

Supplementary Information

Chlorine Transport Governs Chemical Stability at Halide-Sulfide Dual-Electrolyte Interfaces in All-Solid-State Batteries

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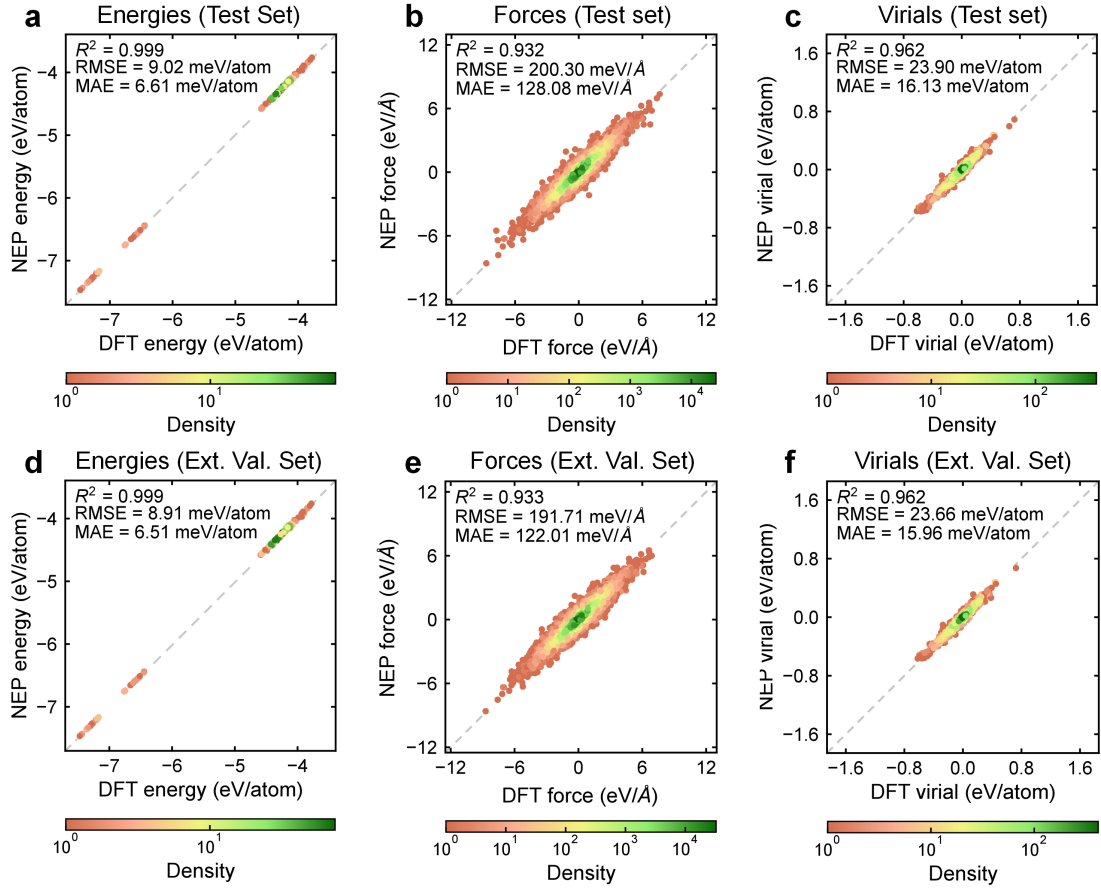
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Supplementary Table S1. DFT-calculated energies of reactants and products used for reaction enthalpy calculations. The structure of Li_2ZrCl_6 (α phase) was taken from Ref. 1, and the structure of $\text{Li}_6\text{PS}_5\text{Cl}$ (48HR-inverted) from Ref. 2, and the structures of the others are taken from Materials Project and their IDs are given.

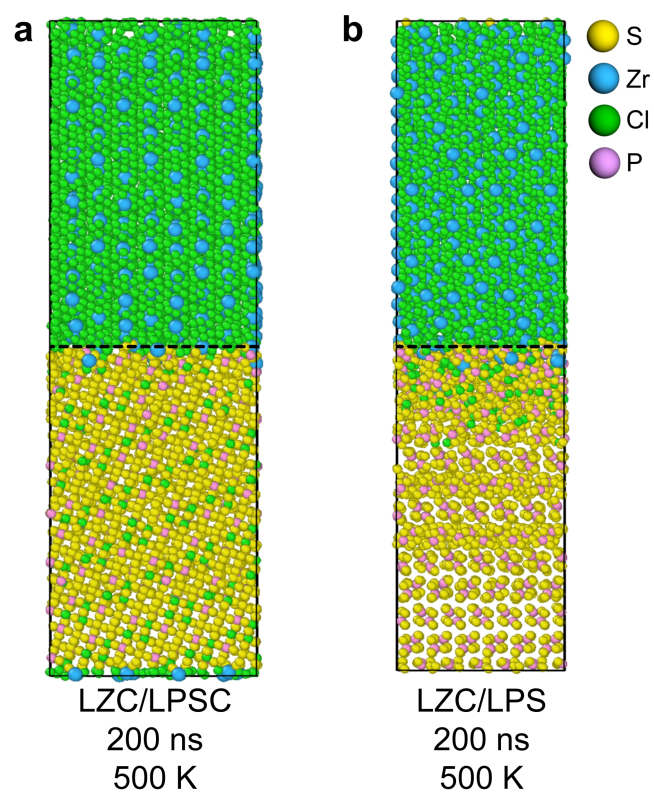
Composition	Energy (eV/f.u.)	Composition	Energy (eV/f.u.)
Li_3PS_4 (mp-985583)	-36.92	$\text{Li}_6\text{PS}_5\text{Cl}$ (48HR-inverted)	-57.34
ZrS_2 (mp-1186)	-22.41		
Li_2ZrCl_6 (α phase)	-41.58	ZrS_3 (mp-9921)	-27.18
ZrP_2S_6 (mp-8203)	-52.64	LiCl (mp-22905)	-7.83
S_8 (mp-77)	-34.53	ZrP_2S_7 (mp-31014)	-57.19

Supplementary Table S2. Comparison of reaction enthalpies ΔH (eV) calculated in this work and reported in Ref. 3 for the LZC/LPS and LZC/LPSC pairings.

