Enhancing ionic conductivity in solid electrolyte by relocating diffusion ions to under-coordination sites

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Solid electrolytes are highly important materials for improving safety, energy density, and reversibility of electrochemical energy storage batteries. However, it is a challenge to modulate the coordination structure of conducting ions, which limits the improvement of ionic conductivity and hampers further development of practical solid electrolytes. Here, we present a skeleton-retained cationic exchange approach to produce a high-performance solid electrolyte of Li$_2$Zr$_2$Si$_2$PO$_{12}$ stemming from the NASICON-type superionic conductor of Na$_2$Zr$_2$Si$_2$PO$_{12}$. The introduced lithium ions stabilized in under-coordination structures are facilitated to pass through relatively large conduction bottlenecks inherited from the Na$_2$Zr$_2$Si$_2$PO$_{12}$ precursor. The synthesized Li$_2$Zr$_2$Si$_2$PO$_{12}$ achieves a low activation energy of 0.21 eV and a high ionic conductivity of 3.59 mS cm$^{-1}$ at room temperature. Li$_2$Zr$_2$Si$_2$PO$_{12}$ not only inherits the satisfactory air survivability from Na$_2$Zr$_2$Si$_2$PO$_{12}$ but also exhibits excellent cyclic stability and rate capability when applied to solid-state batteries. The present study opens an innovative avenue to regulate cationic occupancy and make new materials.

INTRODUCTION

All-solid-state batteries (ASSBs) are attracting ever increasing attention for solving the intrinsic drawbacks of current Li-ion batteries, such as leakage and flammability of liquid electrolytes, and limited energy densities (1, 2). The success of ASSBs depends on solid electrolytes with satisfying Li-ionic conductivities. A high electrochemical stability at the interface of the solid electrolytes with electrode materials in a wide range of working potentials also plays an important role in designing ASSBs, for any electrochemical instability of solid electrolytes may result in interfacial decomposition products with a low ionic conductivity (3, 4). Recent studies on ASSBs have made considerable progress in high-conductivity inorganic solid electrolytes, which are generally classified into sulfide and oxide solid electrolytes (5). The most remarkable features of sulfide solid electrolytes such as Li$_{10}$GeP$_2$S$_{12}$ (6) and Li$_3$PS$_4$X (X = Cl, Br, I) (7, 8) are their high ionic conductivity, comparable with organic liquid electrolytes at room temperatures, but low stability against Li metal to decompose into interfacial side product of Li$_2$S (9). Oxide solid electrolytes such as Li$_2$La$_9$Zr$_5$O$_{12.10}$ and LiPON (11) usually exhibit higher electrochemical stability at the interface in working potentials (12). Despite tremendous research advancements in oxide solid electrolytes, it still faces a large challenge to further improve their ionic conductivity to meet the requirement of practicable application (13).

In the past decades, a great deal of effort has been made for developing oxide solid electrolytes such as LISICON (14), NASICON (15, 16), perovskite (17, 18), garnet (10, 19), and LiPON (20) systems. The basic step in diffusion paths is Li-ion migration between two stable sites through the high-energy transition state. In these compounds, Li-ions usually occupy the lower-energy hexahedral sites and commonly surmounting high-energy and narrow bottleneck (transition state) into tetrahedral sites (Fig. 1A). Reducing the activation energy heights of transition states along the long-range diffusion path is of much importance in increasing ionic conductivity. For many years, optimization of these solid electrolytes has largely proceeded by substituting skeleton structural elements to enlarge the bottleneck and reduce the migration barrier (3, 21), which only achieve the ionic conductivities of the order of 10$^{-6}$ to 10$^{-3}$ S cm$^{-1}$ at room temperature and the activation energy of 0.25 to 0.6 eV. Achieving a low migration barrier requires the bottleneck between two different polyhedrons to satisfy a very specific size. Statistical analysis indicates that those NASION-type lithium solid electrolytes with a bottleneck size of >2.05 Å exhibit a much lower migration barrier (Fig. 1B) (22). Intrinsically, regulating bottleneck size corresponds to change of polyhedron size, which may lead to Li$^+$ occupancy changes from high-coordination to under-coordination sites for retaining structural stabilization (Fig. 1C). Therefore, the regulating coordination structure between Li$^+$ ions and O$^{2-}$ anions provides an important strategy for breaking through this contradiction between occupancy stability and ionic conductivity.

In this work, a skeleton-retained cationic exchange approach based on Na$_2$Zr$_2$Si$_2$PO$_{12}$ (NZSP) is proposed to synthesize advanced solid electrolyte Li$_2$Zr$_2$Si$_2$PO$_{12}$ (LZSP), in which Li$^+$ ions self-adaptively occupy under-coordinated sites and maintain relatively large bottleneck sizes by inheriting the pristine framework. The obtained LZSP...
In the three-dimensional (3D) channels enclosed by SiO$_4$ structure, while the others occupy the octa-coordinated sites ($25^{26}$). Na$^+$ ions perform poor transport activity. Therefore, the pied octahedrons and unoccupied tetrahedrons. However, the octa-coordinated Li$^+$ ions perform well, leading to improved ionic conductivity by following the migration path of occupied sites.

