

Ion diffusions driven by dynamic lattice deformations in perovskite solid electrolyte

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Abstract

Solid electrolyte (SE) is a crucial component of all-solid-state batteries. Development of SE with high ion conductivity needs an in-depth understanding of ion diffusion mechanisms. Recently, the influence of lattice dynamics on ion diffusion in Li-ion conductors has attracted widespread attention. In this study, we intensively investigated the ion diffusion mechanism in $\text{Li}_x\text{La}_{(2-x)/3}\text{TiO}_3$ perovskite by means of highly efficient machine learning-based molecular dynamics simulations. We revealed that dynamic lattice deformation can trigger ion hopping, while local distortions of TiO_6 octahedra adversely affect long-range ion diffusion. Based on the acquired design principles, a new model was constructed, which exhibits an encouragingly high ion conductivity for perovskite SE. Besides, a new concerted diffusion mechanism with lattice deformation as medium has been uncovered. This study provides a new mechanism demonstrating how lattice dynamics contributes to the ion diffusion, potentially paving the way for developing high-performance SEs.

1. Introduction

All-solid-state batteries (ASSBs) utilizing inorganic solid electrolytes (SEs) hold high promise as the next-generation battery systems owing to their enhanced safety and energy density compared to conventional Li-ion batteries that rely on organic liquid electrolytes.^{1,2} The performance of ASSBs is heavily dependent on the quality of the SEs. Understanding the ion diffusion mechanisms in these materials is indispensable for designing SEs with high ion conductivity. To this end, numerous studies have been carried out to reveal the ion transport behavior in SEs.^{3–14} Notably, the atomistic structures of SEs plays a crucial role in determining the hopping site, and diffusion pathways. For instance, Wang *et al.* and Jun *et al.* proposed that body-centered cubic-like anion frameworks in sulfide SEs and corner-sharing frameworks in oxide SEs facilitate the efficient movement of Li ions, resulting in high ionic conductivity.^{5,6}

In addition to the atomistic structure, the dynamics of anion units are believed significantly influence ion diffusion. One exemplary case is the paddlewheel effect, which arises from the the rotational mobility of anions and is associated with enhanced ionic conductivity in borohydrides and *closo*-boranes SEs.^{8,15–17} Recently, Smith *et al.* proposed a low-temperature paddlewheel effect in glassy sulfide materials, which contributes substantially to their high conductivity.^{9,10} Conversely, Xu *et al.* reported that the Li-ion transport is driven by anharmonic coupling between low-frequency Li phonon modes and high-frequency anion modes instead of low-frequency rotational modes of anions.¹⁸ On the other hand, there are a series of important SEs possessing crystal structures with ordered lattice frameworks, including $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ ¹⁹, garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ²⁰ and family of perovskite Li-ion conductors^{21,22}. The dynamics of lattice frameworks are expected to have a significant, yet poorly understood, impact on Li-ion diffusion in these materials.

Perovskite materials with the general formula $\text{Li}_x\text{A}_y\text{BO}_3$ represent an important family of SEs. Among them, $\text{Li}_x\text{La}_{(2-x)/3}\text{TiO}_3$ (LLTO)^{21,23–25} has garnered significant attention due to its high ionic conductivity (10^{-4} - 10^{-3} S/cm). Extensive studies have investigated Li-ion diffusion in both bulk and grain boundaries of LLTO^{26–29}. Furthermore, the relatively simple crystal structure of LLTO makes it an ideal material for exploring the relationship between lattice dynamics and ion diffusion. A schematic illustration of the LLTO structure was shown in Fig. 1a. Experimentally, La ions at the A-sites are observed to alternatively distribute into the La-rich and La-poor layers. When Li concentration is low ($x < 0.3$), the occupancy of A site in the La-rich layer exceeds 90%.^{30–35} As the Li concentration increases ($x \geq 0.3$), the La occupations

in rich and poor layers become more uniform.^{32,34–39} Despite extensive investigations, the precise locations of Li ions in LLTO remain controversial. Some studies reported that the Li ion occupy the center of O4 square window (Fig. 1b),^{30,31,35,40} while others proposed that Li ion reside in the off-center positions and near the A-site (Fig. 1c).^{35,38,41,42} Moreover, for the Li-ion diffusion pathway, several studies have reported that Li ions move by hopping between neighboring O4 center sites in LLTO.^{31,43,44}

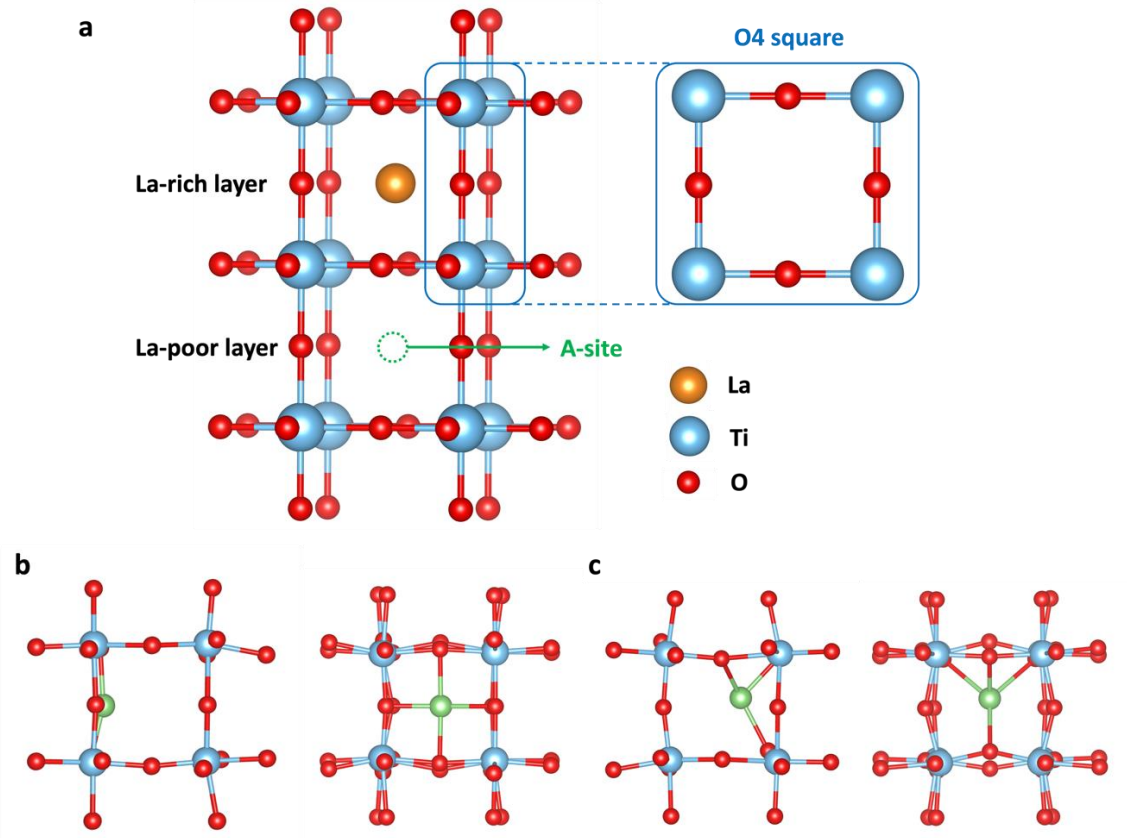


Fig. 1 (a) Schematic illustration of the LLTO structure. Especially, La ions distributed into the La-rich and La-poor layers. The A-site, located at the center of the Ti-O cube is indicated by the dashed circle, while the O4 square, which forms the edge of the cube, is outlined by a blue line. (b, c) Side and top views of Li occupying at (b) the site of O4 center and (c) the distorted site.