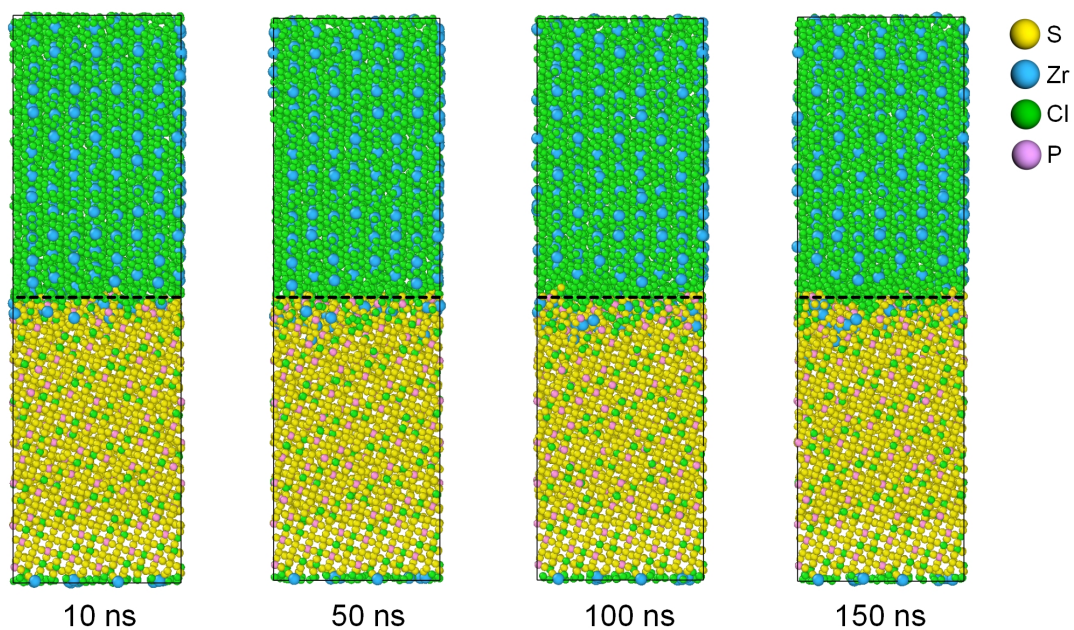
LZC/LPS pairing	ΔH (eV) (This work)	ΔH (eV) (Ref. 3)
$0.5714 \text{ Li}_3\text{PS}_4 + 0.4286 \text{ Li}_2\text{ZrCl}_6 \rightarrow$ $0.1429 \text{ ZrP}_2\text{S}_7 + 0.1429 \text{ Zr}(\text{PS}_3)_2 + 0.1429 \text{ ZrS}_3 + 2.571 \text{ LiCl}$	-0.79	-0.62
LZC/LPSC pairing	ΔH (eV) (This work)	ΔH (eV) (Ref. 3)
$0.4444 \text{ Li}_6\text{PS}_5\text{Cl} + 0.5556 \text{ Li}_2\text{ZrCl}_6 \rightarrow$ $0.2222 \text{ ZrP}_2\text{S}_7 + 0.1111 \text{ ZrS}_2 + 0.2222 \text{ ZrS}_3 + 3.778 \text{ LiCl}$	-1.22	-1.00