Li$^+$ cation coordinating with the N element of the TFSI$^-$ anion, respectively should be satisfied: (i) The selected liquid carrier (EMIIM in this work) is capable of dissolving the lithium compound (LiTFSI in this work) and simultaneously would not dissolve the solid electrolyte precursor; (ii) except for cation exchange, no other chemical reaction takes place. EMIIM and LiTFSI are selected as the solution environment and lithium source, respectively, to drive the cation exchange process. The operation temperature and concentration difference are intrinsically two key driving forces for promoting the cation substitution. Therefore, optimizing concentration difference and operation temperature is of great importance to balance in exchange effectiveness and damaging the skeleton of the solid electrolyte precursor due to inadequate and excessive additive. As shown in fig. S1, Na$^+$ ions inside NZSP are thoroughly replaced by Li$^+$ ions within LiTFSI dissolved EMIIM at 453 K (NZSP is not soluble in EMIIM). Unlike the commonly adopted molten salt ion-exchange method that requires high-temperature calcination (>673 K) ($24^{25}$), this approach can be conducted at a relatively low temperature (≤453 K), giving rise to the ability to restrain phase transition and keep the pristine framework. The usage of liquid carrier, ionic liquid—an essential Li$^+$ ionic conductor, enables the fast removal of Na$^+$ ions and continuous entry of Li$^+$ ions, where liquids without ionic conductivity (e.g., water) may fail. In addition, the NZSP powders are more readily dispersed evenly in ionic liquids than solidified Li$^+$ carrier, which further facilitates the Li$^+$/Na$^+$ ionic exchange.

The textures of “precursor” NZSP and “product” LZSP nanocrystals are determined by diffraction techniques and Rietveld refinement analysis (Fig. 2). The refined powder synchrotron x-ray diffraction (XRD) and neutron powder diffraction (NPD) patterns of NZSP and LZSP nanopowders (Fig. 2, A and B) crystallize with a monoclinic phase, which belongs to the crystal group of C12/c (space group #15). In the locally amplified synchrotron XRD patterns in Fig. 2A (see untruncated data in fig. S2), the peaks of (200) and (400) as well as the (020) and (021) facets all shift to higher angles from NZSP to LZSP, manifesting the lattice contraction of the a and
b axis (a axis: 15.6 → 14.9 Å; b axis: 9.1 → 8.6 Å), respectively. Compared to those peaks, the signal of (111) facet just shows a less offset degree, corresponding to the slight elongation along the c axis (9.2 → 9.3 Å). NPD was then used to investigate the coordination evolution of conductive ions during the replacement of Na⁺ ions with Li⁺ ions. The NPD patterns of NZSP and LZSP (Fig. 2B) are deconvoluted by Rietveld refinements, from which the Wyckoff sites of each atom and the structural parameters consistent with the above results obtained from synchrotron XRD (tables S1 to S4). Particularly, the NPD technique is powerful in revealing the accurate atomic coordination of light elements (e.g., H and Li) (29, 30). Three intense diffraction peaks [(200), (021), and (130) facets] aroused by Na⁺ ions and Li⁺ ions are extracted (Fig. 2B and fig. S3). These characterizations show that the retained skeleton performs a little contraction to accommodate the small size of Li⁺ ions. Scanning electron microscopy (SEM) images (Fig. 2B, inset) exhibit the similar sizes of NZSP and LZSP particles (around 600 nm), indicating the maintained microscopic structure at the submicrometer level during cationic exchange. Energy-dispersive x-ray spectroscopy shows a homogeneous distribution of all constituent elements for NZSP and LZSP solids (fig. S4).

The retained skeleton structure is further supported with ¹⁷O solid-state nuclear magnetic resonance (ssNMR), which is a high-sensitive technique to characterize the local structure of oxides at the atomic level (31, 32). As shown in fig. S5, their alike resonances observed in the ¹⁷O ssNMR spectra show that NZSP and LZSP crystals have a similar skeleton structure. In the skeleton structure, Wyckoff sites of Zr, Si/P, and O ions fully occupy the Wyckoff sites of 8f, 4e/8f, and 8f, respectively (figs. S6 and S7 and tables S1 and S2). In contrast, Na⁺ and Li⁺ occupancy sites in NZSP and LZSP exhibit an obvious difference, respectively. For NZSP, Na⁺ ions are distributed in three Wyckoff sites, fractional occupancy 4d (80%), full occupancy 4e (100%), and 8f (60%), corresponding to hexa-coordinated NaI, octa-coordinated NaII, and hexa-coordinated NaIII (fig. S2 and table S1) (22, 25). These high-coordinated polyhedrons with Na⁺ occupancy are connected with under-coordinated tetrahedrons, forming 3D migration channels such as -octahedron-tetrahedron-octahedron-, -dodecahedron-tetrahedron-dodecahedron-, and -octahedron-tetrahedron-dodecahedron-... When cationic exchange is fully accomplished, Li⁺ ions either invade Na⁺-occupied polyhedrons (LiIV → Na⁺) or create pioneering occupancy in tetrahedrons following the migration channels of -octahedron-tetrahedron (LiIV)-octahedron- and -dodecahedron-tetrahedron (LiIV)-dodecahedron-. These Li⁺ ions in polyhedrons are relaxed into equivalent under-coordination structures with penta-coordinated LiII and tetra-coordinated LiIII, LiIV, and LiV sites (fig. S7 and table S2). Our XRD
and NPD analysis indicates that cationic exchange induces coordination transformation from high-coordinated occupancy (hexa- and octa-coordinated) of Na\textsuperscript{+} ions into under-coordinated occupancy (tetra- and penta-coordinated Li\textsuperscript{+}) of Li\textsuperscript{+} ions. Except for 6% occupancy Na\textsuperscript{III}O\textsubscript{6} → Li\textsuperscript{III}O\textsubscript{6}, most of the Na\textsubscript{III}O\textsubscript{6} octahedrons become vacant and Li\textsuperscript{+} ions are fully occupied in the tetrahedrons connected with two octahedrons. The Li\textsuperscript{+} replacement makes 100% occupancy Na\textsubscript{III}O\textsubscript{6} dodecahedrons into 43.8% occupancy Li\textsubscript{III}O\textsubscript{6} (V denotes vacancy site; fig. S7). As shown in Fig. 2 (C and D), the ionic substitution from Na\textsuperscript{+} to Li\textsuperscript{+} ions does not result in skeleton structure change. However, Na\textsuperscript{+} ions in NZSP occupy high-coordination sites (hexa-/octahedral sites), while exchanged Li\textsuperscript{+} ions in LZSP preferably occupy under-coordination structures such as tetrahedron and pentahedron. Their occupancy structure stability is further discussed in the DFT calculations.

