

Atomic mechanism of lithium dendrite penetration in solid electrolytes

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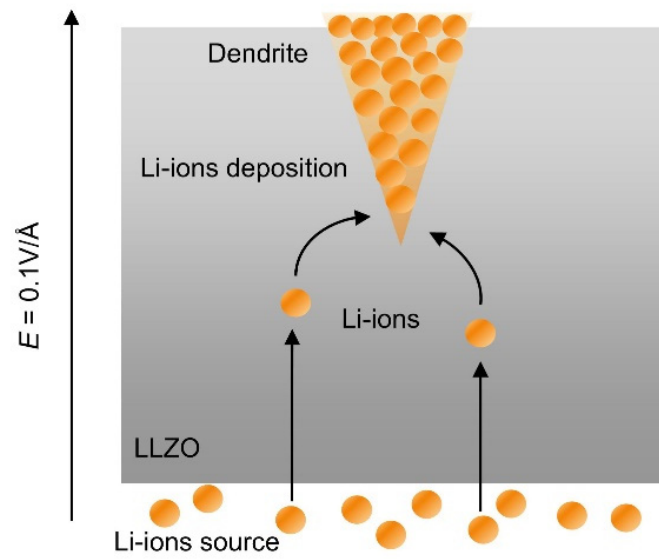
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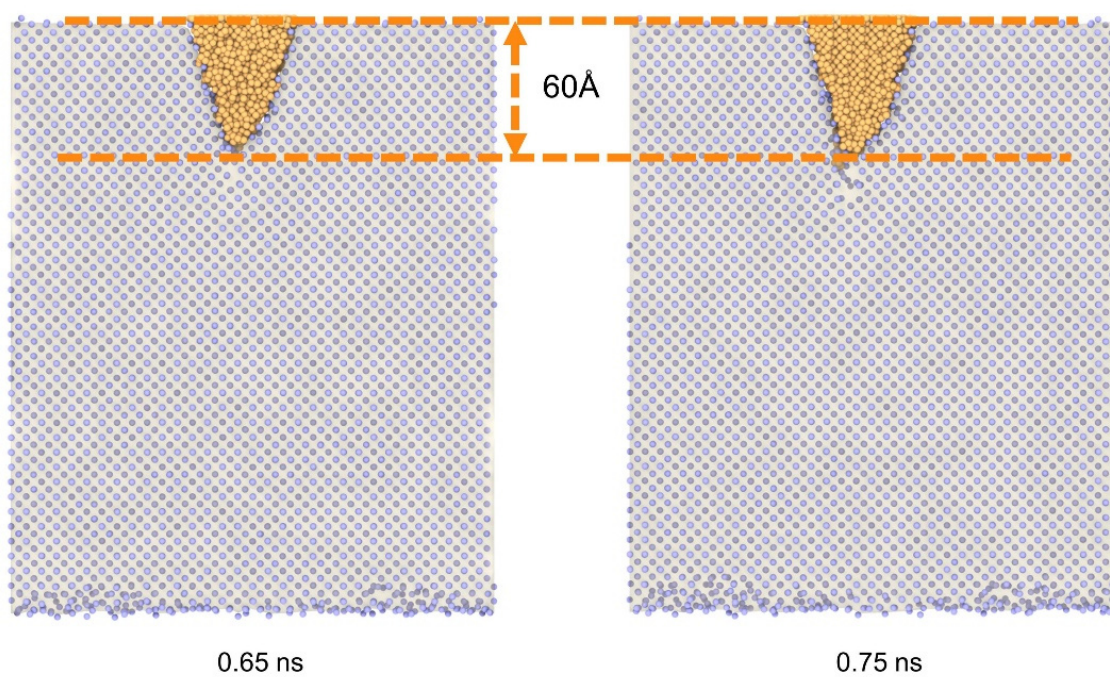
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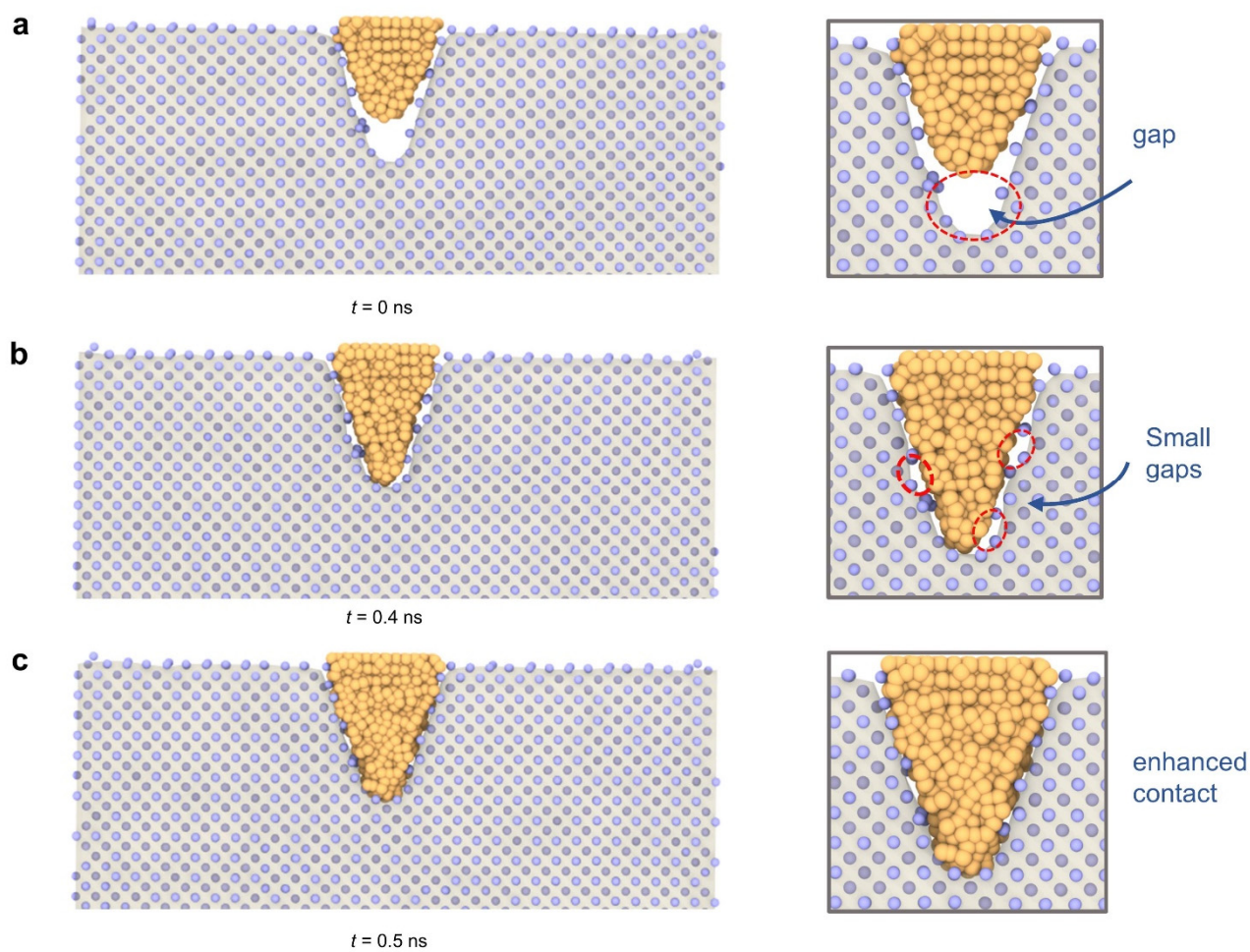
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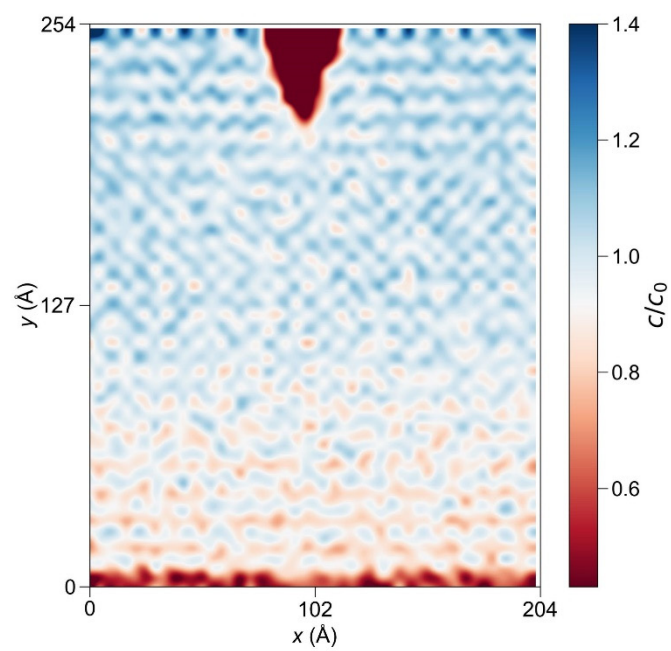
Supplementary Fig. 1 | Schematic illustration of the simulation model for the dendrite penetration in solid electrolyte.



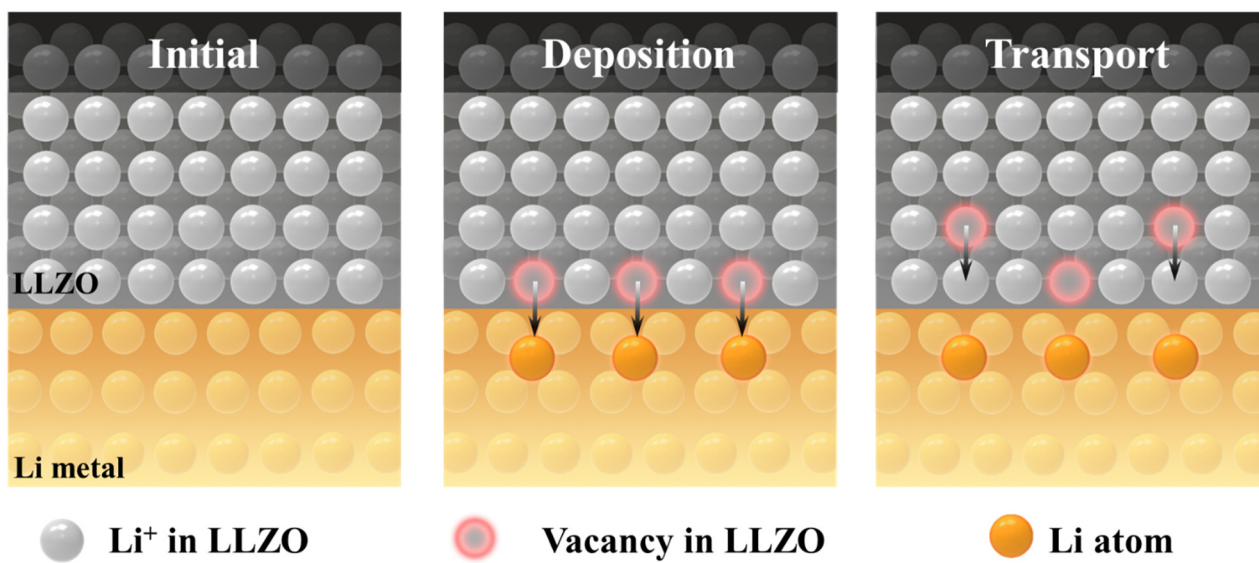
Supplementary Fig. 2 | Snapshots from the dendrite/single-crystal LLZO atomistic model at 0.65 and 0.75 ns. Yellow atoms represent lithium metal atoms. Horizontal yellow dashed lines show no change in dendrite lengths between 0.65 and 0.75 ns.