It is noteworthy that, in ABO_3 perovskites, deformations of BO_6 octahedra have been observed, which are driven by several factors. A small ionic radius at the A-site (Goldschmidt tolerance factor < 1) can lead to the tilting of the BO_6 octahedra. Besides, the second-order Jahn-Teller effect, induced by d^0 transition metals at the B-site, which contributes to an off-center displacement of B-site cation.⁴⁵ The octahedral tilting results in frustrated deformations

of the BO_6 octahedra and complex structural features, such as incommensurately modulated structures, as reported in studies on $\text{Li}_x\text{Nd}_{(2-x)/3}\text{TiO}_3$.^{46,47} Furthermore, Varez *et al.* observed significant thermal vibrations of oxygen atoms in LLTO, which may induce oscillations of TiO_6 octahedra and facilitate the Li-ion mobility.³⁹ They further investigated Al-doped LLTO and found that fluctuations of BO_6 octahedra influence the long-range diffusion of Li ions.⁴⁸ Recently, Kim *et al.* investigated the relationship between La occupancy and bottleneck size formed by four oxygen atoms, further affecting the Li-ion transport.⁴⁹ These findings highlight the critical role of lattice dynamics in facilitating ion diffusion in LLTO.

Theoretical simulations of solid electrolytes offer a powerful tool to reveal the nanoscopic mechanism of Li diffusion in these materials. For instance, Symington *et al.* reported that the significant structural alterations induce the high resistance for Li diffusion at grain boundary based on the molecular dynamics (MD) simulations.⁵⁰ In this study, we conducted an in-depth investigation of Li-ion diffusion behavior in LLTO perovskite SE by means of long-timescale MD simulation enabled by on-the-fly machine learning potentials, aiming to reveal the intrinsic relationship between the dynamics of lattice deformation and ion diffusion. Our results revealed that transitions of tilt modes in TiO_6 octahedra induce the deformation of O4 square thereby facilitating Li-ion hopping. On the contrary, large octahedral distortions hinder long-range ion diffusions. Furthermore, based on established principles for fast ion conductors, we designed a new LLTO model with a significantly improved ionic conductivity at 300 K ($\sigma_{300\text{K}} = 6.83 \text{ mS/cm}$) compared to the low-energy model ($\sigma_{300\text{K}} = 2.29 \text{ mS/cm}$). This improvement is attributed to a newly identified concerted diffusion mechanism, termed “ion-lattice-ion concerted diffusion”. The Nanoscopic diffusion mechanisms uncovered in this work underscore the critical role of lattice dynamics in Li-ion transport.

2. Methods

Two LLTO models with Li concentrations of 0.125 and 0.219 were constructed using $4 \times 4 \times 2$ supercells, each with lattice length exceeding 15 Å. Following experimental observations of La distribution, which indicates that La tend to concentrate in the La-rich layer when $x < 0.3$,³⁵ the La and Li ions were distributed accordingly in each layer in the built models (See Table S1). For each concentration, 40 structures were generated, in which La and Li ions were assigned based on the experimentally observed distributions. These structures were subjected to geometric optimization. The structure with the lowest energy was selected for subsequent MD simulations.

Density functional theory (DFT) method were performed using the Vienna ab initio simulation package (VASP)⁵¹. Electron-ion interactions were described with projector-augmented wave pseudopotentials⁵² and the The Perdew, Burke, and Ernzerhof functional for solids (PBEsol)⁵³ within the generalized gradient approximation⁵⁴ was employed. Compared to the PBE functional⁵⁵, PBEsol provides lattice parameters for LLTO that more closely match experimental values (See Table S2). The Hubbard U value for Ti 3d electrons was not considered as it can be reasonably neglected for early-transition metals.^{29,44,56–58} A plane-wave kinetic-energy cutoff of 600 eV and a k-spacing of 0.25 Å⁻¹ in reciprocal space were used to ensure reliable results. Long-timescale MD simulations were conducted using on-the-fly MLPs⁵⁹ realized in VASP.6, which have been validated for various applications such as calculations of melting points⁵⁹, and simulations of phase transitions in hybrid perovskites⁶⁰. To balance computational efficiency and accuracy, the energy cutoff was reduced to 400 eV and only Γ point was used in the MD simulations. The canonical ensemble (NVT) using the Nosé-Hoover thermostat was chosen. Each simulation spanned 2 ns with a timestep of 2 fs. The temperatures of 300, 400, 500, 600, 700 and 800 K were adopted in the simulations.

The mean squared displacements (MSD) were calculated based on the following equations

$$MSD = \frac{1}{N} \sum_{i=1}^N \langle [r_i(t + t_0) - r_i(t_0)]^2 \rangle \quad (1)$$

where N represents the total number of Li ions. t_0 is the initial time, and $r_i(t)$ represents the displacement of the i -th Li-ion at time t . The self-diffusivities of Li ions (D) were calculated from the time average MSD over a time t using the following equation:

$$D = \frac{MSD}{2dt}, \quad (2)$$

where d represent the dimensionality in the system. It is noteworthy that our previous work has systematically classify the several different type of ion diffusivities.⁶¹ The “self-diffusivity” which also called tracer diffusivity is a more precise terminology in the simulation. The MSD profiles with the time range of 200-1000 ps were used here to calculated the self-diffusivities. Here the activation energy (E_a) is evaluated according to the Arrhenius formula:

$$D(T) = D_0 \times e^{-\frac{E_a}{k_B T}}. \quad (3)$$

where D_0 is the pre-exponential factor, and k_B is the Boltzmann constant. The Li-ion conductivity at specific temperature [$\sigma(T)$] is calculated using Nernst-Einstein equation,

$$\sigma(T) = \frac{e^2 C}{k_B T} D(T) \quad (4)$$

where e is the elementary charge. C indicates the Li⁺ number concentration.

To evaluate the accuracy of the machine learning potentials (MLPs) employed in this study, a series of validation tests were conducted. A total of 100 snapshot structures were uniformly sampled from the 100-2000 ps timeframe of the MD simulations of model-I and model-II. These structures were subsequently analyzed using both DFT and MLP methods. Energy and atomic force comparison plots between the two methods are presented in Figure S1. The mean absolute errors (MAEs) for the energies between DFT and MLP were found to be less than 1 meV/atom, and the MAEs for atomic forces were consistently below 0.12 eV/Å. These errors are minimal and align well with previously reported results for SEs studied using MLPs.²⁹ Therefore, the MLPs are demonstrated to possess sufficient accuracy for their application in the MD simulations of LLTO.