Detailed coordination evolution and ion transport from Na\textsuperscript{+} ions to Li\textsuperscript{+} ions during the cationic exchange were studied through quantitative \textsuperscript{23}Na ssNMR and DFT calculations. As the process of Li\textsuperscript{+} ions substituting Na\textsuperscript{+} ions undergoes, the peaks in the \textsuperscript{23}Na ssNMR spectra move from high frequencies to low frequencies in fig. S8, which means that under-coordinated Na\textsuperscript{+} ions are more preferential to be substituted by Li\textsuperscript{+} ions than high-coordinated ones. The NMR results are in accord with the thermodynamic calculations in fig. S9, in which the formation energies of Li\textsuperscript{+} substituted under-coordinated Na\textsuperscript{+} ions (Na\textsuperscript{+} sites and Na\textsuperscript{III} sites) are about 0.06 eV lower per Li\textsuperscript{+} substituted Na\textsuperscript{+} than those of Li\textsuperscript{+} substituted high-coordinated Na\textsuperscript{+} ions (Na\textsuperscript{II} sites). In addition, except for NZSP and LZSP, two intermediate compounds, Li\textsubscript{2}Na\textsubscript{2}Zr\textsubscript{2}Si\textsubscript{2}PO\textsubscript{12} and Li\textsubscript{2}Na\textsubscript{2}Zr\textsubscript{2}Si\textsubscript{2}PO\textsubscript{12}, were further identified by controlling exchange temperature and time, and then tested with EIS (fig. S10). The presence of intermediates indicates that the skeleton-retained cationic exchange approach can also be used to develop hybrid inorganic superionic conductors (see figs. S10 to S14 and more discussions in text S1).

Ionic conductivity of the LZSP solid electrolyte

Before electrochemical tests, the content of unwrapped Na\textsuperscript{+} ions and residual ionic liquid was determined to evaluate their potential influences. As shown in fig. S15 and table S5, there are no detectable Na, N, and P relevant impurity; their potential influence on electrochemical performances is therefore not considered further. The ionic conductivity of LZSP solid electrolyte was subsequently tested with EIS. In Fig. 3A, the Nyquist plots record from 10^{0} to 60^{0}C comprised one semicircle at the high- to medium-frequency region and a tail at the low-frequency region, which are attributed to the impedance of grain boundary (R\textsubscript{gb}) and the Li\textsuperscript{+} transfer resistance between electrolyte and Au blocking electrodes. The semicircle corresponding to the bulk resistance (R\textsubscript{bulk}) is missing, which is limited by the frequency measuring range. The values of R\textsubscript{bulk} and R\textsubscript{gb}, however, can be fitted with an equivalent circuit of the form R\textsubscript{bulk}, R\textsubscript{gb}, Q\textsubscript{gb}, and Q\textsubscript{electrode}, where R is the resistance and Q is the constant phase element (10, 33). LZSP pellets were used to assemble Au/LZSP/Au symmetric cells. Generally, to densify powdered ceramic solid electrolytes, the most commonly used approach is to press the powders into pellets and then sinter the pellets under high temperatures (typically 1200°C or higher) (19, 34). However, thermal analysis indicates that LZSP powders would undergo phase transition after 742°C (fig. S16). Although its phase stability temperature of 742°C is lower than that (1000°C) of usual NASICON-type solid electrolytes (12, 35), this temperature is much higher than the reported cathode dissociation temperature in the previous literature (36). Therefore, a hot-pressing sintering process at 700°C for 1 hour under a fixed pressure of 70 MPa was carried out to prepare LZSP pellets (the synchrotron XRD and \textsuperscript{17}O ssNMR spectra in fig. S17 prove that the structure of LZSP annealed under 700°C keeps unchanged). The prepared LZSP pellet (fig. S18) is characterized to have a thickness of 2.4 mm and a relative density of about 83% (the porosity is 17%). At 20°C, it exhibits the bulk and total Li\textsuperscript{+} conductivities of 3.59 × 10^{-3} (fig. S19) and 8.75 × 10^{-6} S cm^{-1}, respectively. When temperature is increased to 60°C, the bulk and total Li\textsuperscript{+} conductivities of LZSP are enhanced to 9.0 × 10^{-3} and 1.64 × 10^{-5} S cm^{-1}, respectively. Two approaches could be applied to make denser pellet and improve total ionic conductivity (37–39). On the one hand, we prepared composite pellets for solid-state batteries, where SN and LiTFSI were added to fill the pores between LZSP particles. With a higher relative density of 95%, the total ionic conductivity increases to 8.71 × 10^{-4} S cm^{-1} at 20°C, as shown in fig. S20. On the other hand, the denser LZSP pellet could be prepared through advanced vacuum hot-pressing technique. The outstanding conductivity benefits from the expanded bottleneck sizes and the improved Li\textsuperscript{+} transportation. Moreover, the ionic conductivity increases in line with elevated temperature, which accords with the Arrhenius curves (40). A reliable activation energy for the mobility of Li\textsuperscript{+} ions in LZSP is accordingly normalized to be 0.21 eV (fig. 3B). The comparative study indicates that LZSP has the top value of bulk ionic conductivity among all reported NASICON-type solid electrolytes and is superior to other undoped oxide solid electrolytes (which are marked with horizontal lines in fig. 3C).