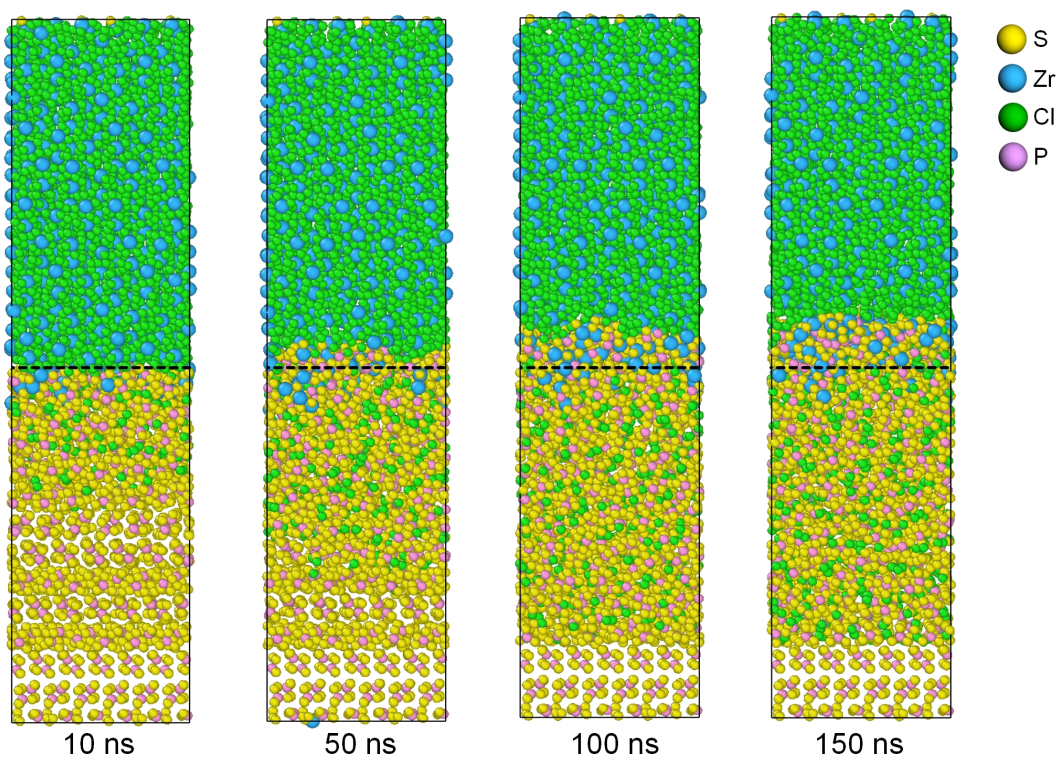
Supplementary Fig. S1. Performance evaluation of the NEP model on the test set and external (Ext.) validation (Val.) set. Parity plots show agreement between NEP-predicted and DFT-calculated values of total energies, atomic forces, and virial stresses for the **a-c** test set and **d-f** external validation set, respectively. The corresponding data-density distributions are shown below.



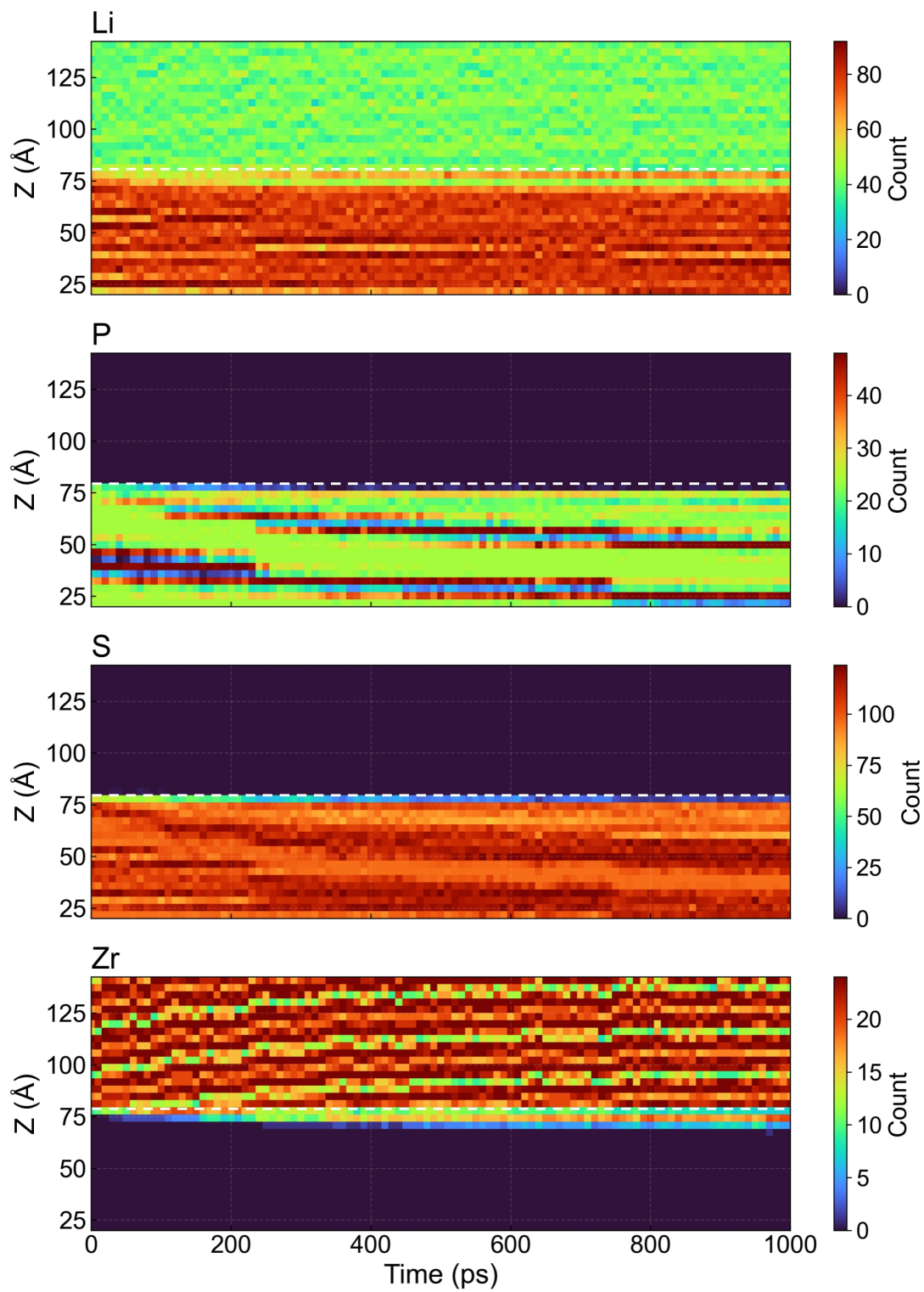
Supplementary Fig. S2. Simulated interfacial structures of **a** $\text{Li}_2\text{ZrCl}_6/\text{Li}_6\text{PS}_5\text{Cl}$ and **b** $\text{Li}_2\text{ZrCl}_6/\text{Li}_3\text{PS}_4$ interfaces at the end of the simulations (200 ns) under NPT ensemble at 500 K. Lithium atoms are omitted for clarity.