3. Results and discussion

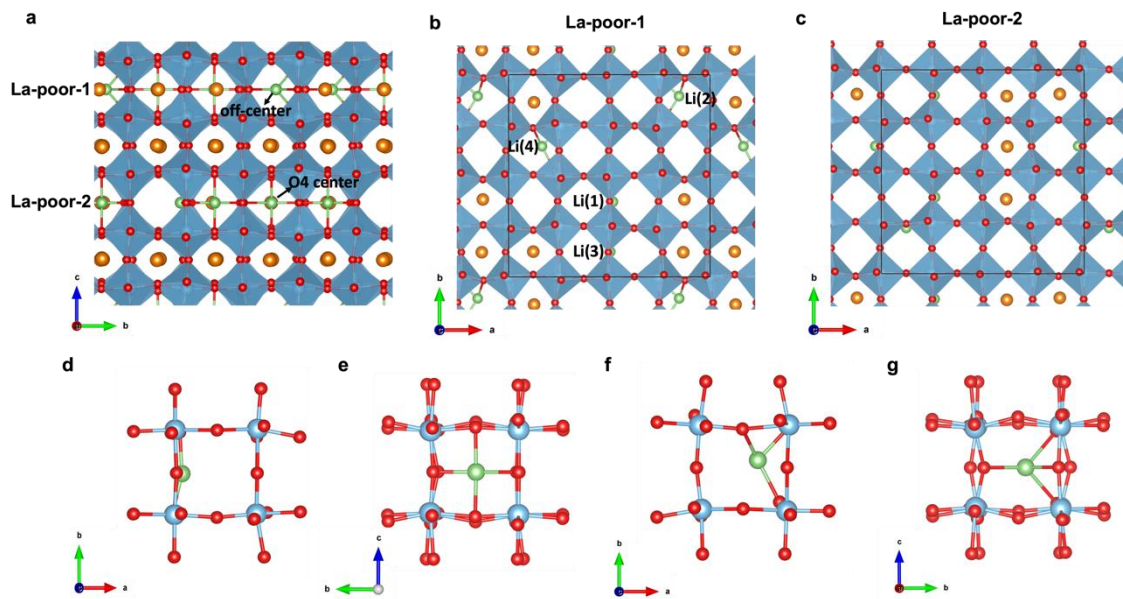


Fig.2 Optimized lowest-energy structure of model-I with composition of $\text{Li}_{0.125}\text{La}_{0.625}\text{TiO}_3$.

Green, orange, light blue and red spheres represent the Li, La, Ti and O ions, respectively. **a** Side view of the structure, which includes two La-poor layers in the cell, labeled “La-poor-1” and “La-poor-2”. **b,c** Top views of (b) La-poor-1 and (c) La-poor-2 layers, respectively. In **b**, the Li ions which will be used in subsequent figures are indexed. **d,e** Top and side views of Li ions located at a O4 center. **f,g** Top and side views of Li ions at an off-center site.

3.1 Atomistic structures.

In order to minimize the interplay between Li ions and simplifying the analysis of ion diffusion behavior, we adopted two $\text{Li}_x\text{La}_{(2-x)/3}\text{TiO}_3$ perovskite models with low Li concentrations ($x=0.125$ and 0.218). The distributions of La and Li in each layer are presented in Table S1.

Through the sampling scheme, the lowest-energy structures of $\text{Li}_{0.125}\text{La}_{0.625}\text{TiO}_3$ and $\text{Li}_{0.219}\text{La}_{0.594}\text{TiO}_3$ were obtained, referred to as model-I (Figure 2) and model-II (Figure S2), respectively. In both models, the La layers are alternatively arranged into La-rich and La-poor layers, with Li ions located in the La-poor layer. We revealed that, in both models, some Li ions occupy the center of the O4 square window (O4 center), while others are positioned at off-center site closer to the A site. These findings help resolve the controversy on the experimental observations regarding the locations of Li ions in LLTO.^{30,31,35,38,40–42} Additionally, distortions of TiO_6 octahedrons were observed in these models, which may influence the Li-ion occupation sites and diffusion behaviors.

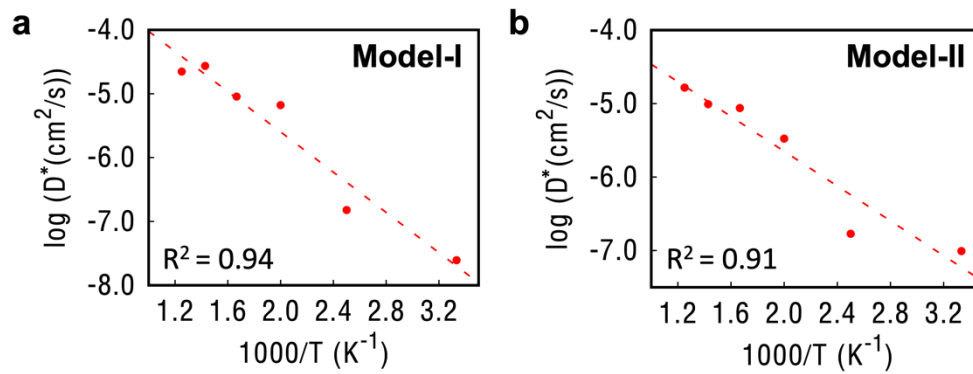


Fig. 3 Calculated self-diffusivities of the constructed models. Arrhenius plots of the self-diffusivities for (a) Model-I and (b) Model-II. The calculated R^2 values indicate good linear fits.

Table 1 Calculated E_a , D^*_{300K} and σ_{300K} of Li ions in Model-I and Model-II.

	E_a	D^*_{300K} (cm^2/s)		σ_{300K} (S/cm)	
		Calculated	Extrapolated	Calculated	Extrapolated
model-I ($\text{Li}_{0.125}\text{La}_{0.625}\text{TiO}_3$)	0.31	2.47×10^{-8}	2.00×10^{-8}	3.30×10^{-4}	2.66×10^{-4}
model-II ($\text{Li}_{0.219}\text{La}_{0.594}\text{TiO}_3$)	0.23	9.86×10^{-8}	5.92×10^{-8}	2.29×10^{-3}	1.38×10^{-3}

3.2 Activation energies and conductivities of Li ions.

Long-timescale MD simulations were performed using on-the-fly machine learning potentials. Li-ion self-diffusivities (D^*) were calculated from the mean square displacement results (Figure S3). The ionic conductivities at 300K (σ_{300K}) and activation energy (E_a), derived from the self-diffusivities of the two models (Figure 3) are summarized in Table 1. The results show that model-II, with a higher Li concentration, exhibits greater self-diffusivity and conductivity than model-I. Correspondingly, the E_a of model-II is lower than that of model-I. Previously reported Li-ion self-diffusivities of $\text{Li}_{0.29}\text{La}_{0.57}\text{TiO}_3$ were $2.6 \times 10^{-8} \text{ cm}^2/\text{s}$ at 295 K and $9.2 \times 10^{-8} \text{ cm}^2/\text{s}$ at 333 K, as determined using the nuclear magnetic resonance (NMR) techniques.^{27,62} These values are comparable to the calculated D^* values of these two models. Notably, the σ_{300K} of model-II ($2.29 \times 10^{-3} \text{ S/cm}$) surpasses the highest experimentally observed value ($\sim 1 \times 10^{-3} \text{ S/cm}$ at room temperature when $x \approx 0.33$)²³. One possible explanation for this discrepancy is related to the adopted atomistic structure as the random distribution of Li and La are confined into a model with hundreds of atoms, which is relatively different with experimental materials. Moreover, the grain boundary will induce the resistance for Li diffusion, lowering the overall Li-ion conductivity. It is noteworthy that such discrepancies between simulations and experiments have been widely reported in previous studies.^{3,9,29,63,64} The adopted parameters in the calculation including pseudopotential and exchange-correlation functional (PBE functional) can have an influence in this discrepancy as well. Furthermore, σ_{300K} values extrapolated from the Arrhenius plot are lower than the directly calculated values in both models. Especially, the extrapolated σ_{300K} for model-II ($1.38 \times 10^{-3} \text{ S/cm}$) is closer to the experimental value. Overall, the self-diffusivity and conductivity results obtained in this study are in reasonable agreement with experimental observations. We should emphasize that the experimental value of Li-ion conductivity is only for reference as the measurement condition is difference between experiments and theoretical calculations.