Diffusion mechanism and kinetics

To reveal the influence mechanism of under-coordinated Li\textsuperscript{+} configuration (tetra-/penta-coordinated Li\textsuperscript{+}) on ionic conductivity of LZSP, DFT calculations combined with ab initio molecular dynamics (AIMD) simulations were carried out to characterize Li\textsuperscript{+} occupancy, structural stability, and ionic conductivity of LZSP. The structural evolution of LZSP was investigated in fig. S14. Compared with the LZSP configuration of Li\textsuperscript{+} ions substituting Na\textsuperscript{+} ions in NZSP without structural relaxation, the LZSP configuration within structural relaxation has a further reduced volume with the contraction from 1.14 to 10.2%. Meanwhile, some of the Li\textsuperscript{+} ions, which take the initial sites of hexa-coordinated Na\textsuperscript{+} sites and Na\textsuperscript{III} sites, move to the sites of tetra-coordinated Li\textsuperscript{IV} sites and the other Li\textsuperscript{+} ions move slightly off the sites of octa-coordinated Na\textsuperscript{II} sites to form penta-coordinated Li\textsuperscript{III} sites with Wyckoff site transformation from 4e to 8f (see fig. S21 and table S7). Compared with hexa-coordinated Li\textsuperscript{+} ion in traditional phosphatic solid electrolytes, the coordination of penta-/tetra-coordinated Li\textsuperscript{+} ions in produced LZSP is decreased. The coordination reduction of Li\textsuperscript{+} ions, accompanied by lattice contraction, leads to a 0.19 eV/formula lower free energy. Furthermore, different LZSP configurations, by tuning Li\textsuperscript{II} occupations from 50 to 31.25% with a constant difference of 6.25%, are built to screen the thermodynamically stable structure. The configuration with 43.8% occupancy Li\textsuperscript{II} sites is found to have the lowest free energy, of which the ab plane is compressed and the c axis is expanded compared with other LZSP configurations (fig. S14). The kinetic stability of screened LZSP configuration was investigated by mean square displacement (MSD) from AIMD simulations in canonical ensemble (NVT). As the temperature increases from 300 to 1000 K, the MSDs of Si/P and Zr atoms are near invariable and the maximal MSD of O...
Intrinsically, the active effect in LZSP plays an important role in not only making the run-through channel network structure but also increasing mobile Li-ion, both of which can effectively enhance ionic conductivity.

The lower migration barrier should be attributed to a suitable bottleneck size for migration ions. Previous studies show that the transition state structure of ionic conduction commonly corresponds to Li\textsuperscript{+} passing through the bottleneck between two polyhedrons (27). According to the Shannon effective ionic radius table, Na\textsuperscript{+} and Li\textsuperscript{+} ions have obviously different critical sizes of the bottleneck, 2.37 Å for Na-O and 1.94 Å for Li-O (41). Those migration paths, of which the bottlenecks are smaller than this critical size, would block the migration of Na\textsuperscript{+}/Li\textsuperscript{+} ions. Since cationic exchange leads to little effect on the bottleneck size, 2.16 Å for the migration path of Na\textsuperscript{+}-Na\textsuperscript{+} and 2.13 Å for the migration path of Li\textsuperscript{+}-Li\textsuperscript{+}, Li\textsuperscript{+} ions are capable of passing through the bottleneck but Na\textsuperscript{+} ions fail. The comparison shows that Na\textsuperscript{+} migration is inactive in NZSP but exchanged Li\textsuperscript{+} migration is active in LZSP.