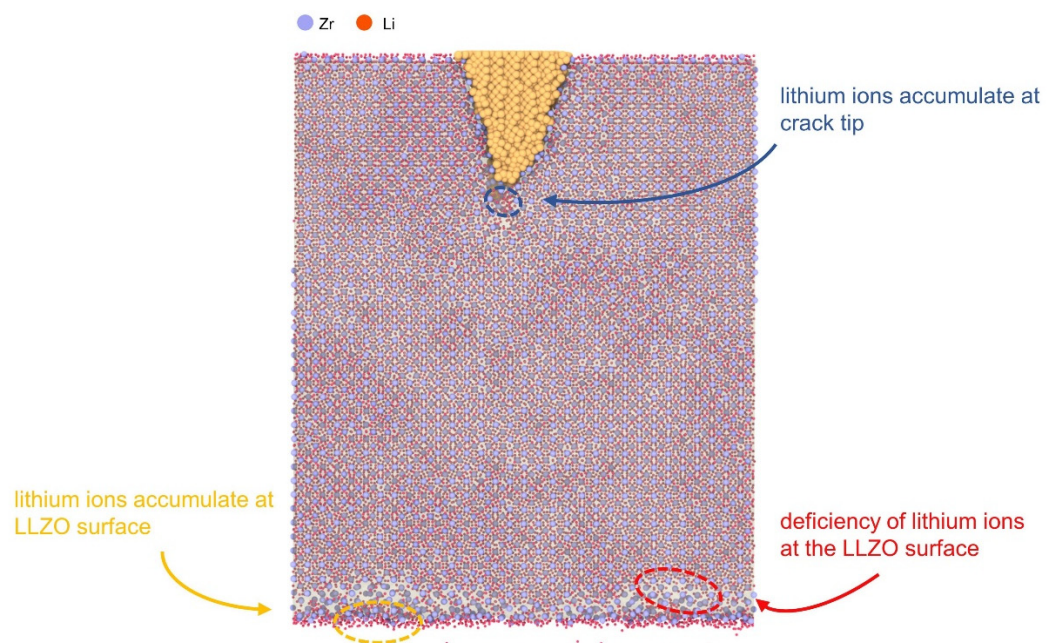
Supplementary Fig. 3 | Contact states between the dendrite and LLZO at specific time intervals: **a** $t = 0 \text{ ns}$, **b** $t = 0.4 \text{ ns}$, **c** $t = 0.5 \text{ ns}$.



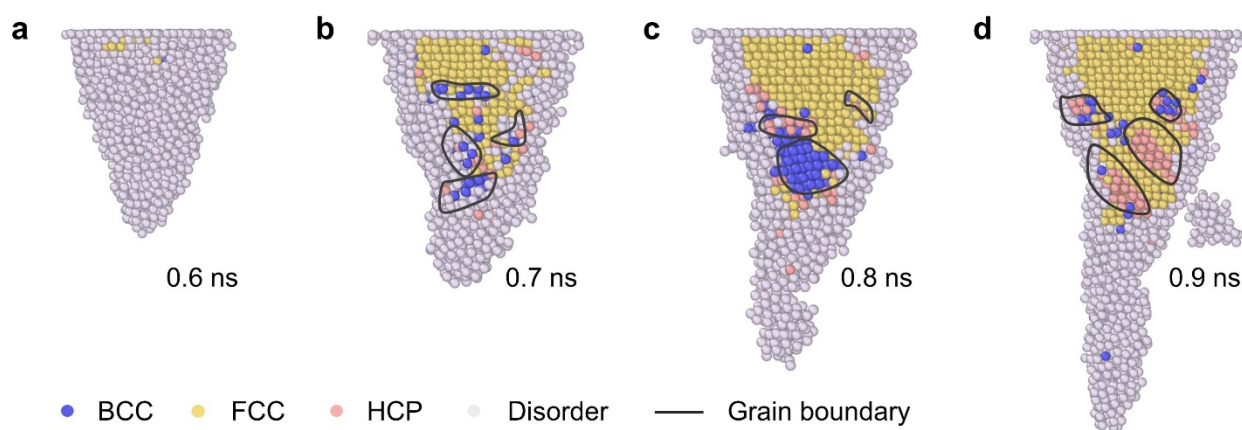
Supplementary Fig. 4 | Distribution of Li-ions concentration at 0.4 ns. The concentration distribution is not significantly different from that at 0.1 ns.



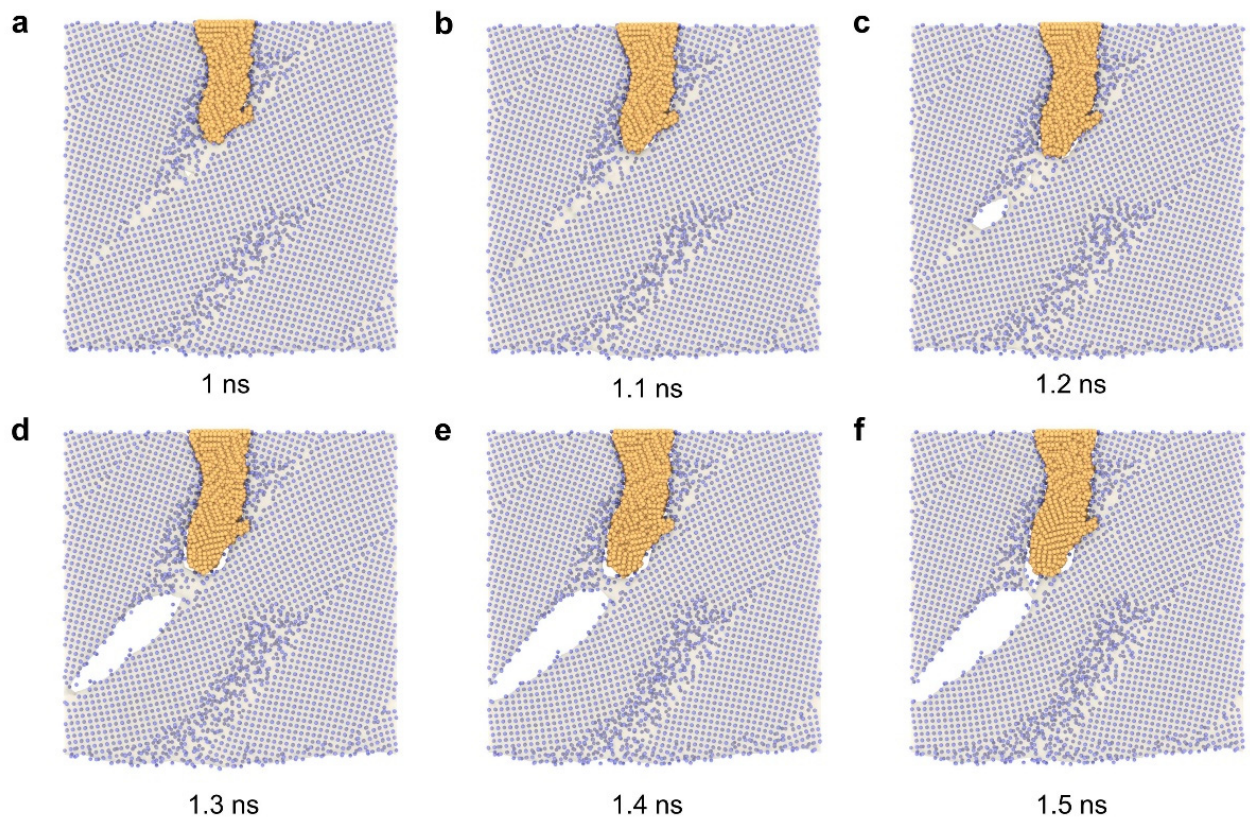
Supplementary Fig. 5 | Schematic of vacancy formation and its resulting localized stoichiometric deviation in LLZO.



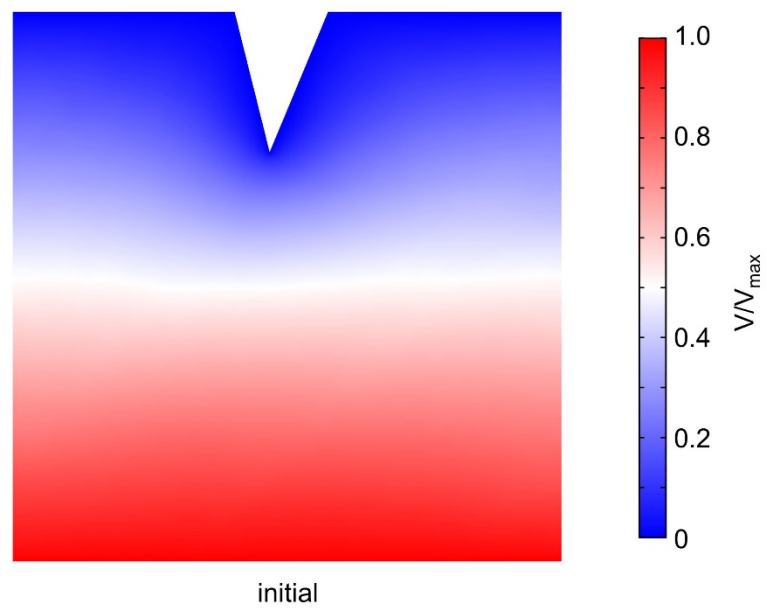
Supplementary Fig. 6 | Snapshot of the dendrite penetration at $t = 0.75$ ns.



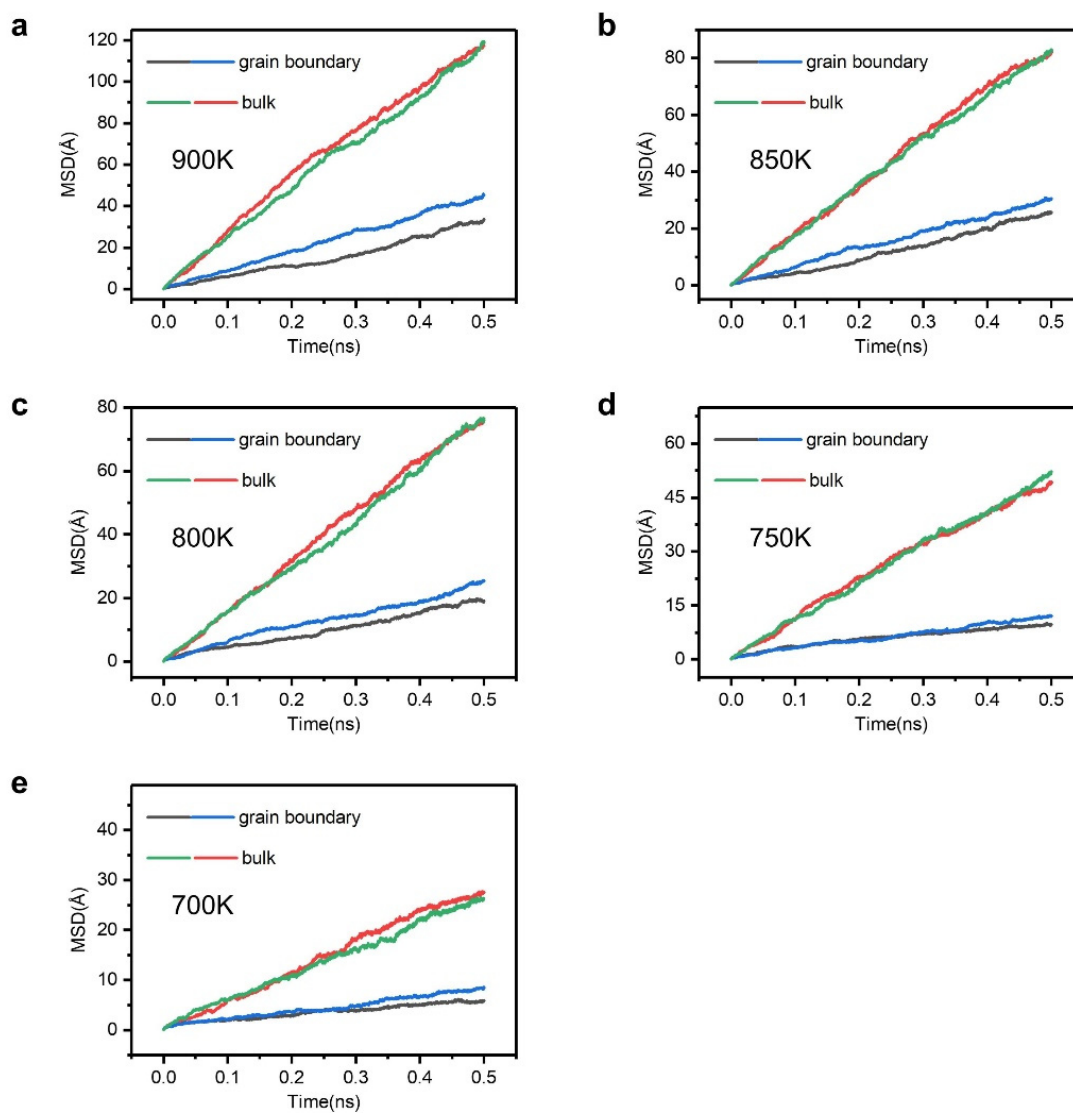
Supplementary Fig. 7 | Atomic structure of lithium metal within dendrites during deposition. There are numerous amorphous phases and grain boundaries within the dendrites.