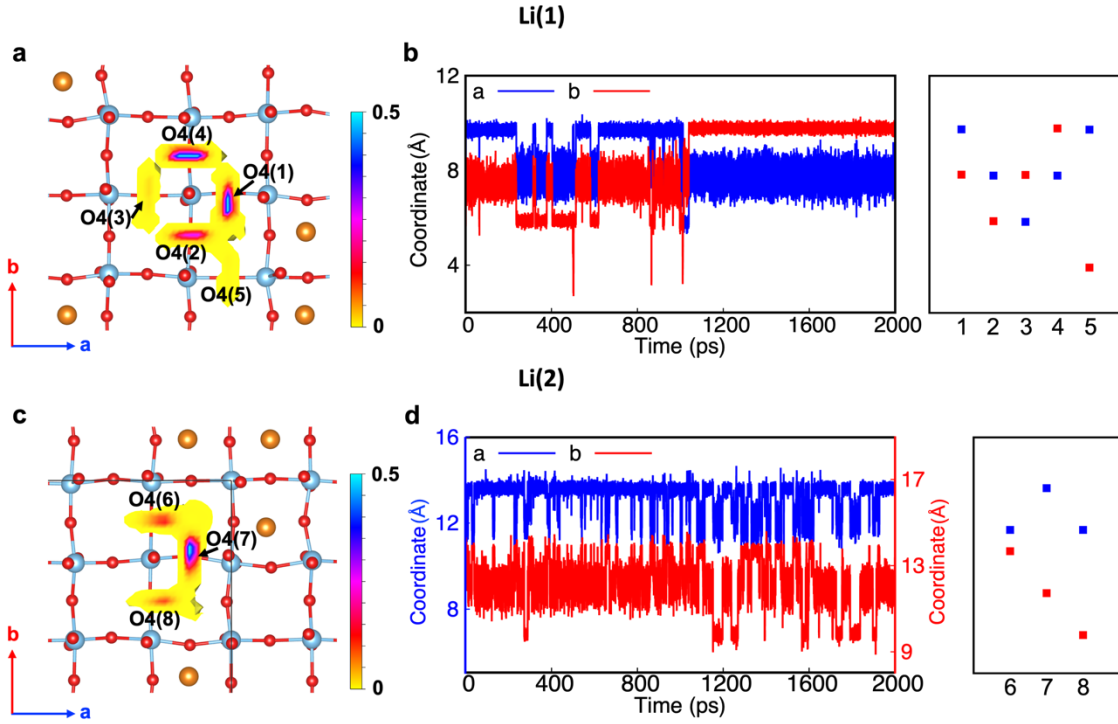


Fig.4 Diffusion trajectories of Li(1) and Li(2) in model-I at 400 K. **a, b** Density of diffusion trajectory and time evolution of coordinate of Li(1), respectively. **c, d** Density of diffusion trajectory and time evolution of coordinate of Li(2), respectively. In panels (**a**) and (**c**), the O4 squares involved in the diffusion pathways are indexed, with their coordinates provided on the right side of panels (**b**) and (**d**) for reference. The atomic coordinate project along a and b axes are shown using blue and red lines, respectively.

3.3 Nanoscopic ion diffusion mechanism.

We carefully analyzed the Nanoscopic diffusion mechanisms of Li ions in the simulated models, with a particular focus on model-I. Moreover, as the hopping event of Li ions is rather rare in the simulations of 300 K, we selected the results of MD simulations at 400 K for the further analysis. The lower Li concentration makes it easier to distinguish individual ion diffusion pathways. The total densities of ion diffusion trajectories within the La-poor-1 (depicted in Fig. 2b) are presented in Figure S4. Specifically, Figures 4a, 4c, S5a and S5c illustrate the diffusion trajectory densities for individual Li ions. Our results reveal that ion movements primarily occurs via hopping between neighbouring O4 centers, consistent with the previous studies.^{31,43,44} Figs. 4b, 4d, S5b and S5d display the time evolution of the coordinates of selected Li ions, revealing distinct diffusion behaviors. Specifically, Li(1) and

Li(3) tend to remain trapped in several O4 centers for extended periods, while Li(2) and Li(4) exhibit significantly higher hopping frequencies.

Two diffusion pathways were identified for Li(1): O4(1)→ O4(2) → O4(3) → O4(4) and O4(1)→ O4(2) → O4(5) (Fig. 4a). The migration barriers for the O4(1)→ O4(4) pathway were calculated using the nudged elastic band (NEB) method, as shown in Figure S6a. The results indicate that this pathway has an energy barrier of approximately 0.6 eV, which is relatively high for SEs. Notably, the O4(2) site was found to be the most stable for Li-ion occupation due to its lowest site energy. However, the diffusion trajectories (Fig. 4a) show higher densities around O4(1) and O4(4), suggesting the preference of Li(1) occupation at these sites. This implies that O4(1) and O4(4) may actually be more stable for Li-ion occupation than O4(2).

To address this apparent discrepancy between NEB calculations and MD simulations, we investigated the structural variations at finite temperatures. Two snapshot structures from the MD simulation at 400K, taken at 235 ps and 1200 ps, were geometrically optimized. The calculated relative energies for Li ions occupying the O4 centers (Fig. S6b) show significant change in stability for these sites under different temperatures. Specifically, in the initial optimized structure, O4(1) is the least stable site; however, it becomes the energetically most stable site at 235 ps under 400 K. To understand the reason for this substantial variation in site stability, we further analyzed the O4 configurations (Figure S7). We found that, in the initial structure, the O4(1) square is visibly distorted (Fig. S7a), which likely increase the energy for Li occupation. Conversely, in the structure at 235 ps under 400 K, the O4(1) square becomes highly ordered, leading to a lower site energy (Fig. S7b). Previous study has reported the relationship between O4 center and diffusion barriers⁴⁹, supporting the current results. These findings indicate that the lattice framework undergoes significant changes at finite temperature, which strongly influence the site stability of Li ions in LLTO.

