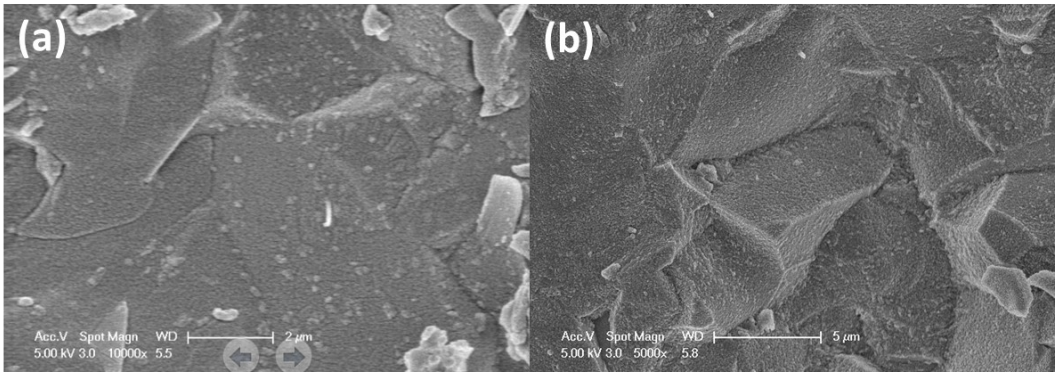
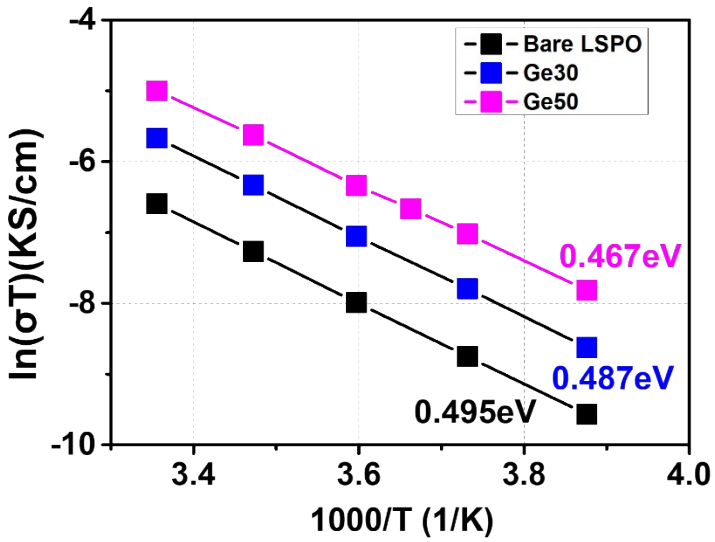
Supplementary Data

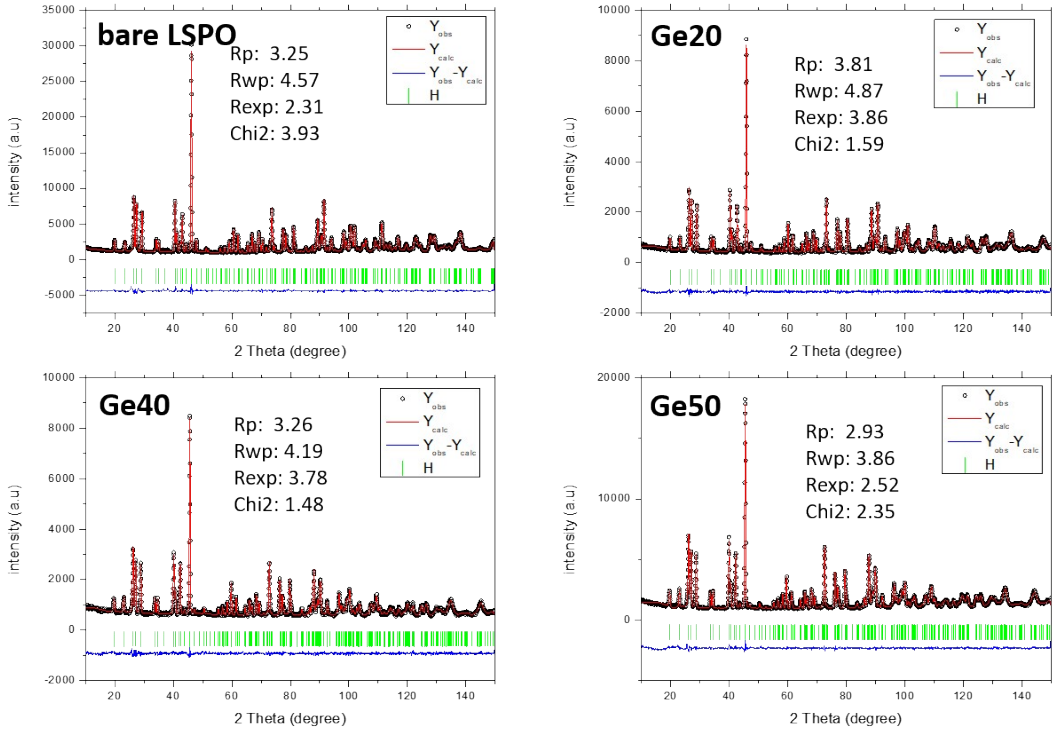
Creating Percolating Li Diffusion Pathways via Ge substitution Enables Thick-Electrode Oxide All-Solid-State Batteries