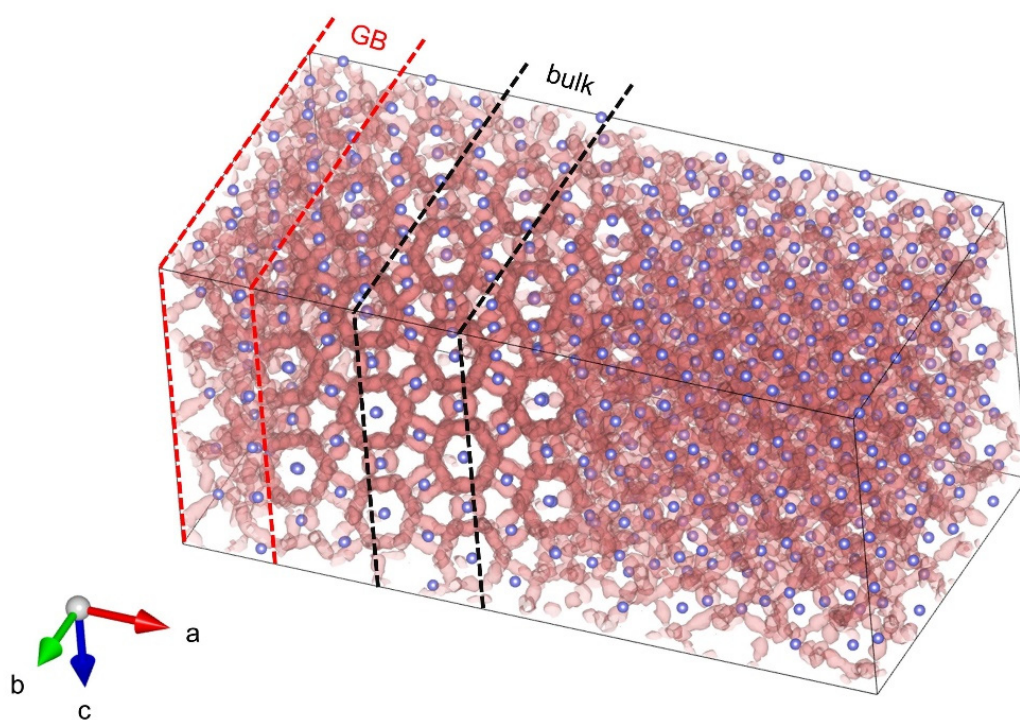
Supplementary Fig. 8 | Unstable crack growth along the grain boundary induced by lithium dendrite. The difference in rates between Li-ions deposition and crack growth causes the dendrite to lag behind the crack.



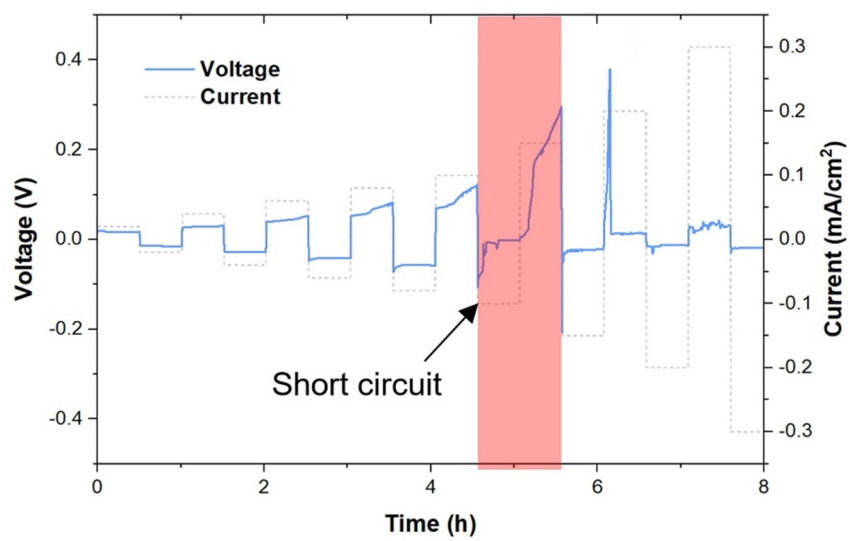
Supplementary Fig. 9 | Normalized potential distribution within the solid-state electrolyte at initial time.



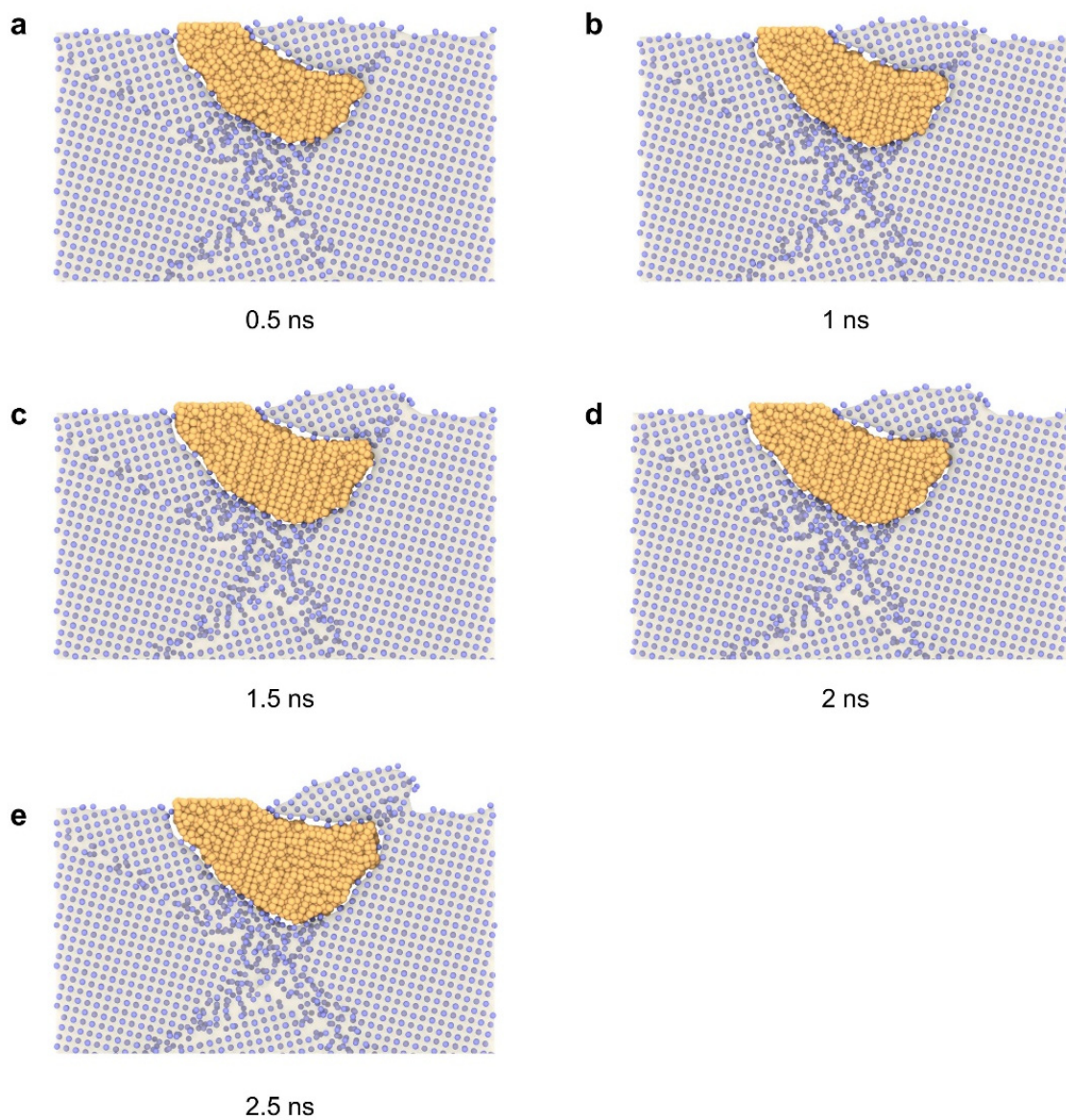
Supplementary Fig. 10 | Li-ions MSD at temperatures from 700 to 900 K versus simulation time of grain boundary and bulk



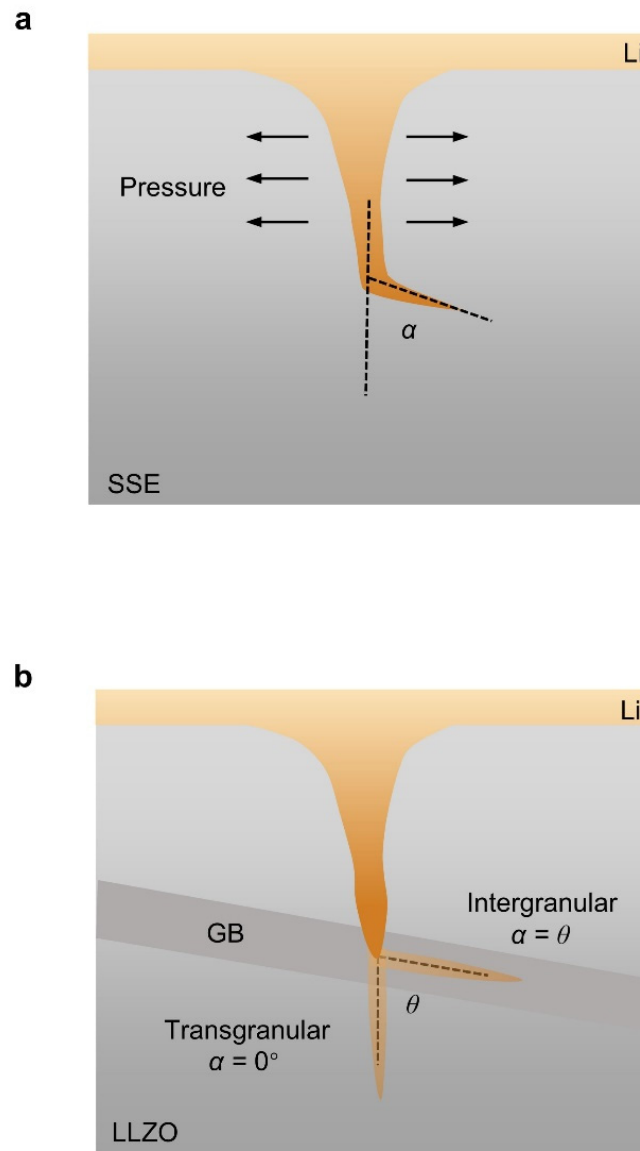
Supplementary Fig. 11 | Li-ions trajectory densities accumulated from the MD simulations for diffusion coefficients calculations. The Li-ions in the bulk phase exhibit three-dimensional diffusion behavior, while the Li-ions at the grain boundaries display more pronounced discontinuous diffusion behavior with a higher proportion of immobile Li-ions.



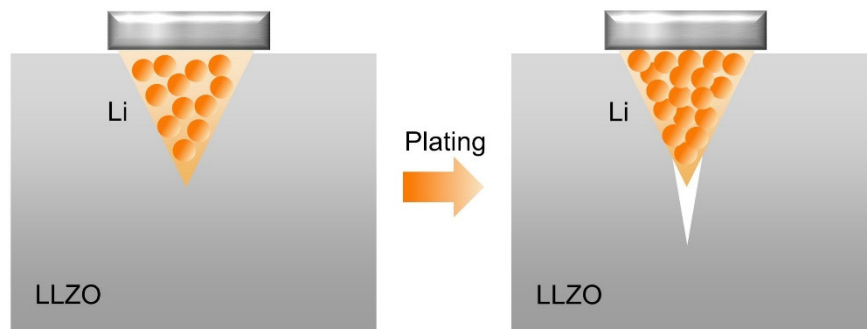
Supplementary Fig. 12 | Critical current density test on Li|LLZO|Li symmetric cell from 0.02 mA cm⁻² to 0.3 mA cm⁻².