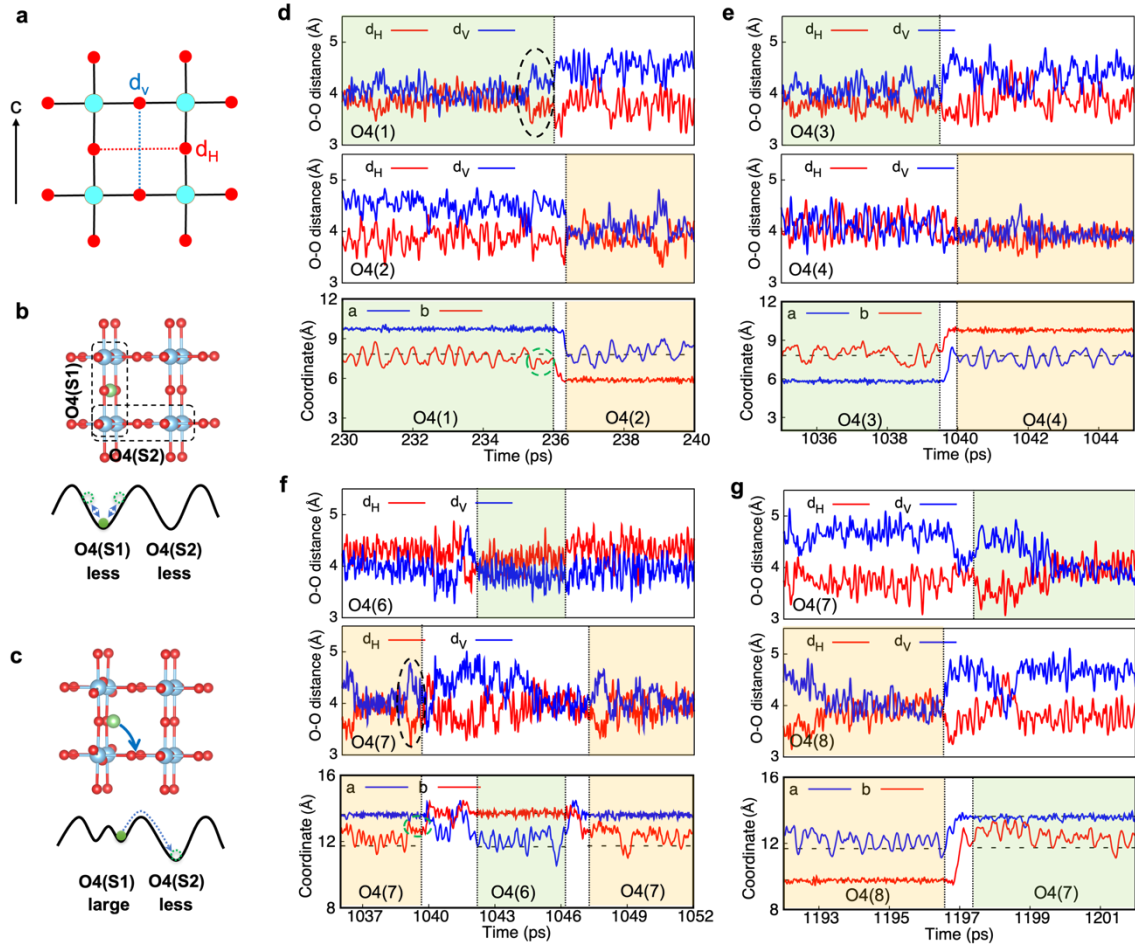


Fig. 5 Relationships between O4 square deformations and Li-ion hopping. **a** Schematic illustration of horizontal (d_H) and vertical (d_V) O-O distances in the O4 square. **b,c** Schematic representations of the Li-ion hopping mechanism in LLTO. Two O4 squares, O4(S1) and O4(S2), enclosed by dashed lines, were defined. In **b**, both O4(S1) and O4(S2) squares are less deformed, resulting in relatively deep energy valleys at the O4 centers on the potential energy surface (PES) shown below. Li ions primarily fluctuate around the O4(S1) center. In **c**, significant deformation of the O4(S1) square alters the PES, raising the energy at the O4 centers and forming local energy valleys near the O4(S1) center (off-center sites). This deformation reduces the diffusion barrier from the off-center site to the O4(S2) center, facilitating Li-ion hopping. **d,e** Time-dependent variations of d_H and d_V for the corresponding O4 squares (top two panels), and the Li(1) coordinate (bottom panel) during jump events of **(d)** O4(1)→O4(2) and **(e)** O4(3)→O4(4) within the selected time ranges. **f,g** Time-dependent variations of d_H and d_V for the corresponding O4 squares (top two panels), and the Li(2) coordinate (bottom panel) during jump events of **(f)** O4(7)→O4(6)→O4(7) and **(g)** O4(8)→O4(7) within the selected time ranges. In **(d-g)**, the time intervals during which Li remains at the center of the respective

O4 square are highlighted with consistent colors in both the Li coordinate plots (bottom panel) and the O4 square deformation plots (top two panels), and atomic coordinate project along a and b axes are shown using blue and red lines in bottom panel of each figure, respectively.

The results above demonstrate that the deformation of the O4 square significantly influences the stability of Li-ion sites located at the O4 center. These deformed sites with lower stability may promote Li-ion hopping.⁶ Therefore, we analyzed the relationship between O4 square deformation and Li-ion hopping, as shown in Figure 5 and Figure S8. Here we divided the distances between two opposite O ions in a O4 square along the horizontal (parallel to the ab plane) (d_H) and vertical (parallel to c axis) (d_V) directions, as illustrated in Fig.5a. The time variations of d_H and d_V in selected O4 squares in the MD simulation of Model-I at 400 K were depicted in the top two panels of Fig. 5d-g. It is found that O ions fluctuate around their equilibrium position due to thermal effects. Intriguingly, beyond typical thermal fluctuations, we observed two distinct deformation states for O4 squares: a “less-deformed” state and a “highly-deformed” state. Transitions between these two states differ from standard thermal fluctuations as these deformation states can persist for relatively long durations, on the order of picoseconds.

We next analyzed the temporal variations of O4 configurations in detail. The hopping event of Li(1) from O4(1) to O4(2) (Fig. 5d) was examined first. When Li(1) occupies the O4 centers, the surrounding O4 squares exhibit less deformation. However, once Li(1) leaves the centers, the O4 squares become highly deformed (See top and middle panels of Fig. 5d). Similar behavior was observed near the hopping event from O4(3) to O4(4) (Fig. 5e). To ensure the generality of these observations, we analyzed the deformation of O4 squares and the occupancy of Li ions across the entire MD simulation. To exclude the fluctuations of O4 squares and Li-ion vibrations induced by thermal effects, we defined an O4 square as being in a highly deformed state if the deformation persisted for at least 0.5 ps. By analyzing the hopping event of Li ions, we found that most of ion hopping can proceed with 0.5 ps. Therefore, the deformation of O4 square persisting at least for 0.5 ps can sufficiently affect the hopping of Li ions. Similarly, an O4 center was considered occupied by a Li ion if the ion remained near the O4 center for more than 0.5 ps. The results are shown in Figure S9. Over the course of the simulation, O4(2) and O4(3) squares predominately remained in a highly deformed state, while O4(1) and O4(4) squares showed a greater tendency to of maintain less-deformed configurations. Correspondingly, Li(1) locates at O4(1) and O4(4) centers most of the time.

These results obviously indicate that Li ion preferentially occupy the centers of less-deformed O4 configurations.