In comparison, the transition state along migration paths Li\textsuperscript{IV}-Li\textsuperscript{I}, Li\textsuperscript{IV}-Li\textsuperscript{II}, and Na\textsuperscript{IV}-Na\textsuperscript{I}, Na\textsuperscript{IV}-Na\textsuperscript{II}, and Na\textsuperscript{IV}-Na\textsuperscript{III} exhibits clear different structures, although they have a similar barrier height (both are 0.17 eV). The former corresponds to the bottleneck structure between tetrahedron and octahedron, whereas the latter corresponds to the hexa-coordinated Li\textsuperscript{I} structure. Their bottleneck sizes are very similar, 2.37 Å for Na\textsuperscript{+} and 2.38 Å for Na\textsuperscript{+}. The transition state structure change shows that such a large-size bottleneck does not inhibit Li\textsuperscript{+} migration. This firstly reported migration mechanism, enlarging the bottleneck size to reduce the migration barrier, is of much importance to design the
Fig. 4. Single-ion migration mechanisms of Na$^+$ ion and Li$^+$ ion from CI-NEB. (A) Energy barriers for single-ion migration of Na$^+$ ion following the NaII-NaIV-NaI-NaIV-NaIII trajectory. (B) Energy barriers for single-ion migration of Li$^+$ ion following the LiII-LiIV-LiI-LiIV-LiIII trajectory. The blue and purple balls stand for Na$^+$ ions and Li$^+$ ions, respectively. The olive, light green, pink, and sky-blue polyhedrons identify the Na$^{\text{IO}}_{8}$ dodecahedron, Li$^{\text{IO}}_{5}$ pentahedron, Na$^{\text{IV}}$O$_{4}$/Li$^{\text{IV}}$O$_{4}$ tetrahedrons, and Na$^{\text{III}}$O/Li$^{\text{III}}$O/Li$^{\text{II}}$O$_{6}$ octahedrons, respectively.

Fig. 5. Diffusion kinetics of NZSP and LZSP from AIMD simulations. (A) Diffusion pathways in monoclinic NZSP at 600 K. (B) Diffusion pathways in monoclinic LZSP at 600 K. (C) Arrhenius plot of Na$^+$ diffusivity $D$ as a function of temperature $T$ in NZSP. (D) Arrhenius plot of Li$^+$ diffusivity $D$ as a function of temperature $T$ in LZSP.
structure of solid electrolytes. Recently, Zhang et al. (27) reported the high-energy site of Na\textsuperscript{IV} in NZSP by increasing the Na\textsuperscript{II}-ion concentration. In this work, we also found low-occupancy Li\textsuperscript{II} sites in LZSP, originating from unoccupied Li\textsuperscript{II} sites. These high-energy sites of Li\textsuperscript{II} increase the coulombic repulsions of Li\textsuperscript{II} ions following the trajectory path of -octahedron-tetrahedron (Li\textsuperscript{IV})-octahedron-and, depending on the concentration of high-energy sites, enhance the correlated migration of Li\textsuperscript{II} ions.

Direct comparison for two DFT-calculated potential energy profiles (Fig. 5) demonstrates that cationic exchange has made a notably lower migration barrier in under-coordinated Li\textsuperscript{II}-Li\textsuperscript{IV} than in high-coordinated Na\textsuperscript{II}-Na\textsuperscript{IV}. To verify the activation effect, AIMD simulations at a temperature of 600 K were performed to reveal the migration path change induced by cationic exchange. The Na\textsuperscript{II} and Li\textsuperscript{II} diffusion pathways of NZSP and LZSP from AIMD simulations under the same simulation conditions are presented in Fig. 5 (A and B), respectively. It is obvious that octa-coordinated Na\textsuperscript{II} sites with 100% occupancy exhibit negligible ionic migration into the Na\textsuperscript{II}-Na\textsuperscript{IV} pathway. But hexa-coordinated Na\textsuperscript{II} and Na\textsuperscript{III} with fractional occupancy present continuous and intertwined diffusion pathways, indicating the 2D migration mechanism. In contrast, LZSP presents the 3D migration mechanism since Li\textsuperscript{II} sites in the corresponding position of Na\textsuperscript{II} become active by forming the Li\textsuperscript{II}-Li\textsuperscript{IV} migration pathway. The activation effect is attributed to the size of the bottleneck located in the under-coordinated Li\textsuperscript{II}-Li\textsuperscript{IV} segment, which is 0.19 Å larger than the sum of Li\textsuperscript{II} and O\textsuperscript{2−} radii.

According to extensive AIMD simulations at different temperatures, diffusion lengths of Na\textsuperscript{II} and Li\textsuperscript{II} ions at different sites in NZSP and LZSP are correlated with simulated temperatures. The fitted activation energies for different sites are also presented in Fig. 5 (C and D). It is obvious that the activation energies from AIMD in Fig. 5 are much lower than the migration barrier of the single-ion direct-hopping mechanism in Fig. 4 because the correlated migration is the preferred conduction mechanism in LZSP and NZSP, which was studied by Zhang et al. (27). The activation energy of Na\textsuperscript{II} (0.22 eV) is nearly twice the values of those of Na\textsuperscript{II} and Na\textsuperscript{III} (0.12 eV). However, the activation energy of Li\textsuperscript{II} is comparable with those of Li\textsuperscript{III}, Li\textsuperscript{IV}, and Li\textsuperscript{V}. Octa-coordinated Na\textsuperscript{II} sites with full occupancy only maintain equivalent vibration and do not exhibit the migration path. In contrast, the Li\textsuperscript{II} sites in the similar position are turned into active ion migration along the Li\textsuperscript{II}-Li\textsuperscript{IV} path, which should be attributed to fractional occupancy and lower migration barrier of Li\textsuperscript{II}. The activation effect plays an important role in not only turning the 2D into 3D migration path but also increasing the percentage of mobile ion rising from 67% in NZSP to 100% in LZSP. As a result of increased mobile ion and decreased migration barrier, the ionic conductivity of LZSP is theoretically predicted as high as 1.46 \times 10^{-2} S cm^{-1}.