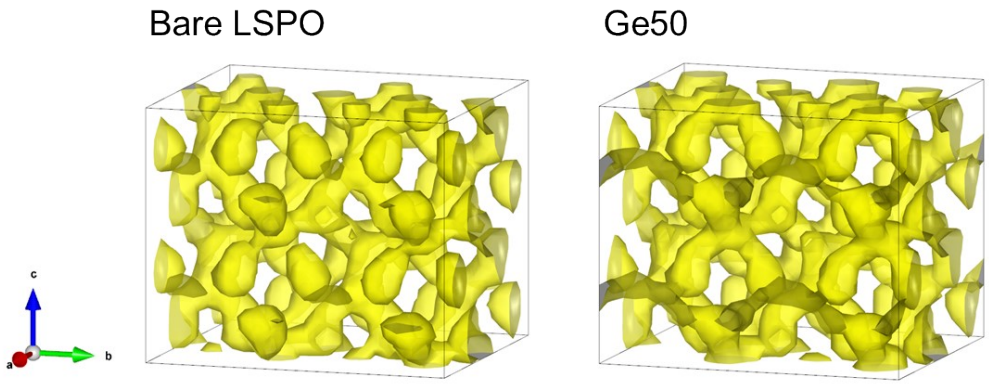
Supplementary Figure S1. Cross-section SEM images of LISICON SEs (a) bare LSPO (b) Ge50



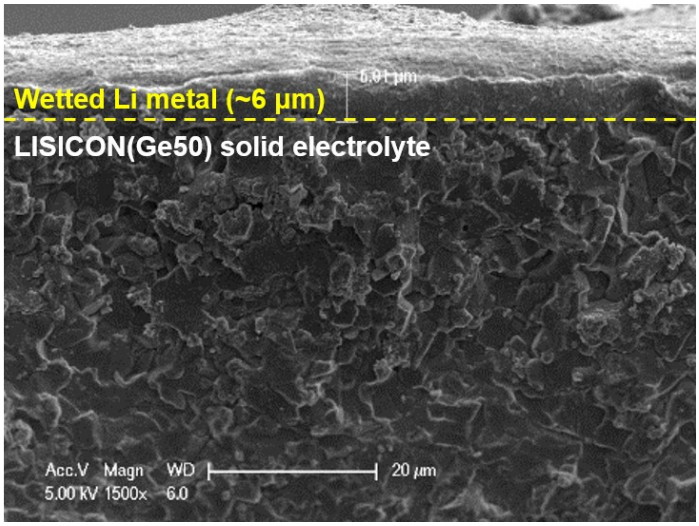
Supplementary Figure S2. Arrhenius plots and corresponding activation energies of bare LSPO, Ge30, and Ge50