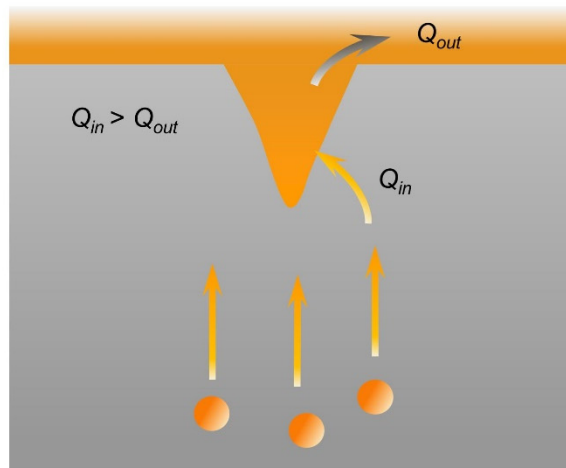
Supplementary Fig. 13 | Snapshots from simulations illustrate the atomic structures of the polycrystalline LLZO surface during peeling.



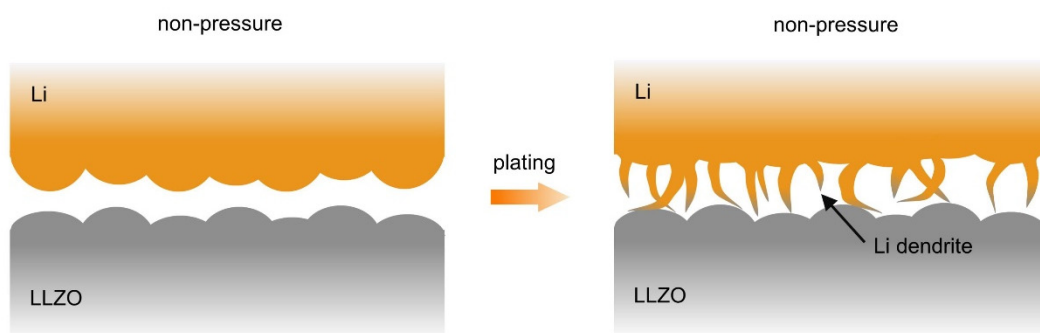
Supplementary Fig. 14 | Fracture mechanics model of dendritic penetration in solid electrolyte (a) and schematic diagram of dendrite transgranular/intergranular penetration in solid electrolyte (b).



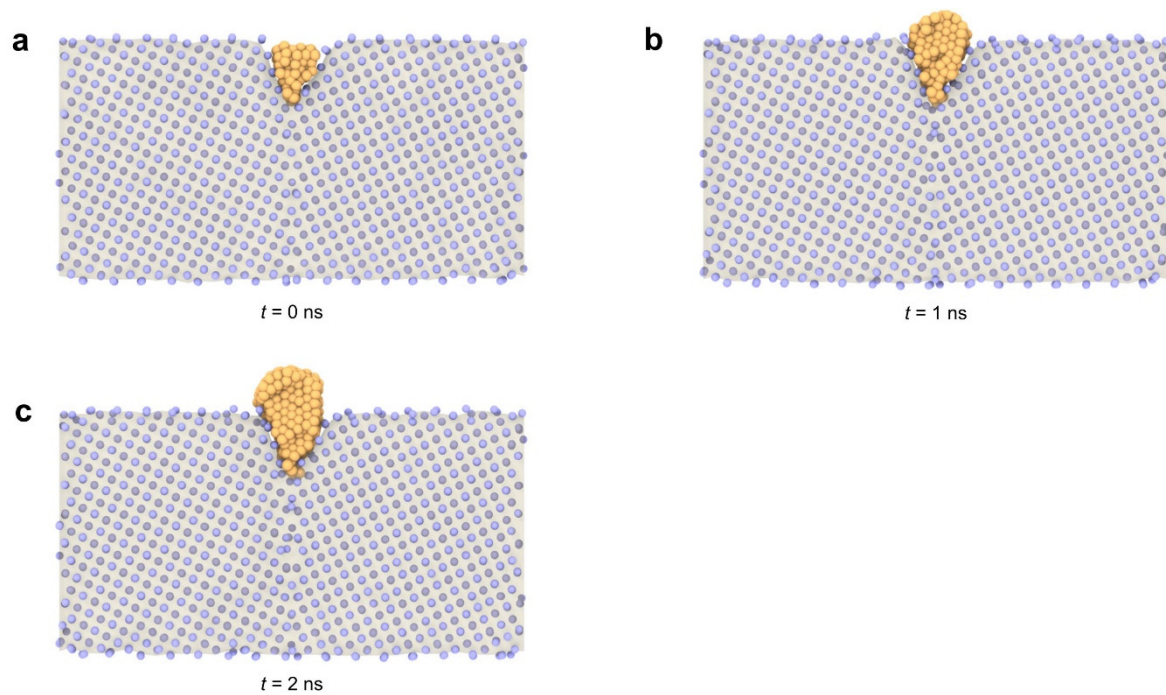
Supplementary Fig. 15 | Schematic of the model with a virtual wall adhered to the LLZO, illustrating dendrite penetration and induced crack.



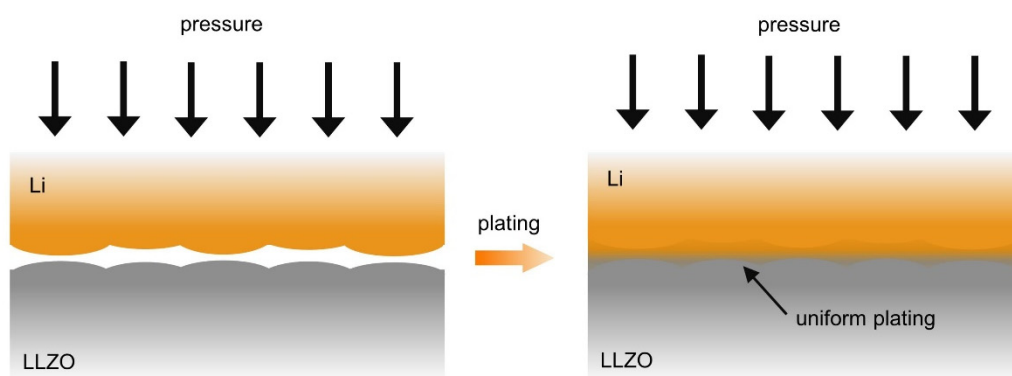
Supplementary Fig. 16 | Schematic of scenarios where the inflow rate of lithium atoms into a defect exceeds the outflow rate.



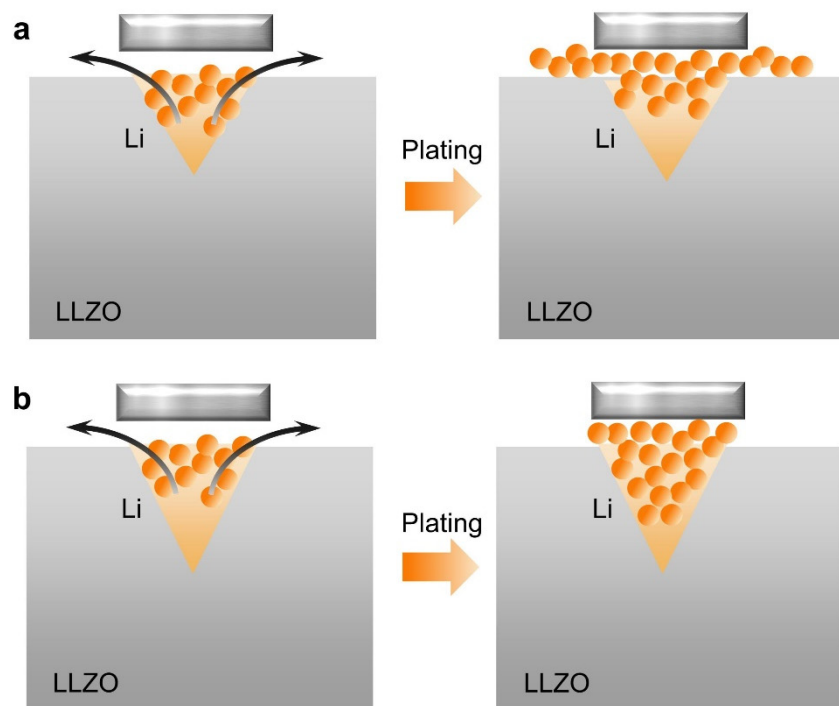
Supplementary Fig. 17 | Schematic of dendrite formation at the interface without external pressure.



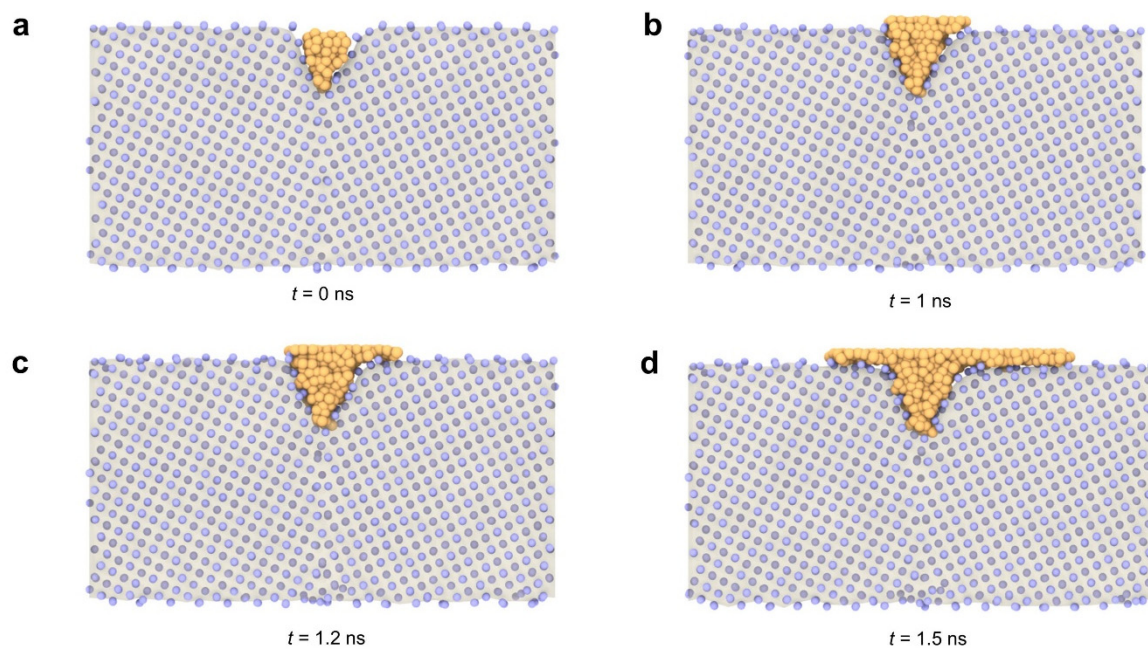
Supplementary Fig. 18 | Schematic of scenarios where the inflow rate of lithium atoms into a defect exceeds the outflow rate.