It is well established that the transition of an O4 square from a less-deformed state to a highly-deformed state can destabilize Li-ion site occupation, thereby facilitating ion hopping. This can also be demonstrated by the diffusion barrier calculations (Fig.S5a), which suggest that the energy barrier for Li-ion diffusion from an off-center position in the deformed O4(1) square to the less-deformed O4(2) center (0.14 eV) is remarkably lower than other diffusion barriers. Further analysis of the hopping event shown in Fig.5d indicates that O4(1) square has undergoes deformation (highlighted by the region enclosed by the black dashed circle in the top panel) about 1 ps before the jump of Li(1). Prior to the jump, Li(1) occupies an off-center position (enclosed by the green circle in the bottom panel) between the O4(1) and O4(2) centers. Similar behavior was observed in the hopping event of Li(2) from the O4(7) center to the O4(6) center (Fig. 5f). Here schematic illustrations (Fig. 5b and 5c) further demonstrate how the transition in the deformation state of O4 squares contributes to Li-ion hopping. This transition increases the site energy, thereby reducing the diffusion barrier and enhancing the likelihood of ion hopping. This ion diffusion mechanism, driven by the lattice deformation, is referred to as the “lattice squeezing effect”. Furthermore, we analyzed the effect of deformation of O4 squares on the Li-ion diffusion in the MD simulations at 300 and 500 K. As shown in Fig. S10, the similar phenomena were observed, suggesting that the lattice squeezing effect is independent with temperature.

The frequencies of deformation state transitions for the analyzed O4 squares were calculated and are presented in Figure S11. Along the O4(1)→O4(4) diffusion pathway of Li(1), although O4(1) exhibits a relatively high transition frequency, the low frequencies of O4(2) through O4(4) impede the hopping of Li(1). In contrast, O4(6)-O4(8) exhibit remarkably higher transition frequencies, facilitating the frequent hopping of Li(2).

Although high hopping frequencies of Li(2) were observed, the hopping of Li(2) remains confined to the local O4 centers [O4(6)-O4(8)], with no evidence of long-range diffusion, as seen in Fig. 4c. Analysis of the diffusion trajectories of Li(2) reveals that the highest densities of diffusion trajectories deviate from the geometric centers of the O4 squares, as also shown in Figs.5f and 5g. Specifically, the equilibrium positions of Li(2) within the O4(6) and O4(8) squares are close to the O4(7) center. This promotes hopping between O4(6)/O4(8) and O4(7) centers due to the shorter jumping distance, while simultaneously impeding hopping between O4(6)/O4(8) centers and other neighbouring O4 centers. This may explain the observed

localized diffusion behavior of Li(2). A similar deviation between the geometric O4 center and the equilibrium position of Li fluctuation was observed in the diffusion trajectory of Li(1) around the O4(1) square (Fig. 4a), where the equilibrium position is closer to the O4(2) square and farther from the O4(4) square, leading to the absence of hopping between O4(1) and O4(4) centers.

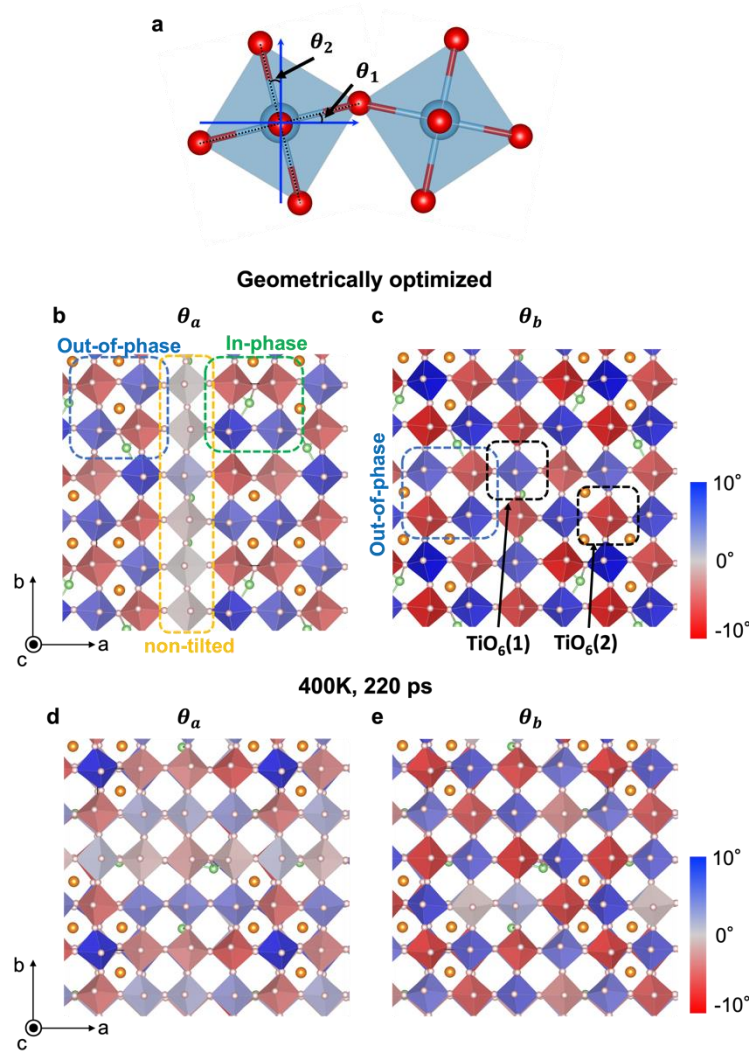


Fig.6 Tilt angle distributions of TiO₆ octahedra in the La-poor-1 layer of Model-I. **a**, Schematic representation of the tilt angles of TiO₆ octahedron, defined as θ_1 and θ_2 . **b,c** Distributions of **(b)** θ_a and **(c)** θ_b in the geometrically optimized structure. Regions enclosed by blue and green dashed rectangles correspond to out-of-phase and in-phase tilt, respectively, while the orange dashed rectangle in **(c)** indicates a non-tilted configuration. The black dashed squares in **(c)** denotes the selected TiO₆(1) and TiO₆(2) octahedra used in Fig. S13. **d,e** Distributions of **(d)** θ_a and **(e)** θ_b in a snapshot structure captured at 220 ps under 400 K.

3.4 Deformation of TiO₆ octahedron.

The achieved results clearly demonstrate that the dynamics of O4 square deformation play a significant role in facilitating Li-ion diffusion in LLTO. This raises the question: what drives the deformation of the O4 square? To address this, it is essential to investigate the deformation mechanisms of the TiO_6 octahedron. As discussed in the Introduction, two key factors influence the deformation of the TiO_6 octahedron: (1) the smaller ionic radius of La, which can cause tilting of the TiO_6 octahedron, the (2) second-order Jahn-Teller effect, which induces off-center displacement of Ti. To quantify these deformations in model-I, we defined two parameters: θ_{TiO_6} , representing the tilting angle of the octahedron, and Δ_{Ti} (Figure S12a), measuring the displacement distance of Ti from the octahedral center. Specifically, for octahedral tilting, two components – θ_a and θ_b – correspond to the rotation angles around the a and b axes, respectively. Moreover, for each octahedron, two angles, θ_1 and θ_2 (Figure 6a), describe the tilting of two different spatial diagonals. The parameter θ_{TiO_6} is the average of θ_1 and θ_2 . Similarly, Δ_{Ti} was decomposed into three components: Δ_a , Δ_b and Δ_c , along the lattice vector directions. The calculated distributions of θ_{TiO_6} and Δ_{Ti} for the TiO_6 octahedra in the La-poor-1 layer are shown in Fig.6b-e and Fig.S12b-g, respectively.