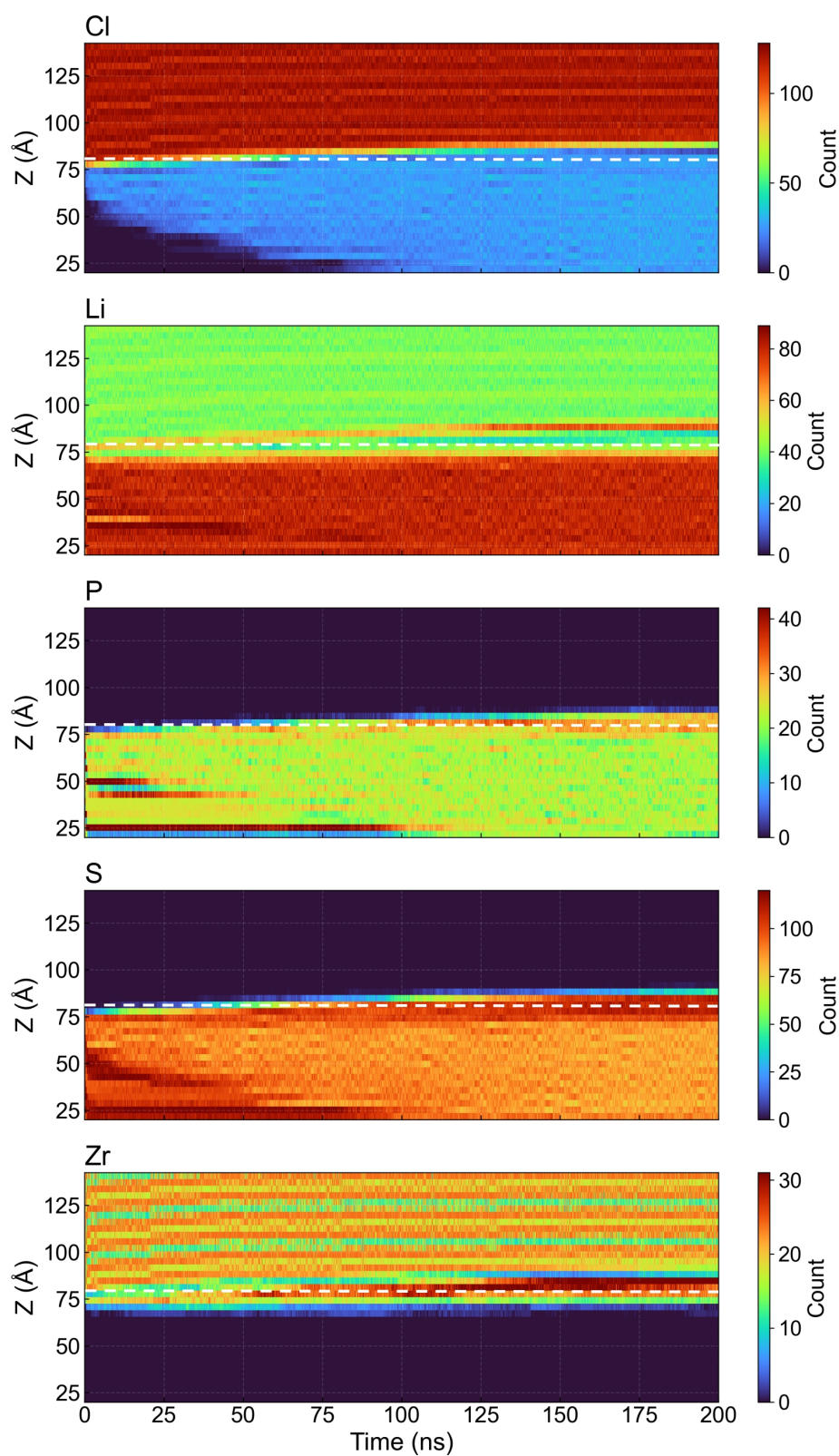
Supplementary Fig. S3. Snapshots (10 ns, 50 ns, 100 ns, and 150 ns) taken from MLMD simulations of the $\text{Li}_2\text{ZrCl}_6/\text{Li}_6\text{PS}_5\text{Cl}$ interface under NPT ensemble at 700 K. Lithium atoms are omitted for clarity.