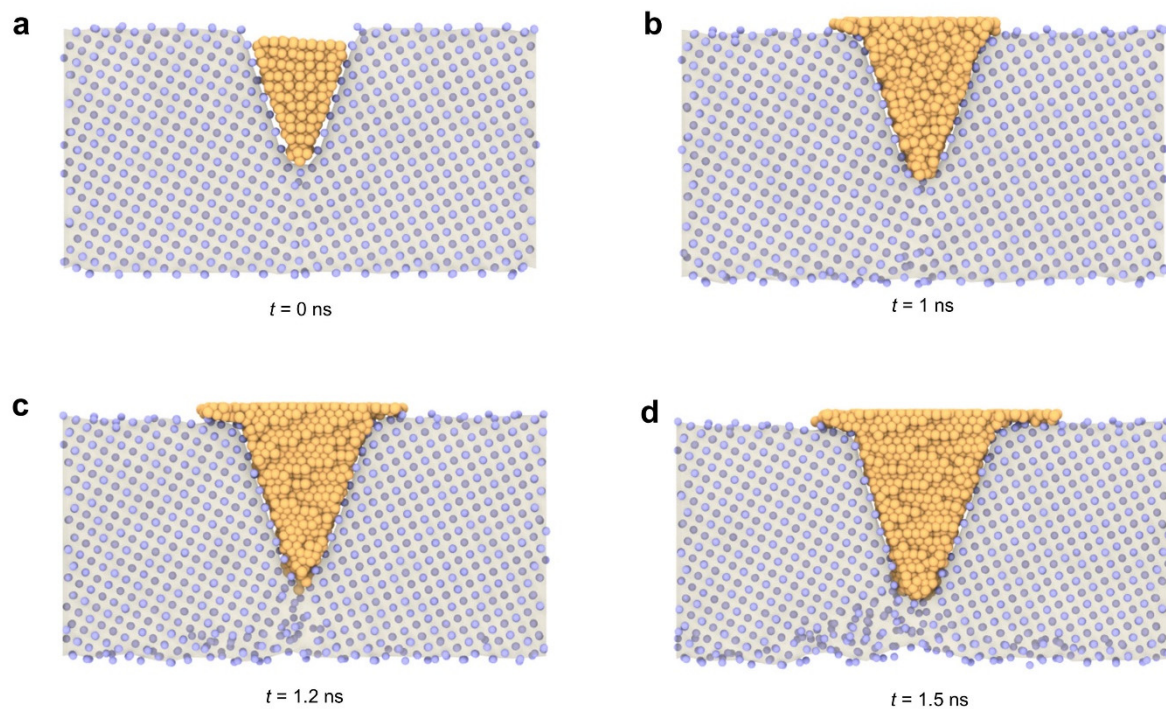
Supplementary Fig. 19 | Schematic of uniform deposition at the interface under external pressure.



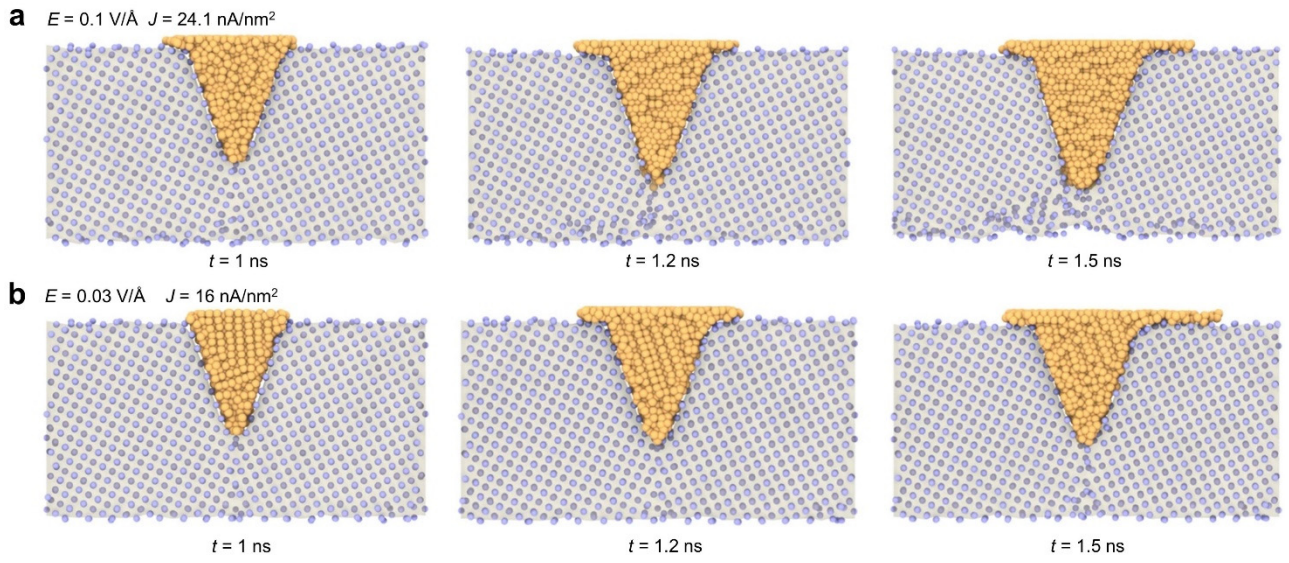
Supplementary Fig. 20 | Schematic of the model with a virtual wall placed above the LLZO, illustrating **a** uniform deposition; **b** dendrite nucleation.



Supplementary Fig. 21 | Progression of uniform deposition with a small defect size at specific time intervals: **a** $t = 0 \text{ ns}$, **b** $t = 1 \text{ ns}$, **c** $t = 1.2 \text{ ns}$, **d** $t = 1.5 \text{ ns}$.



Supplementary Fig. 22 | Progression of dendrite nucleation and growth with a large defect size at specific time intervals:
a $t = 0$ ns, **b** $t = 1$ ns, **c** $t = 1.2$ ns, **d** $t = 1.5$ ns.



Supplementary Fig. 23 | Snapshots of dendrite growth under different current densities at specific time intervals. **a** $E = 0.1 \text{ V/\AA}$, **b** $E = 0.03 \text{ V/\AA}$.

Supplementary Note 1. Details of the force field parameters.

The Buckingham–Coulomb combines the Coulombic potential to describe long-range electrostatic interactions and the Buckingham potential for short-range interactions. The formula for the Buckingham–Coulomb potential is generally expressed as:

$$U_{ij} = A \exp(-r / \rho) - \frac{C}{r^6} + \frac{q_i q_j}{4\pi\epsilon_0 r}, \quad (\text{S1})$$

where A is a pre-exponential factor representing the strength of the repulsive potential; ρ is the distance scaling factor, controlling the decay rate of the repulsive potential; C is the coefficient of the dispersion term, representing the magnitude of the attractive potential; q_i and q_j are the charges of the interacting particles; ϵ_0 is the permittivity of free space.

The parameters are taken from previous work¹, and are listed in Table. S1.

Table. S1 Buckingham–Coulomb potential parameters for LLZO

Species	q (e)	Buckingham pair interaction with oxygen		
		A (eV)	ρ (Å)	C (eVÅ ⁶)
La	2.50	2075.26	0.326	23.25
Li	1.00	1087.29	0.260	0.00
O	-1.65	4870.00	0.267	77.00
Zr	2.65	1650.32	0.311	5.10

The interactions between lithium metal atoms are modeled with the second nearest-neighbor (2NN) embedded MEAM force field. The 2NN MEAM formalism utilizes 14 independent model parameters for pure elements, categorized as follows: four parameters (E_c , r_e , B , d) are designated for the universal equation of state; seven parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$, $t^{(1)}$, $t^{(2)}$, $t^{(3)}$) are assigned to model the electron density; one parameter (A) is used for the embedding function; and two parameters ($C_{\min}$, $C_{\max}$) are for many-body screening. Specifically, E_c , r_e and B represent the cohesive energy, the nearest neighbor distance, and the bulk modulus of the reference structure, respectively. The parameters are taken from literature², and are listed in Table. S2.

Table. S2 2NN MEAM potential parameter sets for Li metal

E_c	r_e	B	d	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$\beta^{(3)}$	$t^{(1)}$	$t^{(2)}$	$t^{(3)}$	A	$C_{\min}$	$C_{\max}$
1.65	3.02	0.13	0.95	1.65	1.00	4.00	1.00	2.30	5.00	0.50	0.16	2.80	0.05

We use the Lennard-Jones (LJ) potential to describe the interactions between lithium atoms and LLZO,

of which the parameters were derived from the modified Universal Force Field (UFF) model. The Lennard-Jones (LJ) potential is expressed as follows:

$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (\text{S2})$$

where r is the distance between two atoms; ε and σ are the energy and distance constants, respectively. The corresponding parameters are listed in Table. S3.

Table. S3 LJ potential parameter sets for LLZO and Li metal

LLZO	Lithium metal	ε (eV)	σ (Å)
Li ⁺	Li	0.00108	2.18
O ²⁻	Li	0.001	2.95
Zr ⁴⁺	Li	0.11	3.7
La ³⁺	Li	0.045	3.65

Supplementary Note 2. Validation of the force field parameters.

The validations including surface energies, elastic parameters, phase change behavior, lattice constants, Li-ion diffusivity for LLZO, and the interfacial adhesion at the Li-LLZO interface.

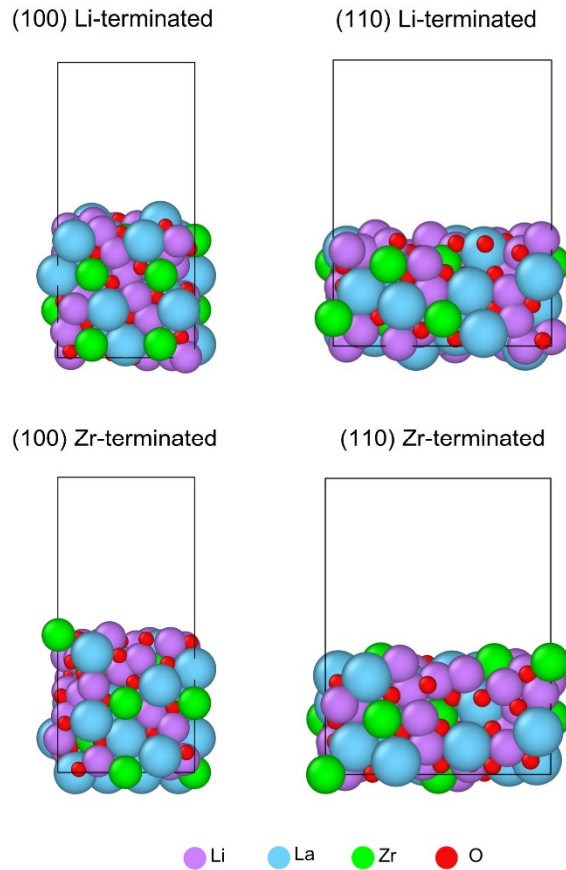
surface energies, elastic parameters:

The surface energy of LLZO are calculated according to previous work³:

$$\gamma = \frac{1}{2A} (E_{\text{slab}} - nE_{\text{bulk}} - \sum_i N_i \mu_i), \quad (\text{S3})$$

where E_{slab} is the total energy of the slab, n is the integer number of stoichiometric formula units in the slab, E_{bulk} is the energy of one formula unit of bulk LLZO, A is the cross-section area, N_i is the number of atoms of type i in the slab in excess of the stoichiometric amount, and μ_i is the chemical potential of element i .

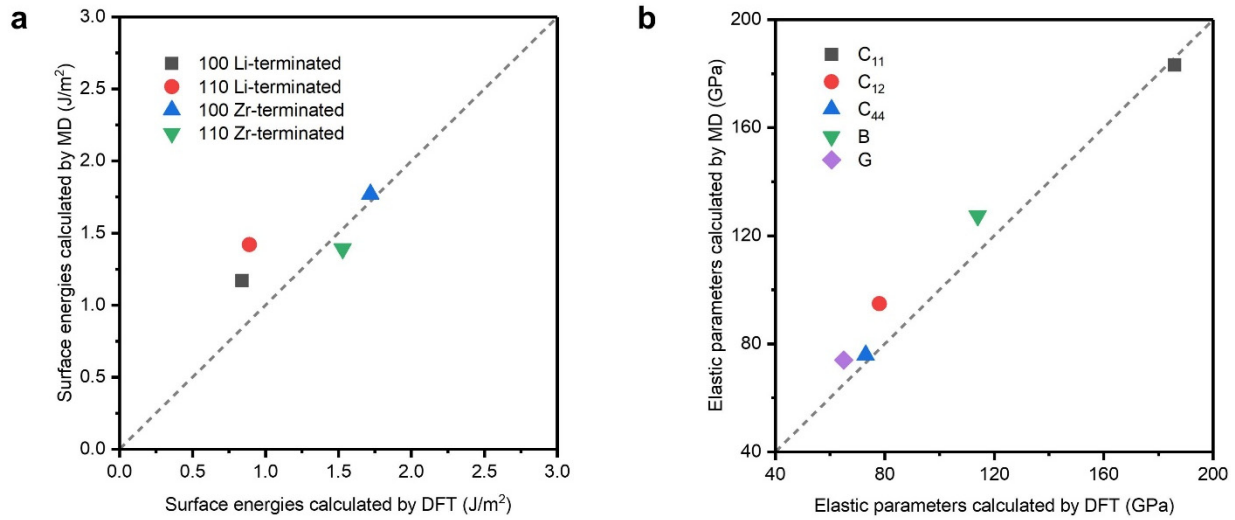
we select four typical surface models conforming to LLZO stoichiometric ratios (Supplementary Fig. 24) and compare them with DFT results. The DFT calculation settings are consistent with those in previous work³.