In addition to thermal stability and ionic conductivity, other properties such as chemical stability against air and the tolerance of voltage are also investigated under electrochemical conditions. At room temperature, the LZSP powders are aged for 0, 100, and 200 hours within air to test the environmental stability. The Li\textsuperscript{II} ssNMR, powder synchrotron XRD, and C 1s x-ray photoelectron spectra (XPS) of these samples were recorded afterward and shown in fig. S25. No Li\textsubscript{2}CO\textsubscript{3} relevant signals (a typical production as a result of air erosion) (42) were observed whenever the aged period was manifesting the excellent stability against air (see more discussion in text S2). Similar to the robust NZSP with the advantage of commendable air survivability (the exchange of protons with the surfaces of NZSP is tough, which prevents air-exposed NZSP powders from deteriorating) (43, 44), the derived LZSP electrolyte inherits its excellent stability against moisture and CO\textsubscript{2} and requires no more extra seal measures if used in practical storage and transportation. To further reveal electrochemical stability, first-principles thermodynamic calculations were used to identify the thermal phase equilibria at different potentials for LZSP. According to our calculated reaction enthalpies, the LZSP is identified to have an electrochemical stability window of ~4 V (fig. S26), which is the top value among all the oxide solid electrolytes. This wide electrochemical window may be attributed to a high endothermicity (4.58 eV) of charge reaction formation of SiO\textsubscript{2} + P\textsubscript{2}O\textsubscript{5} + ZrO\textsubscript{2} + O\textsubscript{2} and a low exothermicity (0.48 eV) of discharge reaction formation of Li\textsubscript{2}Si\textsubscript{3} + Li\textsubscript{3}P + Zr\textsubscript{2}O + Li\textsubscript{2}O.

### Electrochemical test of solid-state batteries

To better eliminate the grain boundary impedance among LZSP nanoparticles, a thermal-assisted cold sintering approach was used to prepare dense LZSP composite pellets (45, 46). Furthermore, to negate the high interfacial resistance between the electrolyte and the electrode, soft polyethylene oxide–ethylene carbonate (PEO-EC) buffer layers were coated on the two surfaces of the LZSP composite pellets in the solid-state cells through an in situ solidification method (see more discussion in text S3 and figs. S27 to S30). A Li/LZSP/Li symmetric cell was fabricated to demonstrate the Li-ion transport capability of the LZSP solid electrolyte. As presented in Fig. 6A, lithium plating/stripping in the symmetrical Li/LZSP/Li cell remains stable for 2000 hours at room temperature with a current density of 0.1 mA cm\textsuperscript{-2}, indicating an excellent stability against lithium metal. In Fig. 6B, measured by an Au/LZSP/Li cell, the electrochemical window of the solid electrolyte is stable up to 6 V versus Li/Li\textsuperscript{+}, which is enough for the requirement of lithium batteries (all the subsistent batteries can withstand a charging voltage of up to 5 V) (47).

High ionic conductivity, good stability against lithium metal and air, and wide stability window make LZSP one of the best candidate electrolytes [e.g., Li\textsubscript{2}La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{12} (LLZO) (10), Li\textsubscript{2}GeP\textsubscript{2}S\textsubscript{4} (6, 48), and Li\textsubscript{3}M(M = Y, Sc, In)Cl\textsubscript{6} (49–53)] for developing commercial solid-state lithium batteries (table S8). A full cell containing the LZSP electrolyte pellet, the buffer layers, the NCM523 cathode, and the anode of Li metal was then designed to make a demonstration. Figure 6C shows the initial charge and discharge curves of the NCM523/LZSP/Li cell at 0.1 C (0.1 C = 15 mA g\textsuperscript{-1}) at room temperature. The discharge specific capacity and coulombic efficiency of the first cycle are 162.0 mAh g\textsuperscript{-1} and 85.8%, respectively. After 100 cycles, there is a minor capacity fading for the cell and it delivered a specific capacity of 146.0 mA h g\textsuperscript{-1}, equal to 90.1% of the initial discharge capacity (Fig. 6D), which surpasses the relevant performance of NCM523-based (cathode) and Li metal–based (anode) batteries using liquid electrolytes (fig. S31). Besides, rate performance was also tested at the current rate of 0.2, 0.5, 1.0, and 2.0 C, respectively, and high specific discharging capacities of 157.5, 141.8, 116.2, and 96.9 mA h g\textsuperscript{-1} were maintained (Fig. 6E). Compared to previously reported NCM523/Li cells based on other solid electrolytes (table S9), without any liquid wetting, the rate capacity, cycling performance, and discharge-specific capacity of this NCM523/LZSP/Li solid-state batteries are in the highest tier.