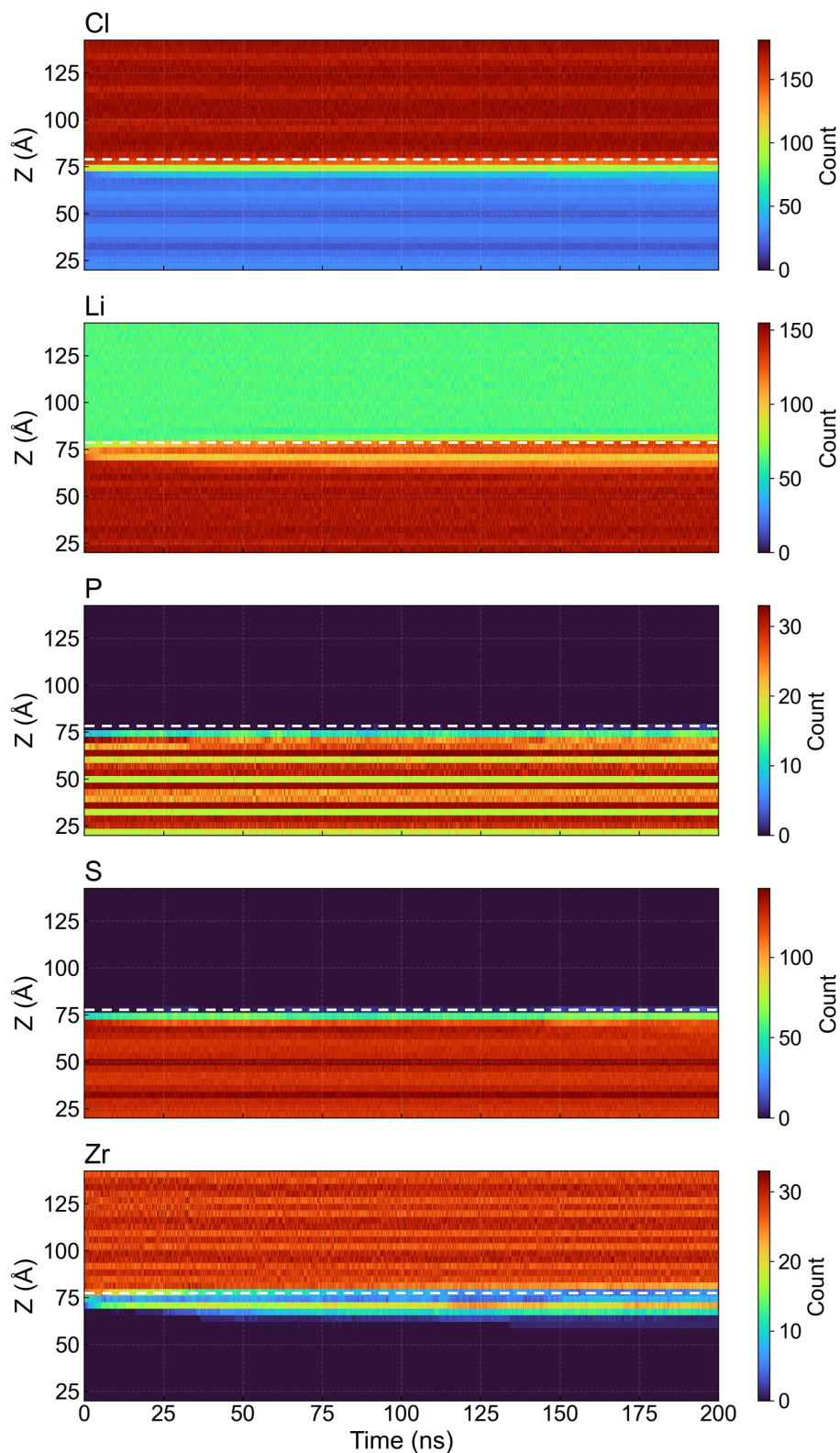
Supplementary Fig. S4. Snapshots (10 ns, 50 ns, 100 ns, and 150 ns) taken from MLMD simulations of the $\text{Li}_2\text{ZrCl}_6/\text{Li}_3\text{PS}_4$ interface under NPT ensemble at 700 K. Lithium atoms are omitted for clarity.



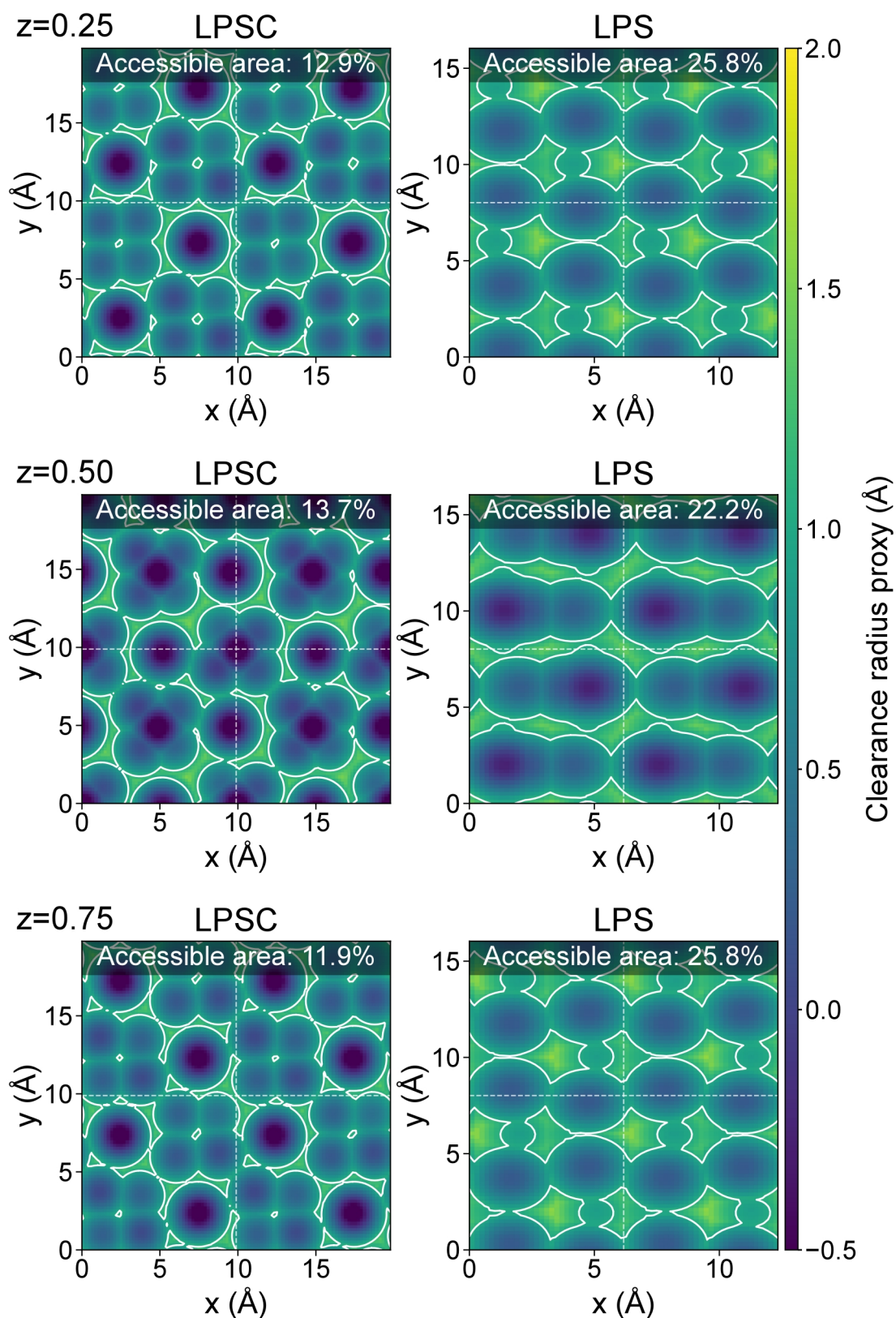
Supplementary Fig. S5. Time-resolved evolution of number density profiles for Li, P, S, and Zr atoms during the first 1000 ps MLMD simulation of the $\text{Li}_2\text{ZrCl}_6/\text{Li}_3\text{PS}_4$ interface at 700 K.