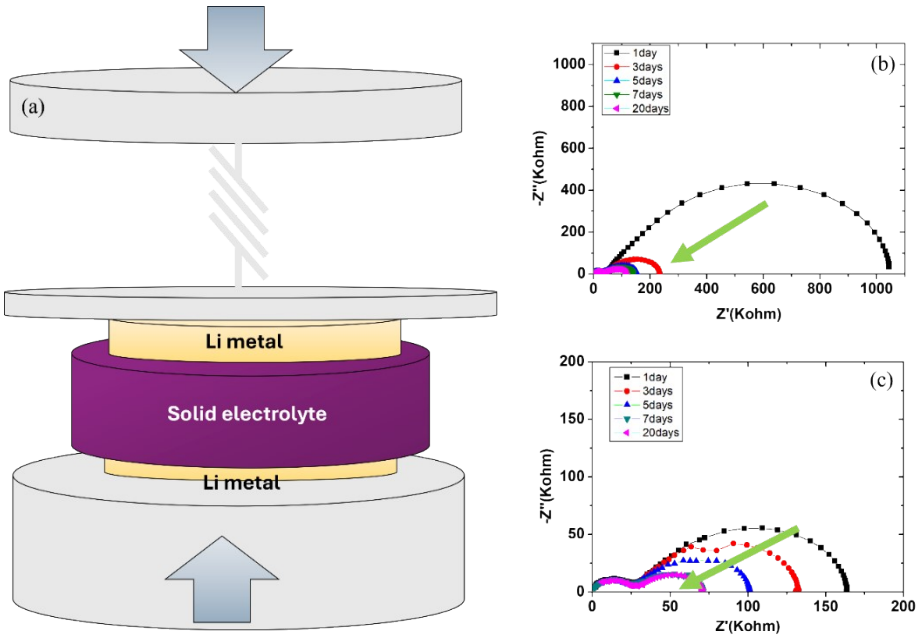
Supplementary Figure S3. Rietveld refinement results of NPD measurement for bare LSPO and Ge-substituted LISICON



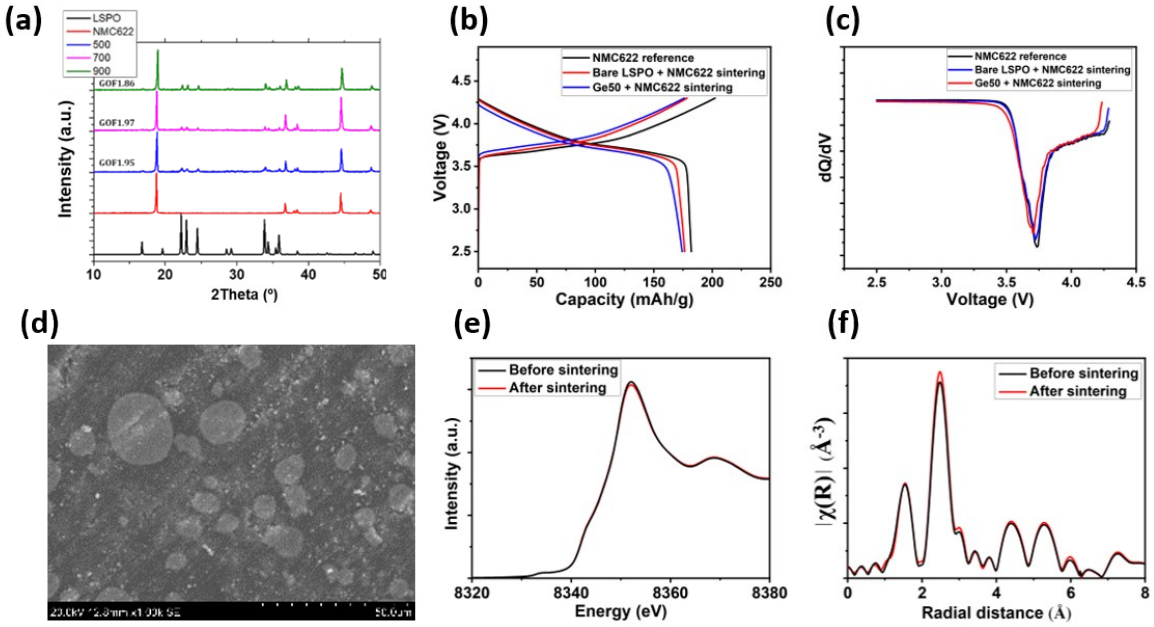
Supplementary Figure S4. Probability density distribution plot of bare LSPO and Ge50



Supplementary Figure S5. Cross-section SEM image of Li-metal-wetted Ge50 solid electrolyte. The wetting process was conducted at 250 ℃, and a thin Li metal layer (~6 μm) was formed by gently wiping the surface of the molten Li metal during the wetting process.