The synthesis approach of skeleton-retained cationic exchange could be commonly used to produce more solid electrolyte, even extensive inorganic materials, by controlling suitable reaction conditions. Several reactions such as Na\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2} (NLP) → Li\textsubscript{3}La(PO\textsubscript{4})\textsubscript{2}...
The conductivity of LZSP is up to $3.59 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature, resulting in low migration barriers for lithium cations to hop along 3D continuous migration channels. As a result, the bulk ionic conductivity is obtained, which is beneficial in regulating the coordination structure of diffusion ions for improving ionic conductivity but also could be used to make new inorganic materials.

**DISCUSSION**

In conclusion, skeleton-retained cationic exchange approach is used to produce a high-performance solid electrolyte with under-coordinated conduction Li$^+$ ions and expanded bottleneck sizes. Using the NASICON-type solid electrolyte NZSP as a precursor, an unreported solid electrolyte, LZSP, with under-coordinated Li$^+$ ions is harvested. The imported lithium cations acclimatize themselves to the relatively large skeleton by the reduction of Li coordination, resulting in low migration barriers for lithium cations to hop along 3D continuous migration channels. As a result, the bulk ionic conductivity of LZSP is up to $3.59 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature, which is the top value among the current oxide solid electrolytes. In addition, the LZSP material not only shows satisfactory environmental survivability but also performs wide electrochemical window and long stability against Li metal in the use of LZSP-based solid-state batteries, indicating it as an advanced solid electrolyte with commercial promise. The present study indicates that the synthesis approach of skeleton-retained cationic exchange not only is effective in regulating the coordination structure of diffusion ions for improving ionic conductivity but also could be used to make new inorganic materials.

**MATERIALS AND METHODS**

**Preparation of NZSP**

The synthesis of NZSP powders is referenced from Zhang et al. (27). Three milliliters of tetraethyl orthosilicate, 10 ml of water, and 5 ml of ethanol were mixed and then stirred at room temperature for 10 min. After adding in 50 ml of water and 17 g of citric acid, the pH value of this mixed solution was controlled at 1.5 with HNO$_3$ dropwise. Stirring at 333 K for 1 hour, a solution consisting of 5.132 g of ZrO(NO$_3$)$_2$$\cdot$2H$_2$O, 2.037 g of NaNO$_3$, and 1.055 g of (NH$_4$)$_2$HPO$_4$ was added while stirring at 353 K. The resulting solution was then transferred into an oil bath pan to evaporate residual water at 353 K for 24 hours. The obtained yellow dried gel was ball-milled at 600 rpm and then calcined at 1073 K in air. After grinding through an agate mortar, white NZSP powders were harvested.

**Process of skeleton-retained cation exchange**

In a typical skeleton-retained cation exchange procedure, 22.996 g of LiTFSI was dissolved in 40 ml of EMIMI in an Ar-filled glove box. The mixture was stirred at 333 K for 30 min and then cooled down to room temperature. Afterward, 2.829 g of NZSP was mixed with the above solution. The resulting white suspension was then sealed in a 100-ml reactor and heated in an oven at 453 K for 24 hours with a swing speed of 50 rpm. Subsequently, the white sediment was centrifuged, washed with ethanol, and dried at 353 K for 6 hours. All these above steps should be performed three times to yield pure LZSP powders (without residual sodium cation). After calcination at 773 K for 5 hours to remove the possible residual EMIM, the target LZSP material is harvested. The exchanged ionic liquid can be reused through renewable process of zeolite adsorption, which is favorable to reduce cost of scale-up production.
Process of $^{17}$O isotopic labeling
In the $^{17}$O isotopic labeling process, 200 mg of NZSP or LZSP was sealed in a glass tube and then annealed at 673 K under $1 \times 10^{-4}$ torr for 3 hours to get rid of surface-adsorbed impurities. Cooling down to room temperature, 90% $^{17}$O-enriched O$_2$ gas (50 mbar, Isotec Inc.) was introduced and the glass tube was sealed again to heat at 673 K for 24 hours. Last, the samples were evacuated at $1 \times 10^{-4}$ torr for 30 min to remove residual $^{17}$O-enriched O$_2$ gas.

Characterization
Synchrotron XRD measurements were performed at the Beamline BL14B1 of Shanghai Synchrotron Radiation Facility (SSRF) in China. A medium-energy (18 keV, $k=0.6887$ Å) x-ray beam (200 μm by 200 μm) is used. The NPD experiments were carried out at room temperature using high-resolution neutron powder diffractometer at China Mianyang Research Reactor. The incident beam with a wavelength $\lambda=1.8846$ Å was vertically focused by a Ge (511) monochromator at a fixed take-off angle of 120°. Diffraction patterns were collected from 10° to 150° with a step increment of 0.06°. $^{23}$Na, $^{17}$O, and $^6$Li magic angle spinning NMR (MAS NMR) measurements were recorded on a 9.4-T Bruker Avance III 400 spectrometer at Larmor frequencies of 105.8, 54.2, and 58.8 MHz, respectively. Dry powders to be measured were packed into 4.0-mm ZrO$_2$ rotors in a N$_2$-filled glove box. $^{23}$Na, $^{17}$O, and $^6$Li NMR shifts were referenced for 3 hours to get rid of surface-adsorbed impurities. Cooling down to room temperature, 90% $^{17}$O-enriched O$_2$ gas (50 mbar, Isotec Inc.) was introduced and the glass tube was sealed again to heat at 673 K for 24 hours. Last, the samples were evacuated at $1 \times 10^{-4}$ torr for 30 min to remove residual $^{17}$O-enriched O$_2$ gas.