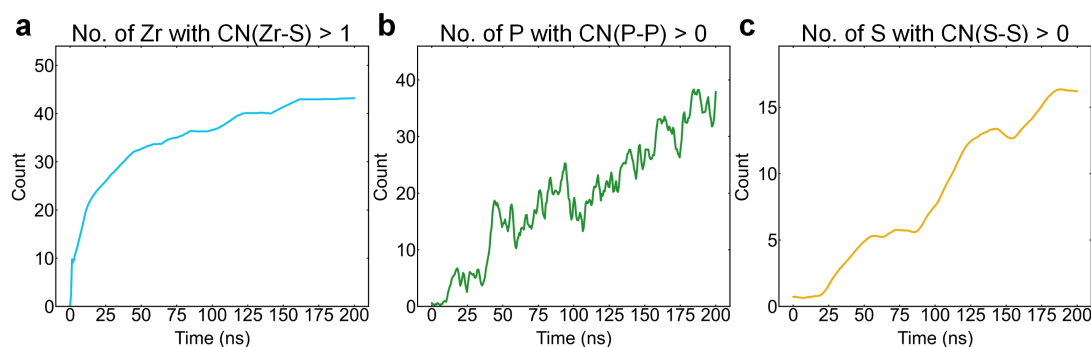
Supplementary Fig. S6. Time-resolved evolution of number density profiles for Cl, Li, P, S, and Zr atoms during the 200 ns MLMD simulation of the $\text{Li}_2\text{ZrCl}_6/\text{Li}_3\text{PS}_4$ interface at 700 K.



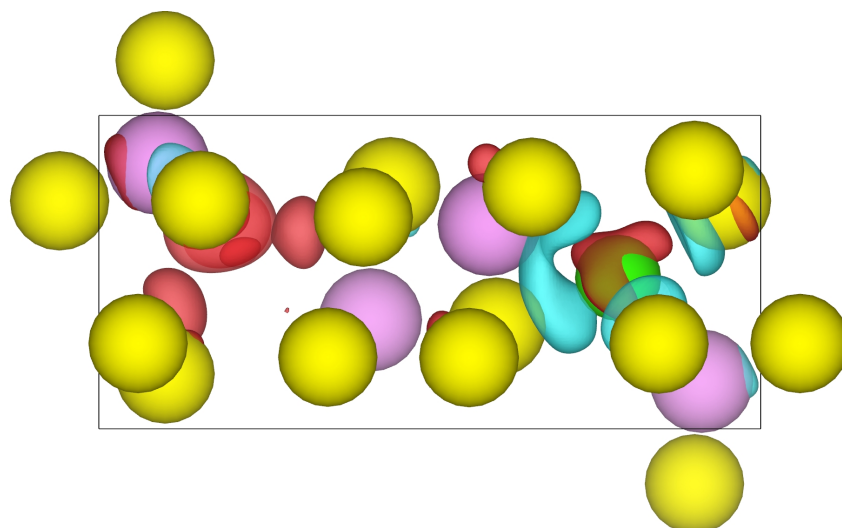
Supplementary Fig. S7. Time-resolved evolution of number density profiles for Cl, Li, P, S, and Zr atoms during the 200 ns MLMD simulation of the $\text{Li}_2\text{ZrCl}_6/\text{Li}_6\text{PS}_5\text{Cl}$ interface at 700 K.



