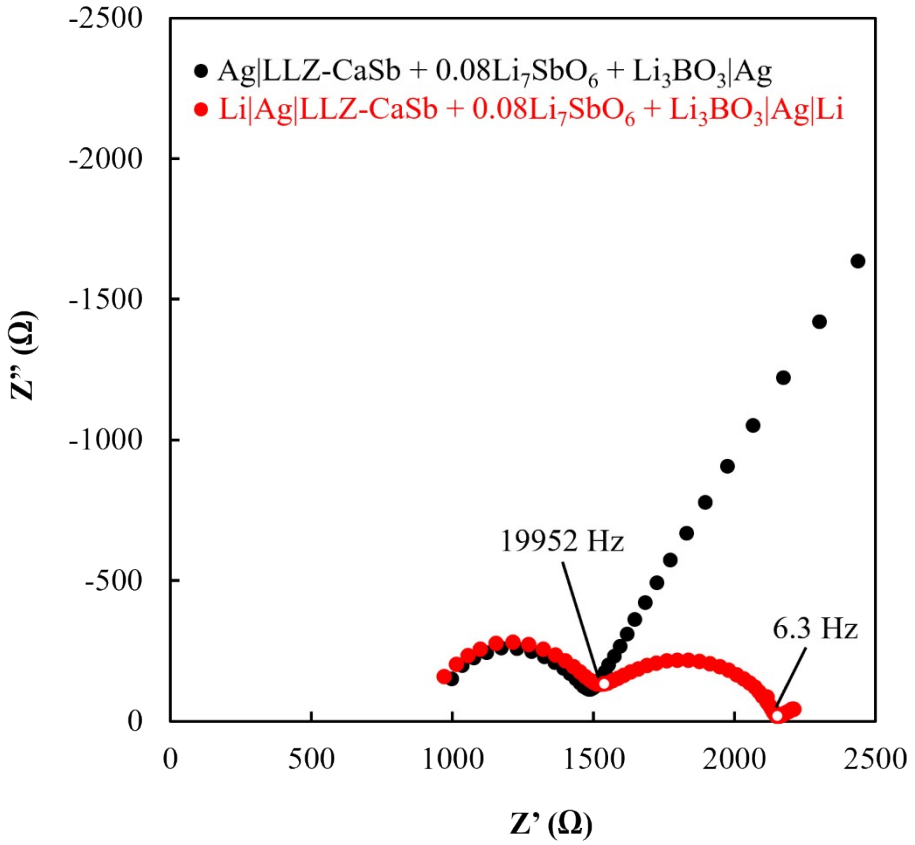

Fig. S10 Nyquist plots of Ag|LLZ-CaSb + 0.08Li_7SbO_6 + Li_3BO_3|Ag and Li|Ag|LLZ-CaSb + 0.08Li_7SbO_6 + Li_3BO_3|Ag|Li.

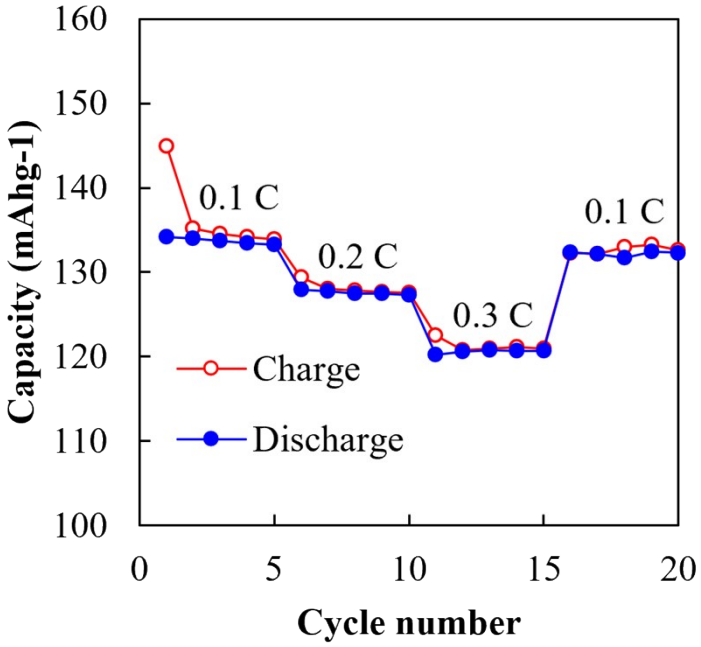

Fig. S11 Rate performance of the Li|LLZ-CaSb + $0.08Li_7SbO_6$|$LiCoO_2$ + LLZ-CaSb + $0.08Li_7SbO_6$ + Li_3BO_3 ASSB at 25 °C.