Supplementary Fig. 24 | Surface slab models for surface energy calculation

The surface energies calculated by MD and DFT are summarized in Supplementary Fig. 25a. Moreover, we have also compared the MD calculated elastic parameters of LLZO with the results of other DFT work

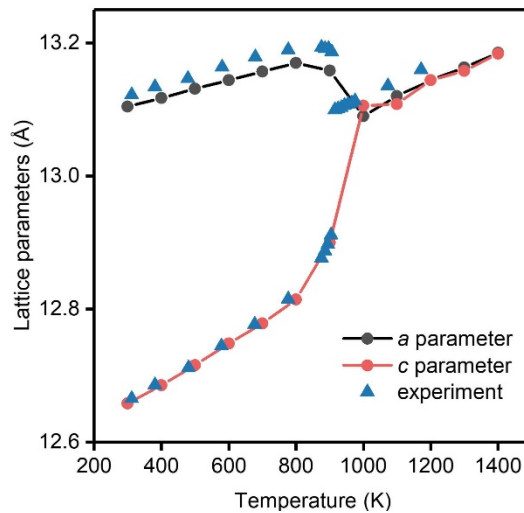
⁴, as shown in Supplementary Fig. 25b. These comparisons collectively validate the accuracy of the force field used in the manuscript.



Supplementary Fig. 25 | Comparisons of the surface energies and elastic parameters of LLZO between MD and DFT. a Comparisons of surface energies between MD and DFT calculations. b Comparisons of elastic parameters between MD calculations and DFT results from work⁴.

Phase change behavior and lattice constants:

The LLZO lattice lengths at different temperatures were determined under the NPT ensemble and compared them with experimental values⁵, as shown in the Supplementary Fig. 26. The simulation results closely match experimental data in terms of lattice parameter changes and phase transition temperature (~900 K), confirming the accuracy of the force field in describing the phase transition behavior of LLZO.



Supplementary Fig. 26 | Lattice parameters calculated by MD as a function of temperature.

Lithium ion diffusivity behavior:

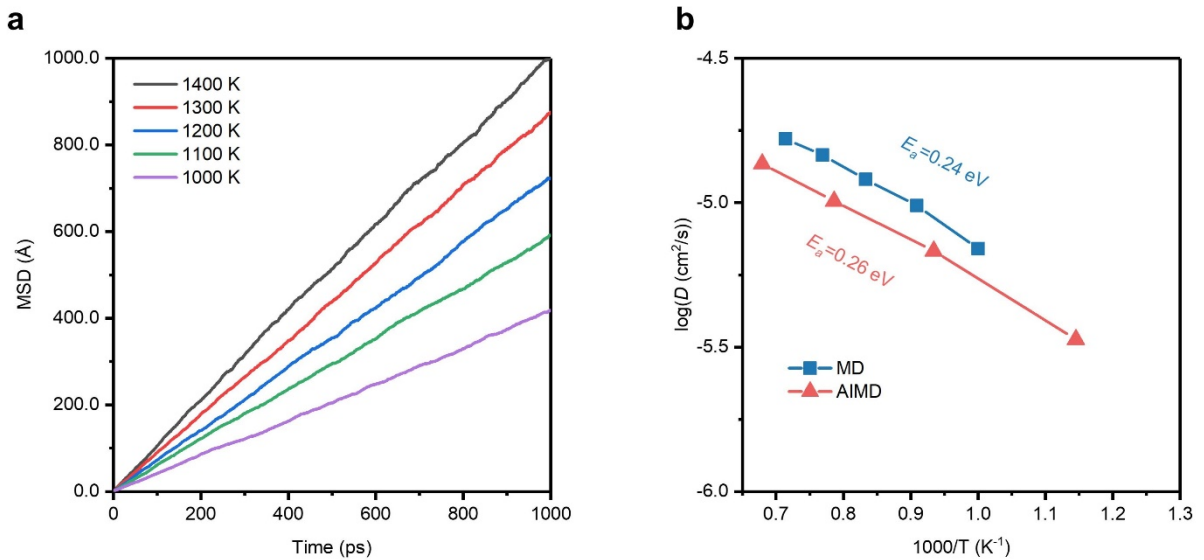
To verify the lithium ion diffusivity in bulk LLZO, we have calculated the mean square displacement (MSD) at five different temperatures (1000, 1100, 1200, 1300 and 1400 K). The MSD data is collected over a 1 ns. The diffusion coefficient is calculated from:

$$D = \frac{1}{2Nd\Delta t} \sum_{i=1}^N \left\langle \left[r_i(t + \Delta t) - r_i(t) \right]^2 \right\rangle, \quad (\text{S4})$$

where N and d refer to the total number of lithium ions and the dimensionality ($d=3$ in our system) in the system, respectively; t_0 is the initial time, and $r_i(t)$ represents the displacement of the i -th lithium ion at time t . Then, the activation energy (E_a) is calculated by fitting the Arrhenius equation:

$$D(T) = D_0 \times e^{-\frac{E_a}{k_B T}}, \quad (\text{S5})$$

where D_0 is the pre-exponential factor, and k_B is the Boltzmann constant. The MSD and diffusion coefficient results are plotted in Supplementary Fig. 27a-b. The E_a obtained by this potential is 0.24 eV, closely matching the 0.26 eV calculated by AIMD⁶, indicating that this potential accurately describes the diffusion behavior of lithium ions in LLZO.



Supplementary Fig. 27 | Validation of lithium ion diffusivity in bulk LLZO. **a** Mean square displacement at different temperatures, and **b** diffusion coefficient as a function of temperature.

Interfacial adhesion between lithium metal and LLZO:

The interfacial adhesion W between lithium metal and LLZO are calculated as:

$$W = (E_{\text{LLZO}} + E_{\text{Li}} - E_{\text{Li-LLZO}})/A, \quad (\text{S6})$$

where A is the total interface area for Li-LLZO interface, $E_{\text{Li-LLZO}}$ is the total energy of the relaxed Li-LLZO interface, E_{LLZO} and E_{Li} are the energies of the separated LLZO slab and Li metal slab, respectively. The interfacial adhesion for Li (100)-LLZO (100) interface is calculated to be 0.56 J/m², closely matching the values obtained from DFT calculations⁷, which range from 0.67 J/m² to 0.98 J/m². This comparison demonstrates that the potential can effectively predict and describe the interactions at the lithium metal/LLZO interface.

Supplementary Note 3. Test for the size effects.

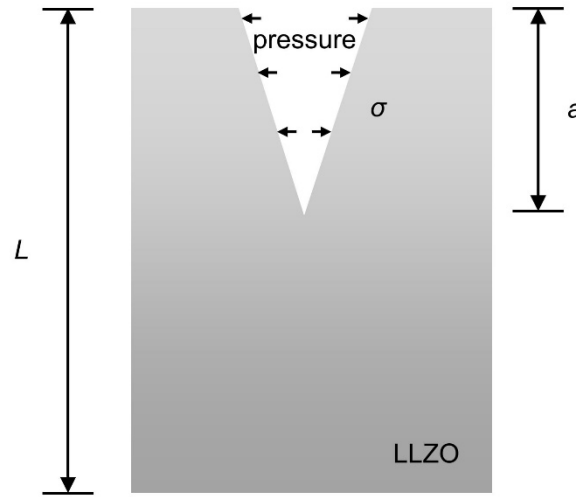
The stress variation along the length direction necessitates consideration of size effects. We use Mode I fracture toughness K_{Ic} as an indicator system size independence and explore the impact of system size on the computational results. The fracture toughness is expressed as follows:

$$K_{Ic} = Y\sigma_c\sqrt{\pi a} \quad (S7)$$

where σ_c represents the critical stress for crack propagation, a is the crack length, and Y is a dimensionless geometric factor. For the single-edge notched model used in our study, the form of Y is:

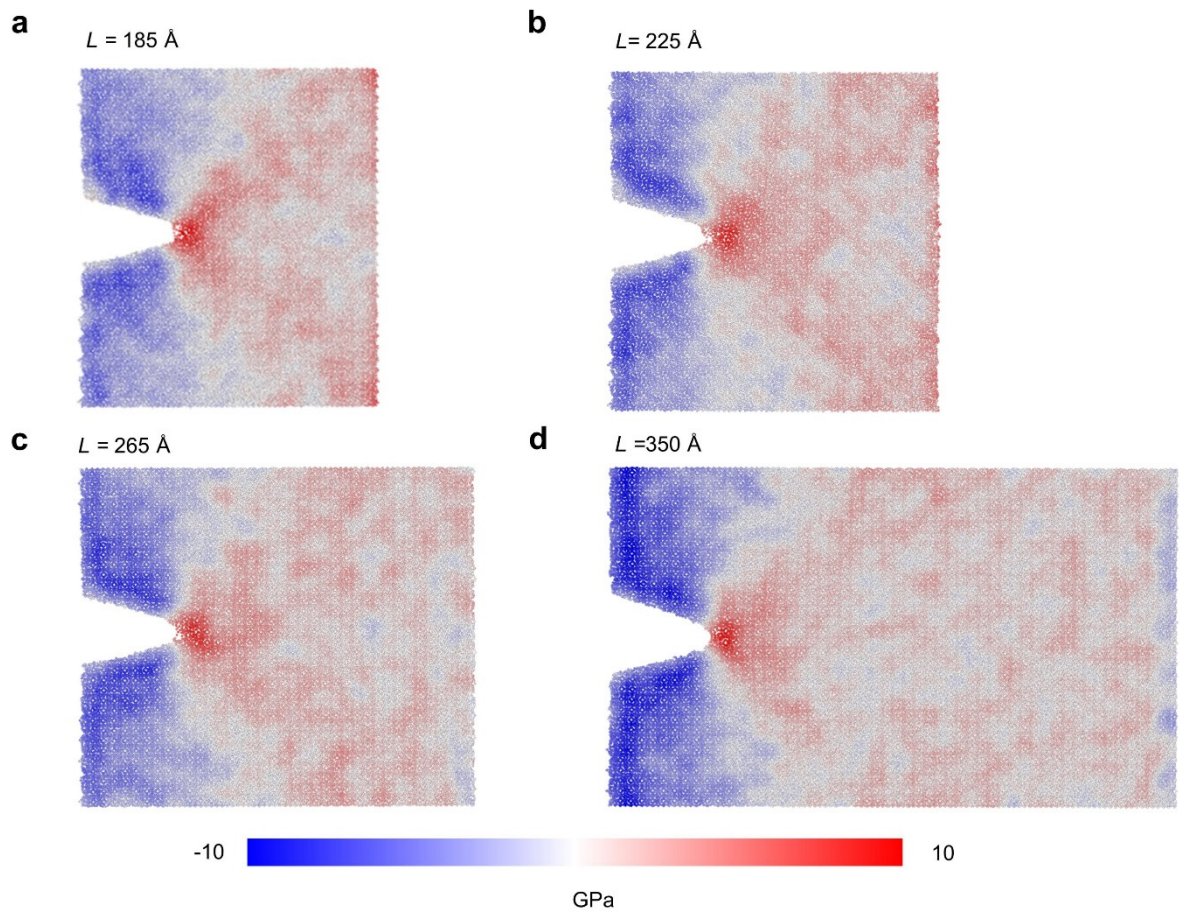
$$Y = \frac{\sqrt{2 \tan(\pi a / 2L)}}{\cos(\pi a / 2L)} \left[0.752 + 2.02 \left(\frac{a}{L} \right) + 0.37 \left(1 - \sin \frac{\pi a}{2L} \right)^3 \right] \sqrt{\frac{L}{\pi a}} \quad (S8)$$

where L is the length of the model, as shown in the Supplementary Fig. 28. To eliminate the impact of lithium ion concentration on fracture toughness, we equate the effect of dendrite growth to an applied internal pressure within the defect.