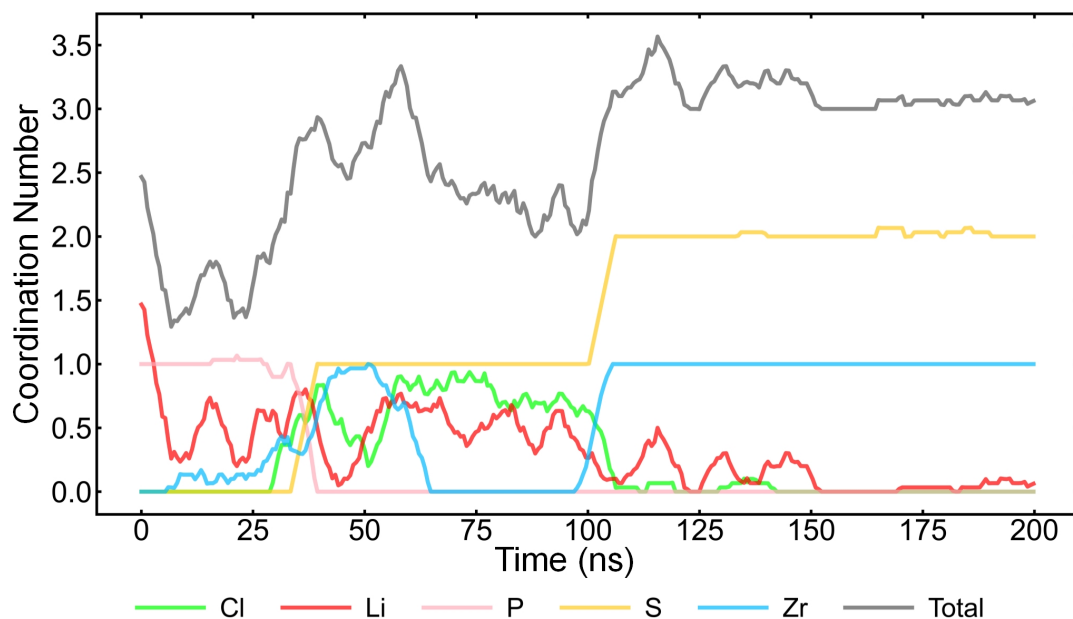
Supplementary Fig. S8. Cross-sectional Cl-probe clearance maps for LPSC and LPS. (Framework atoms are defined as P, S, and Cl, while Li are excluded). White contours mark regions that can geometrically accommodate a Cl probe.



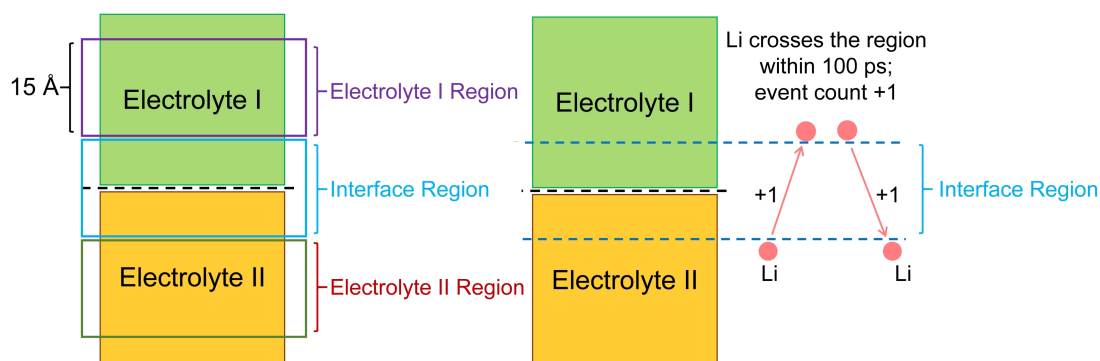
Supplementary Fig. S9. Coordination number (CN) evolution of key atoms during interfacial reactions. **a** Time evolution of the number of Zr atoms with Zr-S coordination number greater than 1 at the LZC/LPSC interface. **b** Time evolution of the number of P atoms with P-P coordination number greater than 0 at the LZC/LPS interface. **c** Time evolution of the number of S atoms with S-S coordination number greater than 0 at the LZC/LPS interface.



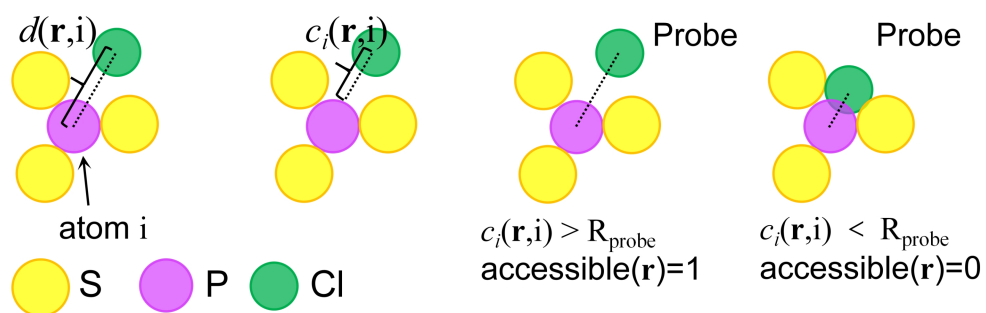
Supplementary Fig. S10. Charge-density difference illustrating charge redistribution in the LPS framework after Cl insertion. Red and blue isosurfaces denote regions of charge accumulation and depletion, respectively. Additional Li was introduced to compensate charge, and Li atoms are omitted for clarity. P, S, and Cl atoms are represented by purple, yellow and green spheres, respectively.