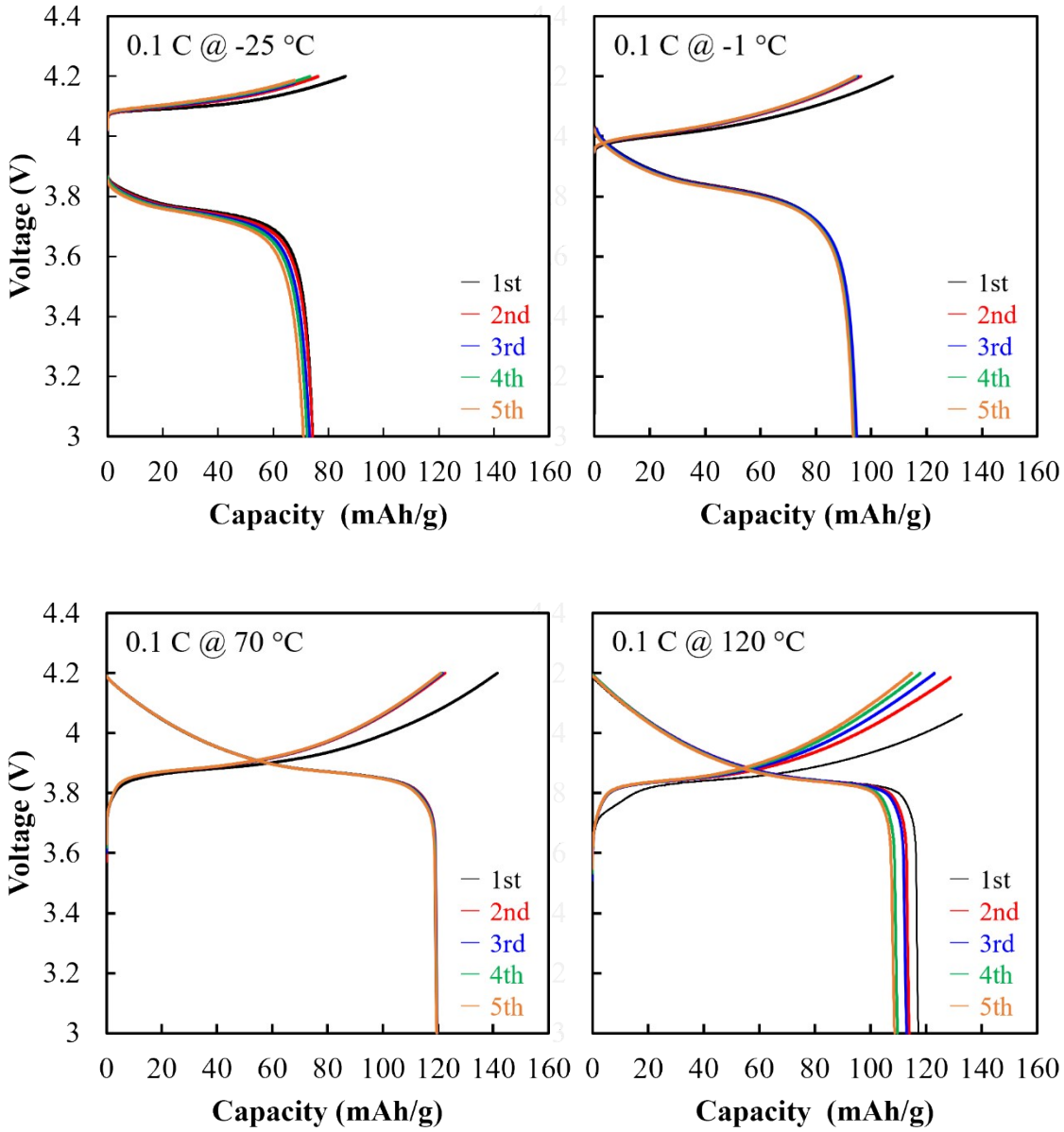

Fig. S12 Temperature-dependent performance of the Li|LLZ-CaSb + 0.08Li_7SbO_6 + Li_3BO_3 ASSB at 0.1C.

Table S1 Manufacturing temperatures, test environments, and performance data of Li plating/stripping tests conducted in the present and previous studies

Study	Sample	Test temperature (°C)	Current density (mA/cm^2)	Test duration	LLZ sintering temperature (°C)
Xu *et al*. (2017)[25]	$Li\|Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}+Li_3PO_4\|Li$	60	0.1	6 h	1140
Huang *et al*. (2018)[42]	$Li\|Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}\|Li$	25	0.1–0.3	300 h	1250
Song *et al*. (2018)[43]	$Li\|Li_{7.2}La_3Zr_{1.8}Gd_{0.2}O_{12}\|Li$	25	0.05	90 h	1220
		25	0.1	90 h	
		25	0.2	90 h	
Alexander *et al*. (2018)[44]	$Li\|Al\|Li_{6.28}Al_{0.24}La_3Zr_2O_{12}\|Al\|Li$	25	0.03	7.2 h	1200
Indu *et al.* (2019)[45]	$Li\|Au\|Li_{6.5}La_3Zr_{1.75}Te_{0.25}O_{12}\|Au\|Li$	25	0.1	900 min	1100
Koshikawa *et al*. (2019)[46]	$Li\|Au\|Li_{6.25}Al_{0.25}La_3Zr_2O_{12}\|Au\|Li$	25	0.05	6 h	1200
Su *et al*. (2019)[47]	$Li\|Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}\|Li$	27	0.4	600 h	1150
Dong *et al*. (2020)[48]	$Li\|Li_7La_3Zr_{1.75}Ce_{0.25}O_{12}\|Li$	60	0.0125	100 h	1050
		60	0.025	50 h	
		60	0.05	50 h	
Present study	Li|Au|LLZ-CaSb+0.08Li_7SbO_6+Li_3BO_3|Au|Li	25	0.05	150 h	750