Electronic Supplementary Information

Understanding the Anion Disorder Governing Lithium Distribution and Diffusion in Argyrodite Li₆PS₅Cl Solid Electrolyte

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Fig. S1 Relative energies of all investigated $\text{Li}_6\text{PS}_5\text{C1}$ (LPSC) structures as a function of *x*, which represents the degree of S/Cl disorder.



Fig. S2 Potential energy surfaces for the migration of single Li ions along doublet jump (T5 \rightarrow T5a \rightarrow T5), intracage jump (T5 \rightarrow T2 \rightarrow T5), and intercage jump (T5 \rightarrow T4 \rightarrow T5) paths at (a) x = 0% and (b) 50%. The climbing image nudged elastic band method¹ was used to calculate the potential energy surface.



Fig. S3 Average number of S and Cl ions around Li ($N_{\text{Li}-\text{S}}$ and $N_{\text{Li}-\text{S}}$) in the most stable LPSC structure at each *x*.



0 eV





Fig. S4 Two LPSC structures at x = 50%: (a) the lowest-energy structure with $N_{S-Li} = 7$ and $N_{Cl-Li} = 5$ and (b) one of the structures with $N_{S-Li} = 6$ and $N_{Cl-Li} = 6$. For each structure, X ions (X = S and Cl) that occupy the 4d/4a sites and their nearest Li ions are displayed.



Fig. S5 Projected density of states (PDOS) of Li, P, S, and Cl in the most stable LPSC structure at each *x*.





Fig. S6 Mean-square displacements (d_{ms}) of Li ions as a function of time in the most stable LPSC structure at (a) x = 0%, (b) 25%, (c) 50%, (d) 75%, and (e) 100%.



Fig. S7 Logarithmic diffusivities $(\ln D)$ of Li ions as a function of inverse temperature in the most stable LPSC structure at each x.





Fig. S8 Conductivity (σ) and activation energy (E_a) as a function of time in the most stable LPSC structure at (a) x = 0%, (b) 25%, (c) 50%, (d) 75%, and (e) 100%.



Fig. S9 Mean-square displacements (d_{ms}) of Li ions as a function of time in LPSC structures with energies approximately 0.3 eV higher than the lowest-energy structures at (a) x = 0%, (b) 50%, and (c) 100%.



Fig. S10 Logarithmic diffusivities (ln*D*) of Li ions as a function of inverse temperature in LPSC structures with energies approximately 0.3 eV higher than the lowest-energy structures at x = 0%, 50%, and 100%.



Fig. S11 Conductivity (σ) and activation energy (E_a) as a function of time in LPSC structures with energies approximately 0.3 eV higher than the lowest-energy structures at (a) x = 0%, (b) 50%, and (c) 100%.

x (%)	a (Å)	<i>b</i> (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	vol (Å ³)
0	9.93	9.70	9.70	90.7	90.8	90.9	934.8
25	9.82	9.75	9.60	88.4	90.2	91.0	918.7
50	9.71	9.83	9.71	89.0	89.3	89.9	925.8
75	9.70	9.76	9.78	91.2	90.3	88.6	925.5
100	9.90	9.81	9.69	90.1	89.0	90.9	939.8

Table S1 Lattice parameters of the most stable LPSC structure at each x.

	lowest-energy structure		higher-energy structure		
<i>x</i> (%)	$E_{\rm a}({\rm eV})$	$\sigma({ m mS~cm^{-1}})$	$E_{\rm a}({\rm eV})$	$\sigma ({ m mS \ cm^{-1}})$	
0	0.31	0.4	0.31	0.4	
50	0.25	4.6	0.25	4.8	
100	0.28	2.9	0.27	2.8	

Table S2 Activation energies (E_a) and conductivities (σ) in the lowest-energy LPSC structures and approximately 0.3 eV higher-energy structures at x = 0%, 50%, and 100%.

References

1 G. Henkelman, B. P. Uberuaga and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901–9904.