Supplementary Fig. 28 | Schematic of internal pressure loading.

Supplementary Fig. 29 compares the critical stress states at fracture in LLZO with a fixed initial crack length (a) and varying lengths (L) of 185, 225, 265, and 350 Å. The calculated K_{Ic} for different model sizes are 1.18, 1.27, 1.28, and 1.26 MPa·m^{1/2}, respectively. When the model length exceeds 225 Å, the fracture toughness K_{Ic} tend to stabilize. The current dendrite penetration simulation uses a model length of 265 Å, a size that mitigates the impact of size effects and ensures the reliability of our results.



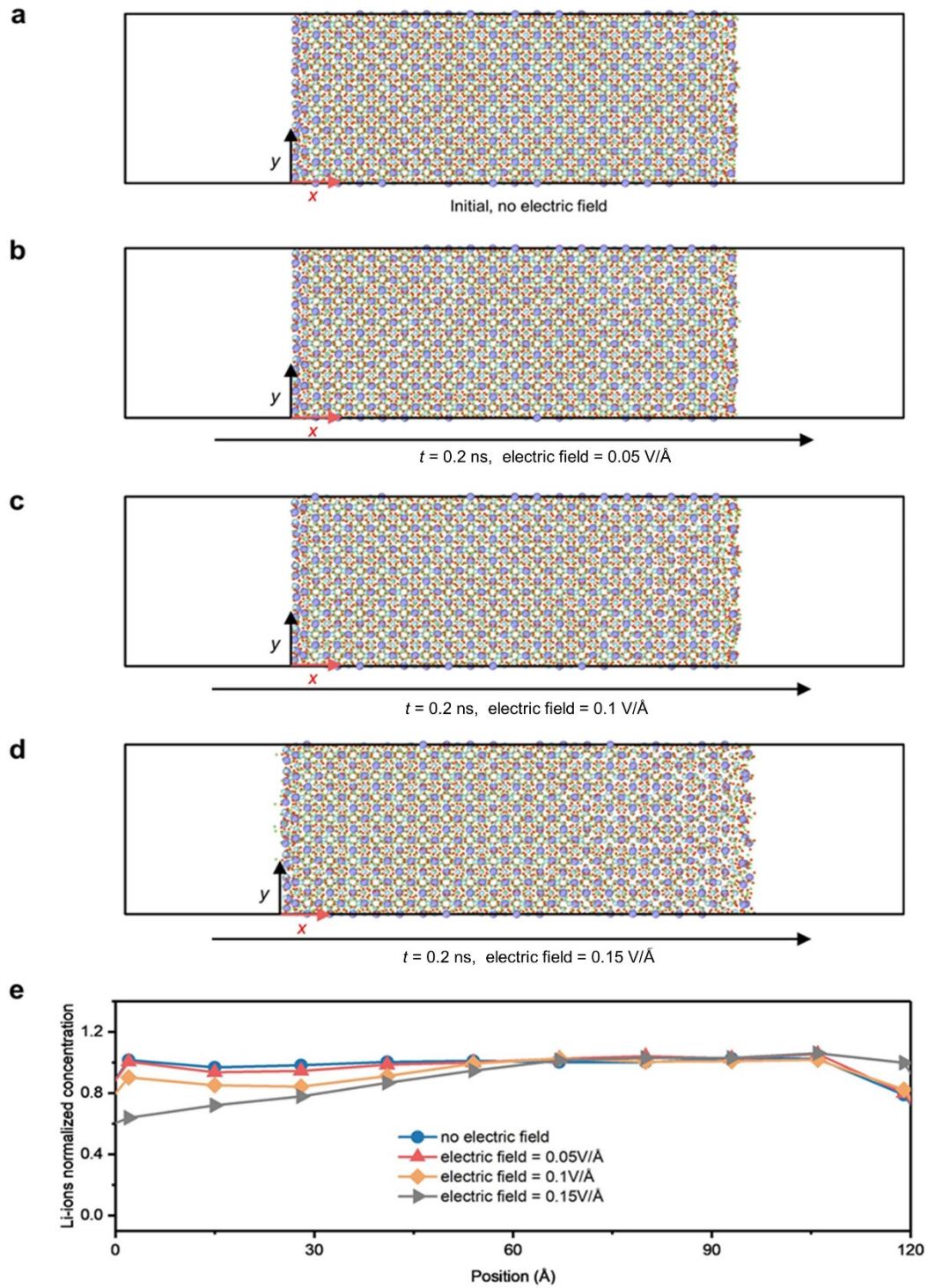
Supplementary Fig. 29 | Normal stress distribution in the LLZO under internal pressure loading with different lengths: **a** $L = 185 \text{ Å}$, **b** $L = 225 \text{ Å}$, **c** $L = 265 \text{ Å}$, **d** $L = 350 \text{ Å}$.

Supplementary Note 4. Test for the electric field strength.

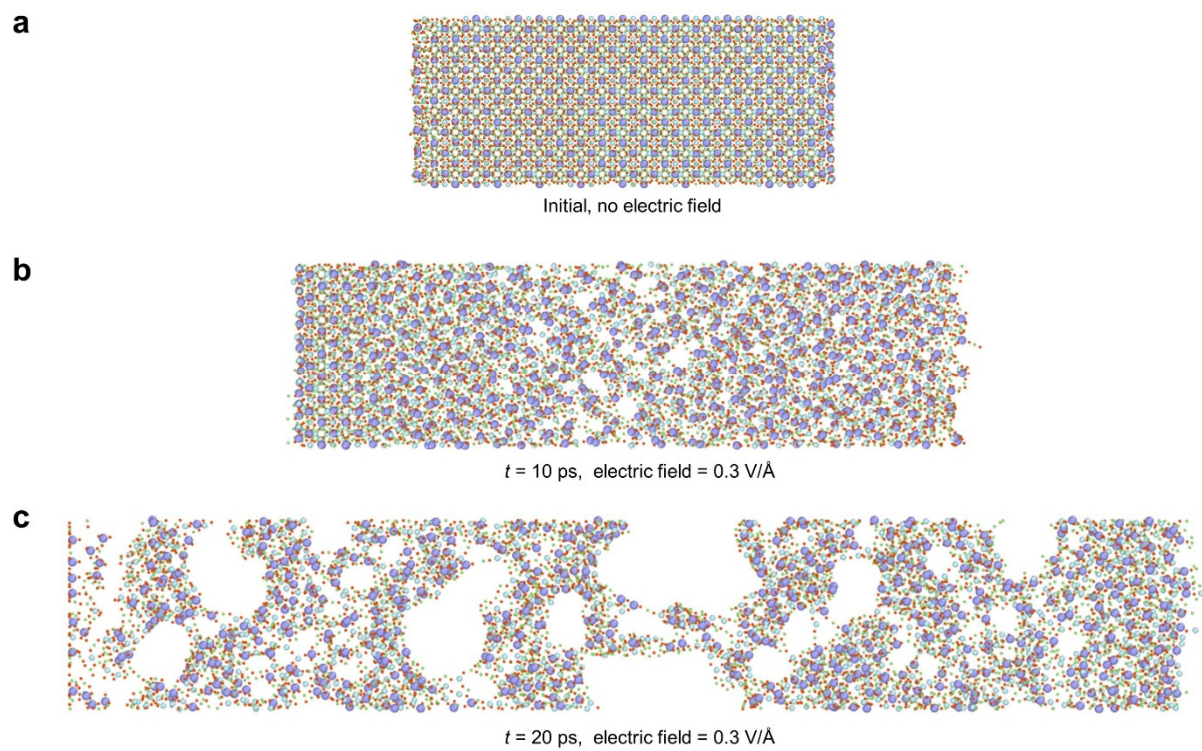
In MD simulations of the lithium battery charging process, a weak electric field may not provide sufficient driving force for ion motion, resulting in low computational efficiency. Conversely, an excessively high electric field may separate cations and anions, potentially damaging the material. For these reasons, commonly selected applied electric field ranges from 0.1 V/Å to 0.75 V/Å^{8,9}.

To justify the applied electric field, four different values are selected: 0.05V/Å, 0.1V/Å, 0.15V/Å, and 0.3V/Å. The distributions of lithium ions in LLZO under these electric fields at $t = 0.2$ ns are shown in the Supplementary Fig. 30. Under an electric field of 0.05V/Å (see Supplementary Fig. 30b and Supplementary Fig. 30e), the distribution of lithium ions shows little change compared to the condition without an electric field. When the electric field exceeds 0.1V/Å (see Supplementary Fig. 30c-e), lithium ions visibly move toward the counter electrode under the influence of the electric field. When the electric field reaches 0.3V/Å, LLZO fails to maintain its original lattice structure within 20ps (see Supplementary Fig. 31a-c).

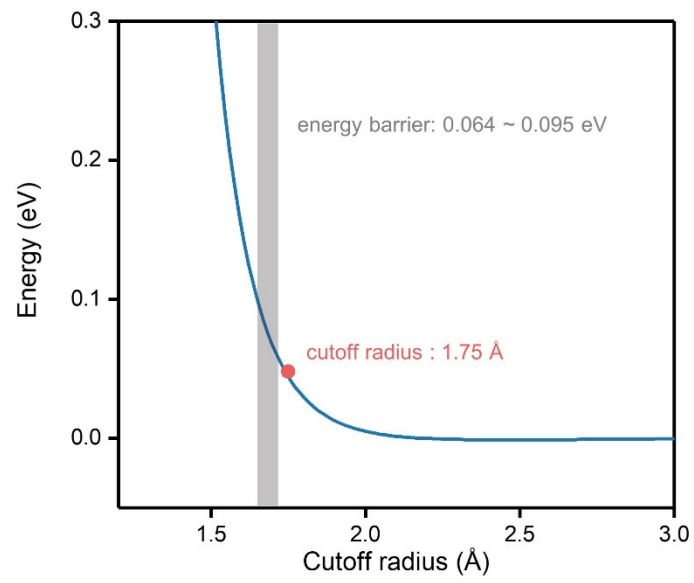
Based on the discussion above, an electric field of 0.1V/Å is selected. This value provides an optimal balance between computational efficiency and structural integrity.



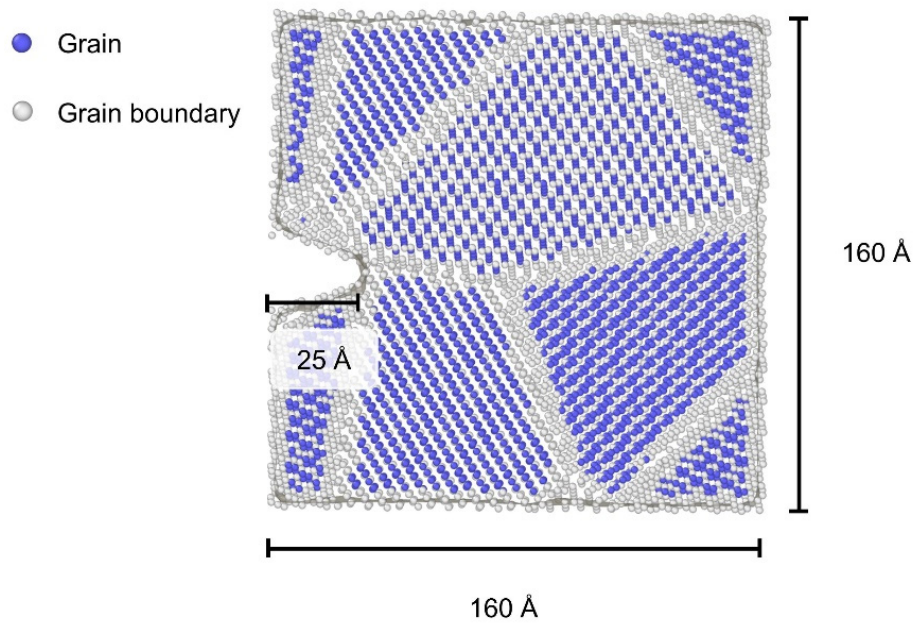
Supplementary Fig. 30 | Snapshots and lithium ion distributions of LLZO under different electric fields: **a** no electric field, **b** 0.05 V/Å, **c** 0.1 V/Å, **d** 0.15 V/Å, **e** lithium ion distributions at $t = 0.2$ ns under different electric fields.