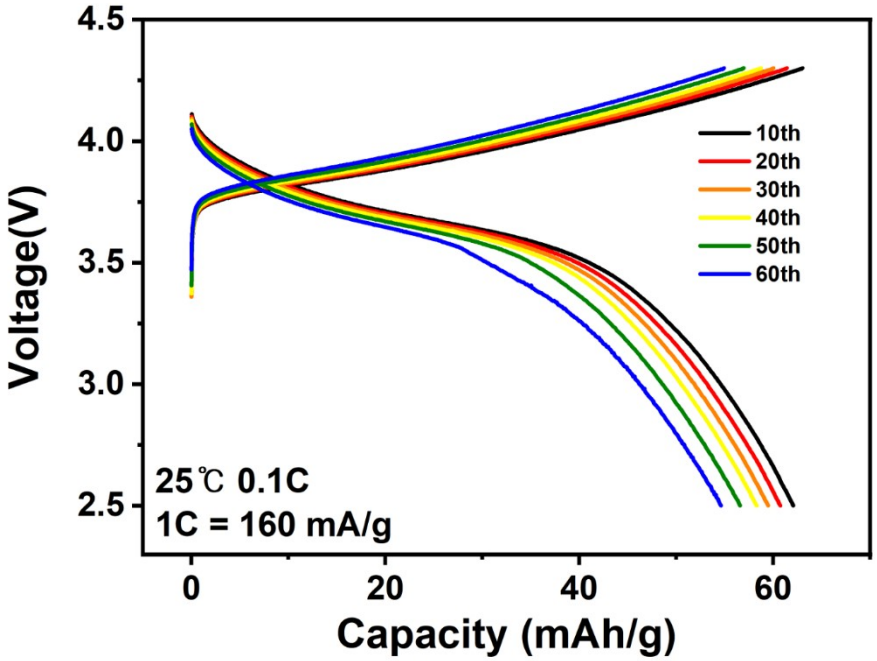


Supplementary Figure S6. Time-dependent impedance spectra of Li|SE|Li symmetric cells measured using a (a) Swagelok-type cell. EIS result of (b) Li|bare LSPO|Li and (c) Li|Ge10|Li. The bulk resistance remains unchanged, while the interfacial resistance gradually decreases, indicating stable interfacial behavior.



Supplementary Figure S7. Chemical & electrochemical stability confirmation test. (a) XRD patterns of bare LSPO, $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$(NMC622), and *ex-situ* analysis of the co-sintered NMC622 with the Ge50 at 500℃, 700℃, and 900℃. (b) Voltage curves and (c) dQ/dV plots of the NMC622 sample, and the NMC622 co-sintered samples with bare LSPO and Ge50. (d) Cross-section SEM image of the NMC622 co-sintered pellet with Ge50. (e), (f) XANES, EXAFS data of the NMC622 co-sintered sample with Ge50.

The co-sintered NMC622 samples with Ge50 even at 900 ℃ did not show any impurity phases. The crystalline structures of both Ge50 and NMC622 phase were well maintained without any secondary phases. Electrochemical properties of the co-sintered samples were evaluated by using electrochemical cell test with liquid electrolyte with the voltage range from 4.3V to 2.5V at 0.1C rate at room temperature. A slight polarization was observed in the co-sintered samples, but no noticeable change occurred in the electrochemical reaction behavior of NMC622. Ni oxidation number and local structure remained nearly unchanged before and after the heat treatment, confirming that Ge-substituted LISICON maintains excellent chemical/ electrochemical compatibility with NMC622.