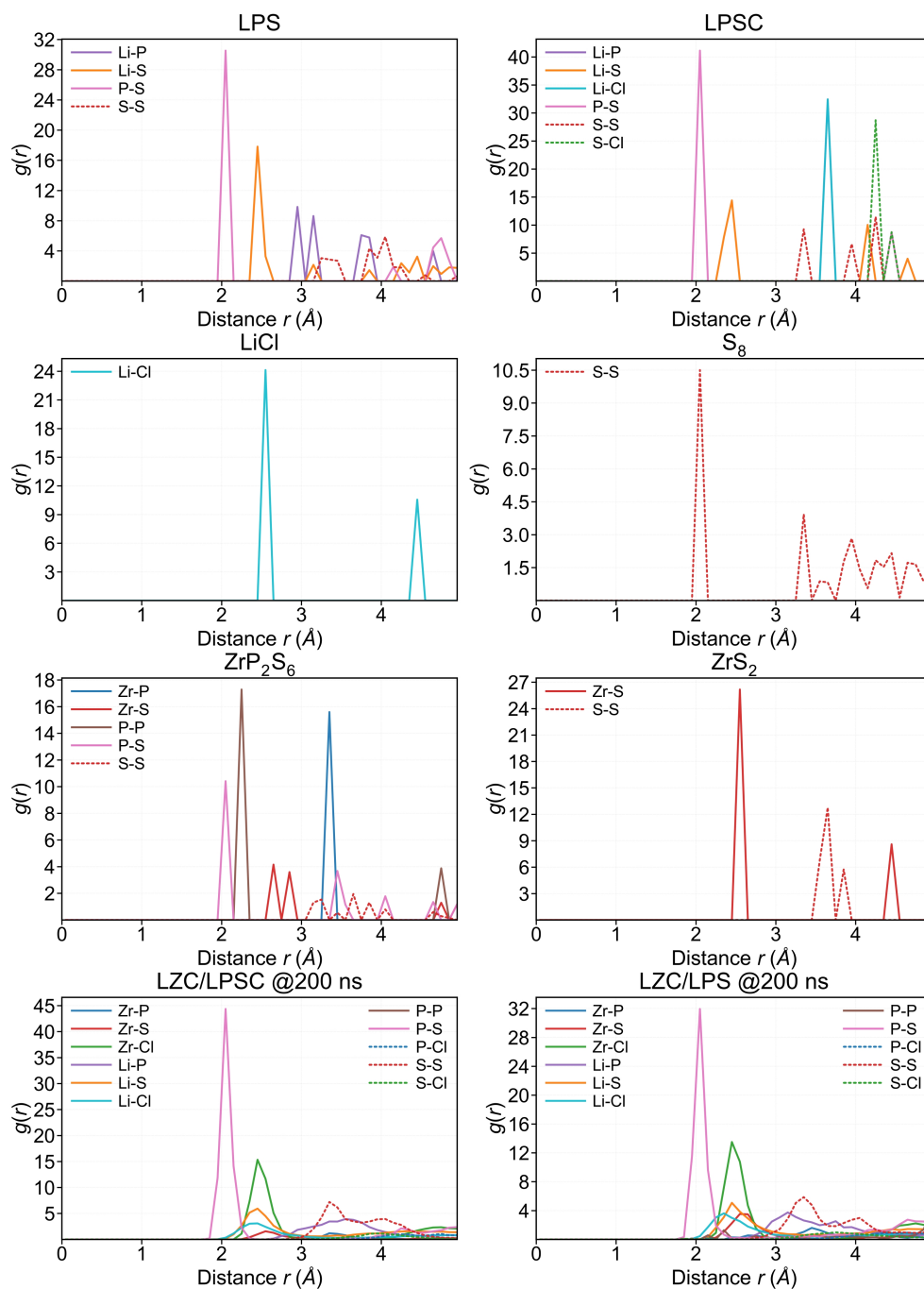
Supplementary Fig. S11. Time evolution of the selected sulfur coordination shell, highlighting the transition from PS_4^{3-} to S_x ($x=2$ or 3). This evolution reveals the growth process of sulfur chains, with occasional Zr coordination during the intermediate stages, suggesting that elemental sulfur (S_8) formation proceeds through polysulfide-anion-like intermediates.



Supplementary Fig. S12. Schematic illustration of the interface region used for the count of crossing events.



Supplementary Fig. S13. Schematic illustration of the definitions used to calculate the Cl-accessible clearance, including $d(\mathbf{r},i)$, $c_i(\mathbf{r})$, and $\text{accessible}(\mathbf{r})$.



Supplementary Fig. S14. Radial distribution functions (RDFs) and local structural fingerprints in LPS, LPSC, potential reaction products (LiCl, S_8 , ZrP_2S_6 , ZrS_2) together with those of the reacted interfacial systems extracted from the final snapshots of the MLMD simulations. All pair-specific coordination-number criteria used in this work were determined from the corresponding RDF profiles, with the cutoff distances taken from the first minima of the RDFs.

References

1. Wang, K. *et al.* A cost-effective and humidity-tolerant chloride solid electrolyte for lithium batteries. *Nat. Commun.* **12**, 4410 (2021).
2. Pustorino, G. *et al.* Mechanical and Electronic Properties of Bulk and Surface Li₆PS₅Cl Argyrodite: First-Principles Insights on Li-Filament Resistance. *Chem. Mater.* **37**, 313–321 (2025).
3. Pennebaker, T. *et al.* Establishing the Compatibility of Anolytes and Catholytes in Dual Electrolyte Solid-State Batteries. Preprint at <https://doi.org/10.26434/chemrxiv-2025-chtzv> (2025).