Supplementary Fig. 31 | The response of LLZO under electric field strength of $0.3 \text{ V/\AA}$. **a** no electric field, **b** $t = 10$ ps, **c** $t = 20$ ps.

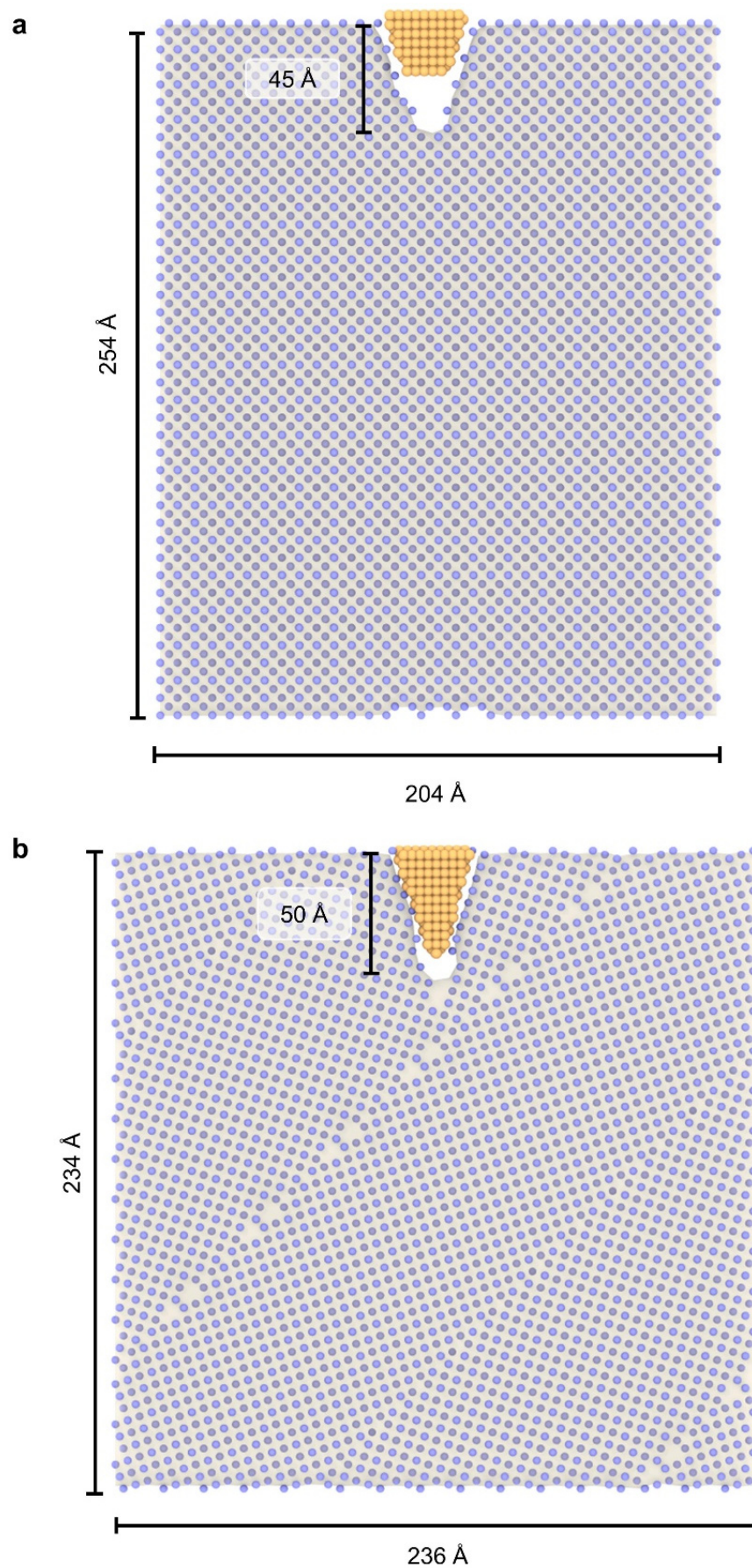


Supplementary Fig. 32 | Relationship between lithium deposition energy barrier and cutoff radius.

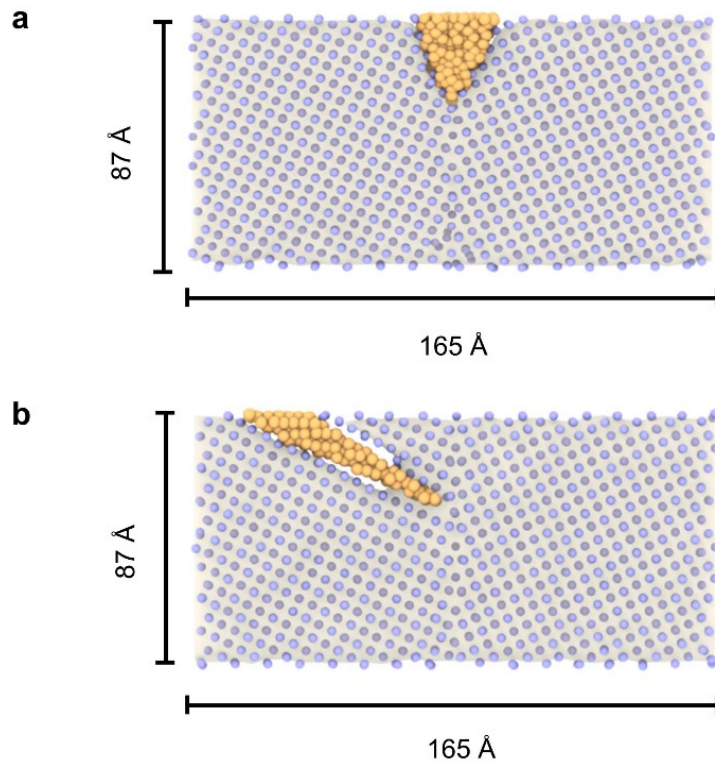


Supplementary Fig. 34 | Random grain boundaries model for calculating Mode I fracture toughness K_{Ic}^{gen} of LLZO.

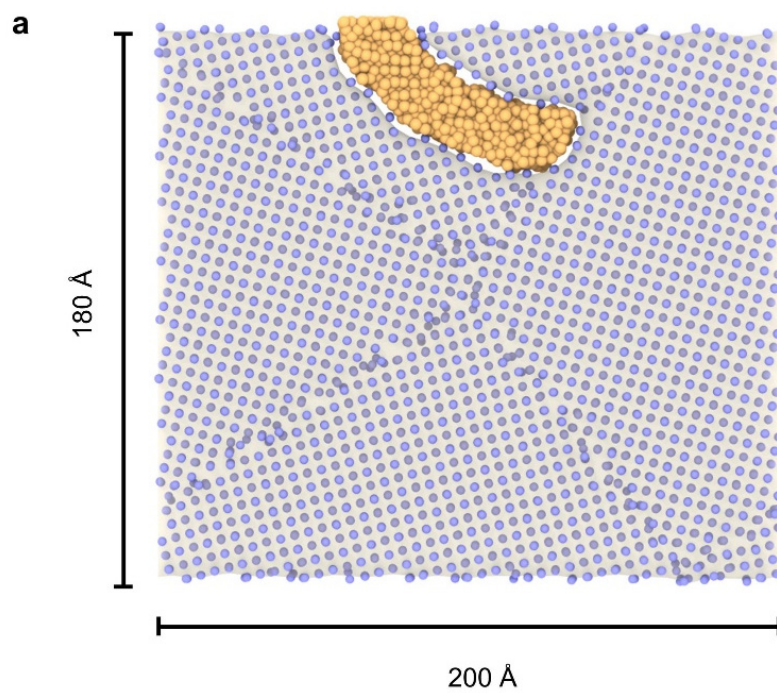
This parameter is used to plot Fig. 7d.



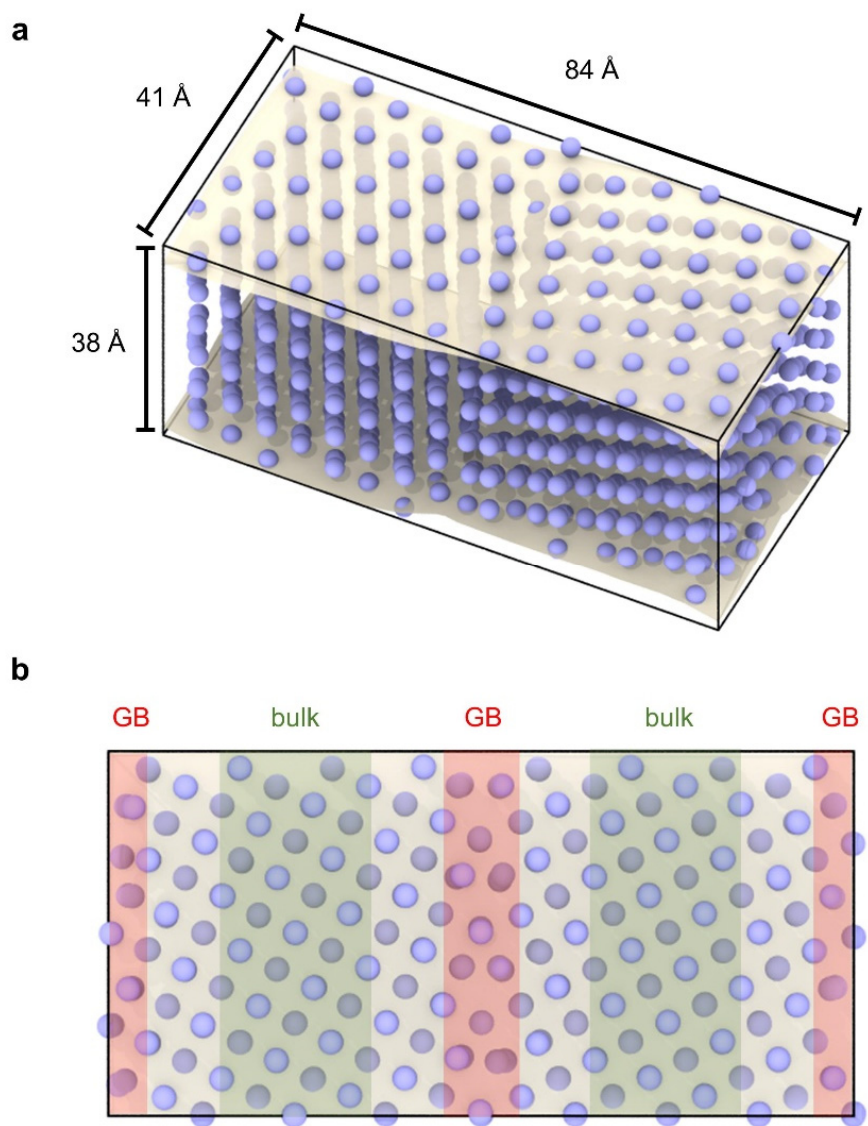
Supplementary Fig. 35 | Simulation models for dendrite penetration in single-crystal LLZO (a) and polycrystalline LLZO (b).



Supplementary Fig. 36 | Simulation models with dendrite at angle of incidence 0° (a) and 60° (b) to the grain boundary.



Supplementary Fig. 37 | Simulation model for dendrite induced surface peeling. The grain boundaries are random.



Supplementary Fig. 38 | Atomistic model for calculating the diffusion coefficients of bulk and $\Sigma 5(310)$ grain boundary. The region corresponding to the grain boundary accounted for 20% of the solid electrolyte volume.

Supplementary References

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