Supplementary Figure S8. Voltage-capacity profile of Figure 7(c)

Sample	Density *(g cm⁻³)*	Calculated density (g cm⁻³)	Relative density (%)
LSPO	2.400	2.4050	99.79
Ge10	2.476	2.4805	99.82
Ge20	2.512	2.5560	98.28
Ge30	2.559	2.6315	97.24
Ge40	2.648	2.7070	97.82
Ge50	2.748	2.7825	98.76

Supplementary Table S1. Density profiles of sintered LSPO and Ge-substituted LSPOs pellets.

All pellets exhibited high relative densities in the range of 97.2–99.8%, indicating comparable densification among the samples.

$Li_{3.5}Si_{0.5}P_{0.5}O_4$						
$S.G.:Pnma;$		$Z = 4$				
$a = 10.5924$Å		$b = 6.1188$Å		$c = 5.0028$Å	$V = 324.248$Å^3	
$R_p = 3.25\%$		$R_{wp} = 4.57\%$		$R_{exp} = 2.31\%$	$\chi^2 = 3.93$	
Atomic position						
Atom	Wyckoff position	x/a	y/b	z/c	Occupancy	Biso
Li1	8d	0.33249	-0.00201	0.81732	0.775	1.204
Li2	4c	0.57026	0.25000	0.81399	0.390	0.968
Li3	4c	0.58040	0.25000	0.62280	0.088	0.932
Li4	8d	0.47918	0.46324	0.93008	0.135	0.932
Li5	8d	0.66486	0.45007	0.35474	0.198	3.443
Li6	4c	0.75923	0.25000	0.59158	0.077	1.341
O1	8d	0.34059	0.03820	0.21980	1.000	-
O2	4c	0.05205	0.25000	0.27983	0.500	-
O3	4c	0.41068	0.25000	0.64254	0.500	-
Si1	4c	0.41007	0.25000	0.32511	0.250	-
P1	4c	0.41007	0.25000	0.32511	0.250	-
Ge1	-	-	-	-	-	-

$Li_{3.6}Ge_{0.2}Si_{0.4}P_{0.4}O_4$						
$S.G.:Pnma;$		$Z = 4$				
$a = 10.6613$Å		$b = 6.1474$Å		$c = 5.0377$Å	$V = 330.164$Å^3	
$R_p = 3.81\%$		$R_{wp} = 4.87\%$		$R_{exp} = 3.86\%$	$\chi^2 = 1.59$	
Atomic position						
Atom	Wyckoff position	x/a	y/b	z/c	Occupancy	Biso
Li1	8d	0.33421	-0.00286	0.81966	0.767	1.174
Li2	4c	0.56978	0.25000	0.81565	0.391	0.744
Li3	4c	0.63443	0.25000	0.59547	0.098	1.055
Li4	8d	0.48564	0.45502	0.93915	0.141	0.932
Li5	8d	0.65571	0.47037	0.36863	0.200	3.596
Li6	4c	0.74115	0.25000	0.52992	0.093	5.414
O1	8d	0.33963	0.03530	0.22301	1.000	-
O2	4c	0.05433	0.25000	0.27699	0.500	-
O3	4c	0.41048	0.25000	0.65201	0.500	-

Si1	4c	0.41080	0.25000	0.33039	0.200	-
P1	4c	0.41080	0.25000	0.33039	0.200	-
Ge1	4c	0.41080	0.25000	0.33039	0.100	-

$Li_{3.7}Ge_{0.4}Si_{0.3}P_{0.3}O_4$						
$S.G.:Pnma;$		$Z = 4$				
$a = 10.72227$Å		$b = 6.17173$Å		$c = 5.0753$	$V = 335.855$Å^3	
$R_p = 3.26\%$		$R_{wp} = 4.19\%$		$R_{exp} = 3.45\%$	$\chi^2 = 1.48$	
Atomic position						
Atom	Wyckoff position	x/a	y/b	z/c	Occupancy	Biso
Li1	8d	0.33609	-0.00104	0.82233	0.754	1.461
Li2	4c	0.56643	0.25000	0.82791	0.384	0.908
Li3	4c	0.60684	0.25000	0.62886	0.097	0.245
Li4	8d	0.47009	0.48095	0.92467	0.145	0.787
Li5	8d	0.66874	0.47209	0.36647	0.237	3.596
Li6	4c	0.69910	0.25000	0.53841	0.093	1.627
O1	8d	0.33914	0.03023	0.22530	1.000	-
O2	4c	0.05643	0.25000	0.27743	0.500	-
O3	4c	0.41108	0.25000	0.66187	0.500	-
Si1	4c	0.41278	0.25000	0.33484	0.150	-
P1	4c	0.41278	0.25000	0.33484	0.150	-
Ge1	4c	0.41278	0.25000	0.33484	0.200	-