There are two types of octahedral tilt arrangement in perovskite structures: in-phase tilt, where two adjacent octahedra along the rotation axis rotate in the same direction (indicated by the green dashed square in Fig. 6c), and out-of-phase tilt, where adjacent octahedra rotate in the opposite directions (indicated by the blue dashed square in Fig. 6c). The distributions of TiO_6 octahedral tilting in the La-poor-1 layer (Fig. 6c-f) vary significantly along the a and b axes. In the geometrically optimized structure, the octahedra exhibit an out-of-phase tilt along the b axis (Fig. 6d), while along the a axis, a more complex distribution is observed, containing both in-phase and out-of-phase tilts, was observed along the a axis, (Fig. 6c). Notably, along the a axis, a line of nearly non-tilted octahedra is observed (indicated by the yellow rectangle in Fig. 6c). In the snapshot structure at 220 ps and 400 K, the distributions of octahedral tilts differ from those in the initial optimized structure. Different in-phase and out-of-phase tilts are present along the a axis (Fig. 6e). Along the b axis, the out-of-phase tilt persists, although the direction of tilting for each octahedron switches (Fig. 6f).

Further analysis revealed that the distribution of octahedral tilts is influenced by the La ions. As shown in Fig. 6b-e, the TiO_6 octahedra near the Li-ion accumulation region exhibit stronger tilting, with higher absolute values of θ_a and θ_b , compared to those located farther from the La ions. To illustrate this, we selected two representative TiO_6 octahedra— $\text{TiO}_6(1)$ and $\text{TiO}_6(2)$ —indicated in Fig. 4b, which are positioned near and far from the La ions, respectively. The time

variations of θ_a and θ_b for these two octahedra were plotted in Fig. S13. The results indicate that the tilt fluctuation amplitude for $\text{TiO}_6(2)$ is greater than that of $\text{TiO}_6(1)$. Moreover, distinct switches in the tilt angle of $\text{TiO}_6(2)$ were observed, which are related to the deformation state transitions of the O4 square.

For Δ_{Ti} , in the initial optimized structure, the TiO_6 octahedra near the La ions exhibit larger absolute values of Δ_a and Δ_b (Fig. S12a and b). Notably, Δ_{Ti} for most TiO_6 octahedra near the La ions point away from the La ions, as schematically illustrated in Fig. S14a. This octahedral distortion influences the distance between neighbouring O atoms [$d(\text{O-O})$] in a TiO_6 octahedron. Time variations of $d(\text{O-O})$ values in selected TiO_6 octahedra were analyzed as shown in Fig. S15. The results manifest that the averaged $d(\text{O-O})_1$ and $d(\text{O-O})_4$, corresponding to d_1 in Fig. S14a, are shorter than other $d(\text{O-O})$ values corresponding to d_2 and d_3 . A schematic diagram of two neighbouring O4 squares is provided in Fig. S14b. The shorter d_1 indicates that the O4 squares are closer to each other, increasing the likelihood of Li-ion hopping between these O4 centers. Conversely, the longer d_2 and d_3 suggest that O4 squares are relatively farther apart, hindering the Li-ion hopping between these centers. These findings explain the diffusion densities of Li(2) shown in Fig. 4c. Additionally, Fig. S14c presents a schematic of the local distortion of O4 squares around diffusion trajectory of Li(2), showing that Li(2) becomes trapped between O4(6)/O4(8) and O4(7) squares due to the shorter distance between these squares. Similarly, the localized diffusion behavior of Li(4) (Fig. S5c) can also be explained by the local surrounding structure.

3.5 Design of high-conductivity LLTO SEs.

Based on the established diffusion mechanisms, the following principles are proposed for designing high-conductivity LLTO SEs:

1. Enhance the available pathways for Li-ion diffusion by increasing the accessible diffusion area.
2. Promote frequent deformation state transitions of O4 square originating from the octahedral tilting.
3. Minimize Li-ion hopping localization caused by octahedral distortions.

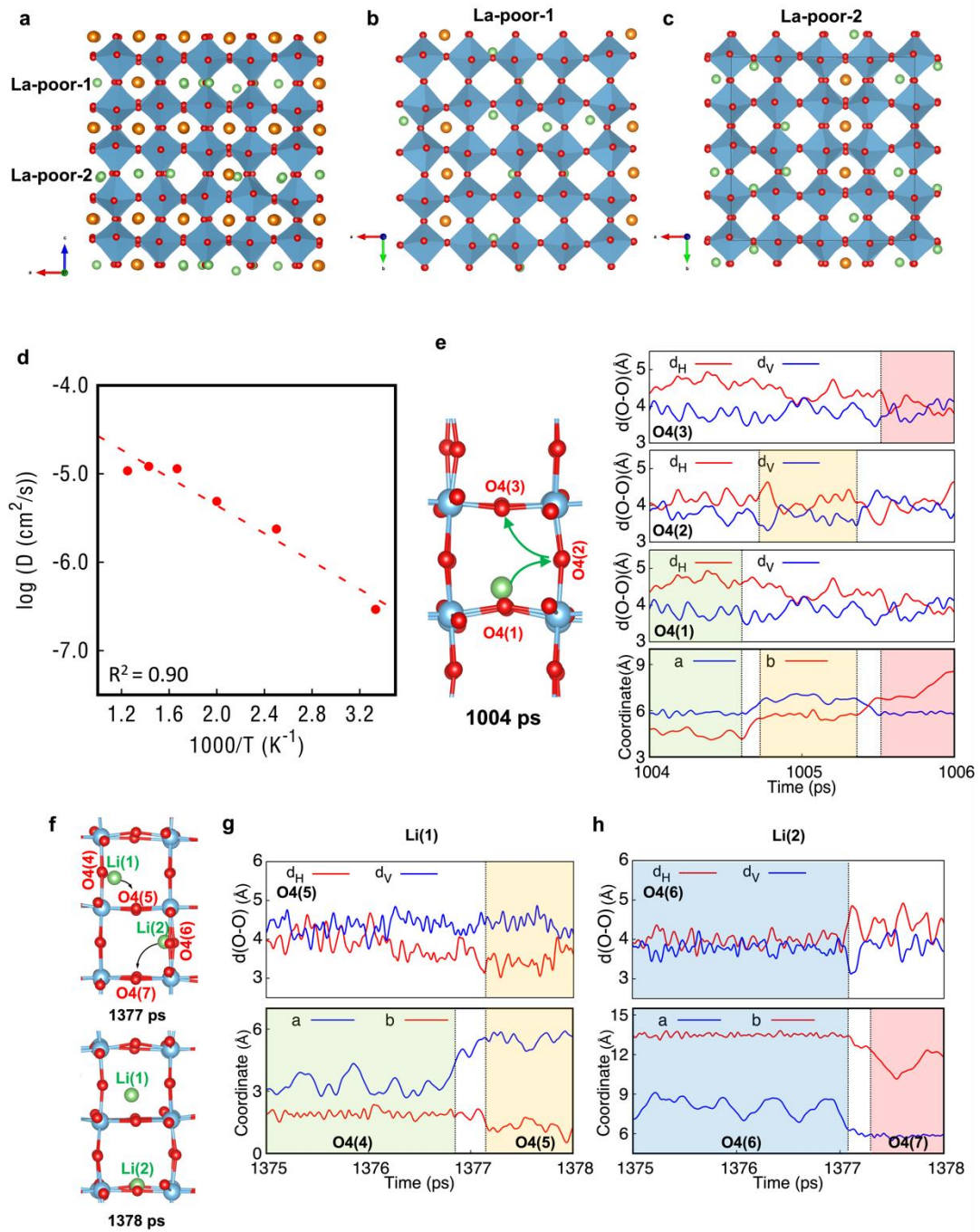


Fig.7 Results of the designed high-conductivity LLTO model. **a** Side view of designed structure, featuring two La-poor layers labeled as “La-poor-1” and “La-poor-2”. **b,c** Top views of (b) La-poor-1 and (c) La-poor-2 layers. **d** Arrhenius plot of the self-diffusivities for the designed model. **e** Left panel: Local configurations of snapshots at 1004 ps during the MD simulation at 400 K, showing three O4 squares labeled O4(1)-O4(3). Arrows indicate the directions of Li-ion motions. Right panel: Time variations of d_H and d_V in O4(1)-O4(3) squares, along with the coordinates of a selected Li ion within the 1004-1006 ps time range. **f** Local configurations of snapshots at 1377 and 1378 ps, highlighting two Li ions, Li(1) and Li(2), and