Computational methods
First-principles calculations were used to calculate the structural and electronic properties as implemented in the Vienna Ab initio Simulation Package (54). The plane-wave projector-augmented wave method (55, 56) with an energy cutoff of 400 eV and Monkhorst-pack $k$-meshes (57) were used to investigate the structural and transport properties by using generalized gradient approximation with Perdew-Burke-Ernzerh exchange-correlation functional (58). All atomic coordinates and lattice parameters are fully relaxed until the force convergence of 0.01 eV Å$^{-1}$ and the energy convergence of $10^{-4}$ eV atom$^{-1}$ are achieved. AIMD calculations were carried out in the canonical ensemble (NVT) using a Nosé thermostat at 300, 600, 800, 1000, and 1200 K with a time step of 3 fs for 30 ps to calculate MSDs and at 600 K for an appropriate time to investigate the diffusion pathways of conductive ions (59). AIMD and climbing image nudged elastic band (CI-NEB) (60) calculations revealed the transport properties of Na$^+$ and Li$^+$ ions via a correlated migration mechanism.

Fabrication of LZSP pellets
A hot-pressing sintering process was applied to obtain pure LZSP pellets. The LZSP powders were placed into the mold for dry pressing and sintered at 700°C under a fixed pressure of 70 MPa for 1 hour. After natural cooling to room temperature, the LZSP electrolyte pellet with a diameter of 10 mm was obtained. To better eliminate the grain boundary impedance among LZSP nanoparticles in the pure LZSP pellets, a thermal-assisted cold sintering approach was used to prepare dense LZSP composite pellets (45, 46). First, succinonitrile (SN) and LiTFSI with a mass ratio of 85:15 were mixed uniformly. Second, the LZSP powders were added and ground for 30 min. Last, the composite powders (90 weight % (wt %) LZSP, 10 wt % SN, and LiTFSI) were pressed at 130°C for 1 hour, and 810-MPa uniaxial pressure was applied. After natural cooling to room temperature, the LZSP composite pellet with a diameter of 10 mm was obtained. All operations were carried out in a drying room with a dew point at ~40°C.

Pure LZSP pellets prepared by the hot-pressing sintering process were used to measure the ionic conductivities. LZSP composite pellets prepared by the thermal-assisted cold sintering approach were used to measure other electrochemical properties.

Electrochemical tests
The ionic conductivities of the electrolyte pellets were calculated from Nyquist plots, which were performed on an electrochemical workstation (Bio-Llogic, VSP-300) with an AC amplitude of 50 mV from 7 MHz to 0.1 Hz by sputtering Au blocking electrodes on both sides of the pellets. The bulk and total ionic conductivities were obtained by fitting results using the ZView software. The ionic conductivities were calculated through $\sigma = \frac{L}{R \cdot S}$, where $\sigma$, $L$, $R$, and $S$ denote the ionic conductivity, the thickness of the pellet, the resistance, and the effective area of the electrode, respectively. For the Li/LZSP/Li symmetric cells, to improve the interface contact between the electrolyte and electrode, a PEO-EC buffer layer precursor solution was prepared by dispersing PEO (M$_{\text{PEO}}$ = 600,000, Sigma-Aldrich) and EC (99.0%, Adamas) in dimethyl carbonate and stirred for 30 min at 60°C. The PEO-EC buffer layer precursor solution was casted onto one side of the LZSP composite pellet and naturally volatilized for 12 hours to remove the dimethyl carbonate solvent, and two lithium foils were pasted on the buffer layers. The Li/LZSP/Li symmetric cells were investigated using a LAND battery tester (CT2001A, Wuhan LAND Electronics) under a current density of 0.1 mA cm$^{-2}$.

The Au/LZSP/Li coin cells were assembled with a lithium foil pasted on the buffer layer as the counter electrode and a gold film sprayed on the other side of the pellet as the working electrode. The electrochemical window measurement was scanned in a range of −0.5 to 6.0 V at 1 mV s$^{-1}$ at room temperature using a CHI604E electrochemical workstation.

The charge-discharge properties were evaluated by NC523/LZSP/Li cells with soft PEO-EC buffer layers adhered to both sides of the LZSP composite pellet. The NC523 cathode was composed of 77 wt % NC523, 10 wt % Super P, 10 wt % polyvinylidene difluoride, and 3 wt % LiTFSI. The NC523/LZSP/Li cell was tested between 2.8 and 4.3 V at current densities of 15, 30, 75, 150, and 300 mA g$^{-1}$.

**SUPPLEMENTARY MATERIALS**
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