$Li_{3.75}Ge_{0.5}Si_{0.25}P_{0.25}O_4$						
$S.G.:Pnma;$		$Z = 4$				
$a = 10.7436$Å		$b = 6.19161$Å		$c = 5.0857$Å	$V = 338.301$Å^3	
$R_p = 2.93\%$		$R_{wp} = 3.86\%$		$R_{exp} = 2.52\%$	$\chi^2 = 2.35$	
Atomic position						
Atom	Wyckoff position	x/a	y/b	z/c	Occupancy	Biso
Li1	8d	0.33229	0.00318	0.82241	0.740	1.375
Li2	4c	0.56997	0.25	0.8311	0.382	1.593
Li3	4c	0.61167	0.25	0.60856	0.107	0.245
Li4	8d	0.47749	0.48802	0.9416	0.165	0.787
Li5	8d	0.66927	0.4695	0.36407	0.242	0.778
Li6	4c	0.71094	0.25	0.50432	0.105	2.885
O1	8d	0.33936	0.02995	0.22662	1.000	-
O2	4c	0.05848	0.25	0.2761	0.500	-
O3	4c	0.41144	0.25	0.66536	0.500	-
Si1	4c	0.41312	0.25	0.33819	0.125	-
P1	4c	0.41312	0.25	0.33819	0.125	-
Ge1	4c	0.41312	1/4	0.33819	0.250	-

Supplementary Table S2. Rietveld refinement results of NPD measurement for bare LSPO, $Li_{3.6}Ge_{0.2}Si_{0.4}P_{0.4}O_4$(Ge20), $Li_{3.7}Ge_{0.4}Si_{0.3}P_{0.3}O_4$(Ge40), $Li_{3.75}Ge_{0.5}Si_{0.25}P_{0.25}O_4$(Ge50)

$S.G.:Pnma$			
Lattice parameter	a	b	c
Bare LSPO	10.594	6.116	5.006

500℃	10.576	6.118	5.006
700℃	10.586	6.120	5.006
900℃	10.598	6.118	5.011

Units: Å

$S.G.: R-3m$			
Lattice parameter	a	c	c/a
NMC622	2.870	14.226	4.953
500℃	2.867	14.212	4.957
700℃	2.867	14.213	4.953
900℃	2.869	14.217	4.955

Units: Å

Supplementary Table S3. Refined XRD patterns' lattice parameters of supplementary figure S4(a)

	Item	Information
Materials properties	Cathode material	$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622), ρ = 4.7 g cm^{-3}
	Solid electrolyte(SE)	$Li_{3.75}Ge_{0.5}Si_{0.25}P_{0.25}O_4$ (Ge50), ρ = 2.65 g cm^{-3}
	Anode material	Li metal, ρ = 0.53 g cm^{-3}
Electrochemical properties	Discharge capacity	122 mAh g^{-1}
	Areal capacity	4.490 mAh cm^{-2}
	Areal energy	16.89 mAh cm^{-2}
ASSB components	Cathode composite	Thickness = 140 μm, volume = 0.00704 cm^3 , mass = 27.7 mg
	SE disk	Thickness = 50 μm, volume = 0.00251 cm^3 , mass = 6.66 mg
	Li metal anode	Thickness = 6 μm, volume = 0.000302 cm^3 , mass = 0.16 mg
	Total stack	Volume = 0.009862 cm^3, Mass =34.52 mg
Energy density	Volumetric	860.88 Wh L^{-1}
	Gravimetric	245.94 Wh kg^{-1}

Supplementary Table S4. Detailed component information for energy density calculations