four O4 squares, O4(4)-O4(7). Arrows indicate the Li-ion motion directions. **g** Time variations of d_H and d_V in the O4(5) square (top panel), along with the Li(1) coordinates (bottom panel) within 1375-1378 ps. **h** Time variations of d_H and d_V in the O4(6) squares, along with Li(2) coordinates within 1375-1378 ps.

Based on the proposed design principles, we constructed several LLTO models. Encouragingly, one designed model with a composition equivalent to model-II ($x=0.219$) shows high ion conductivity. In this structure (Fig. 7a-c), three La ions are aligned in a row within each La-poor layer to minimize the impact of octahedral distortions (See Fig. S16). The calculated energy of the designed structure is only 1.5 meV/atom higher than that of model-II. Ion self-diffusivities were calculated from MSD profiles (Fig. S17). The activation energy, derived from the Arrhenius plot of self-diffusivities, is 0.16 eV, which is remarkably lower than the values for model-I and model-II. Moreover, the calculated ionic conductivity at 300 K ($\sigma_{300K} = 6.83 \times 10^{-3}$ S/cm) is much higher than that of model-I and model-II, indicating that this newly constructed model is a promising candidate for high-performance of Li-ion conductors.

The analyzed Li-ion diffusion trajectories (Fig. S18) reveal a continuous diffusion path, while the trajectory of a selected Li (Fig. S19) exhibits long-range diffusion behavior. To better understand the high ionic conductivity of this structure, we investigated the relationship between ion diffusion and lattice deformations. As shown in Fig. 7e, the diffusion pathway of the selected Li-ion follows the sequence O4(1)→O4(2)→O4(3). The deformations of O4(1), O4(2) and O4(3) squares show significant variations, suggesting that ion diffusion is facilitated by the observed effect.

Furthermore, concerted diffusion mechanisms were also observed in this model. As depicted in Fig. S20, Li(3) hops to the site previously occupied by Li(4), displacing Li(4) to a neighboring site, demonstrating a knock-off diffusion mechanism^{11,12,65}. Interestingly, a novel diffusion mechanism was observed during 1377-1378 ps, as depicted in Fig. 7f. Specifically, the selected Li(1) hops from the O4(1) center to the O4(2) center, resulting in a decrease in d_H of O4(2) (Fig. 7g). Since O4(2) and O4(3) share a common edge, this causes a significant increase in the d_H of O4(3), leading to severe deformation of this O4 square. The destabilized O4(3) center prompts Li(2) to diffuse to O4(4) centers. This mechanism is referred to as “ion-lattice-ion concerted diffusion”. These findings reveal that correlated diffusions play key roles in determining the high conductivity of this designed LLTO material. Moreover, the concerted

diffusion behavior for Li-ion is reflected in the calculated distinct part of van Hove correlation function ($G_d(t,r)$) (Fig. S21). The gradual accumulation of $G_d(t,r)$ over time further confirms the presence of correlated Li-ion diffusion.

3.6 Discussion

In this study, we have unveiled the critical role of lattice deformation dynamics in facilitating Li-ion diffusion within LLTO SE. Specifically, the observed off-center displacement of Ti in TiO_6 octahedron induces the localization of Li-ion diffusion, while deformation state transitions of the O4 square, driven by TiO_6 octahedral tilting, generate a lattice squeezing effect that enhance Li-ion hopping possibility. Furthermore, the concerted diffusion mechanisms observed in the designed model, including knock-off diffusion and ion-lattice-ion concerted diffusion, significantly contribute to improved Li-ion conductivity. It is noteworthy that, as the transition of O4 deformation states isn't involved in the NEB calculations of Li-ion hopping process. This induces the higher diffusion barriers of Li ions in the NEB calculations. The dynamics of lattice framework have a significant influence on the ion diffusion in LLTO SEs.

To further understand the dynamics of Li ions and the lattice framework, we calculated the power spectra of the velocity autocorrelation function^{9,66} for Li and O ions in model-II and the designed model, as shown in Fig. S22. Previous studies have proposed that lower vibration frequencies of Li ions correlate with higher self-diffusivities.^{7,9} We observed a peak at approximately 3.90 THz in the power spectra of Li in model-II, whereas the designed model exhibited two distinct peaks at 2.69 and 3.91 THz. These findings suggest a reduction in the vibration frequencies of Li ions in the designed model compared to model-II, consistent with the enhanced Li-ion conductivity observed in the designed model. Additionally, the power spectra of O show negligible differences between the two models. It is worth noting that the frequency of deformation state transition is on the order of 10^{-2} - 10^{-1} THz (See Fig. S11), which is significantly lower than the vibration frequencies induced by thermal effects.

The critical role of anion lattice dynamics in enhancing Li-ion diffusion in SEs have been reported in a series of works. We should emphasize that the diffusion mechanism revealed in this work differs from the previously proposed paddlewheel effect, which relies on the reorientation of anion units such as PS_4 . In this study, we demonstrate that the lattice framework deformations can facilitate ion diffusions in LLTO SE, introducing a novel “lattice squeezing effect” mechanism. Based on these findings, we propose two potential strategies for designing high-conductivity SE in the $\text{Li}_x\text{A}_y\text{BO}_3$ perovskite family. The first strategy involves

rearranging the A-site cations, as demonstrated in the designed model. The second strategy focuses on selecting a suitable B-site element to enhance the frequency of deformation state transitions in O4 squares.

4. Conclusions

In summary, we have conducted a comprehensive theoretical study on Li-ion diffusion in LLTO perovskite SEs by means of long-timescale MD simulations enabled by highly efficient on-the-fly MLPs. Our findings revealed that frequent deformation state transitions of O4 square significantly enhance the likelihood of Li-ion hopping, while the off-center displacements of Ti in TiO_6 octahedra impede long-range ion diffusion. Based on these insights, we designed a new structural model exhibiting a remarkably high ion conductivity of 6.83×10^{-3} S/cm. The enhanced diffusion behavior in this model is attributed to concerted diffusion mechanisms, including the knock-off diffusion and a novel ion-lattice-ion concerted diffusion. This work highlights the critical role of lattice dynamics in Li-ion diffusion and provides valuable guidance for designing high-conductivity SE materials for ASSBs.

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Author contributions

B. G. and Y. T. conceived the study with the help of R. J. Calculations were performed by B. G. Contributions were made by Y. T. and R. J. in relation to the analysis and discussion of the results. The paper was written by B. G. with comments from other authors.

Competing interests

The authors declare no competing interests.

Data availability

All data are available in the paper and from the author upon request.

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