Understanding Ionic Conductivity Trends in Polyborane Solid Electrolytes from Ab Initio Molecular Dynamics

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Supporting Information

ABSTRACT: Polyborane salts based on B_{12}H_{12}^{2−}, B_{10}H_{10}^{2−}, CB_{11}H_{12}^{−}, and CB_{9}H_{10}^{−} demonstrate high Li and Na superionic conductivity that makes them attractive as electrolytes in all-solid-state batteries. Their chemical and structural diversity creates a versatile design space that could be used to optimize materials with higher conductivity at lower temperatures; however, many mechanistic details remain enigmatic, including reasons why certain known modifications lead to improved performance. We use extensive ab initio molecular dynamics simulations to explore the dependence of ionic conductivity on cation/anion pair combinations for Li and Na polyborane salts. Further simulations are used to probe the influence of local modifications to chemistry, stoichiometry, and composition. Carbon doping, anion alloying, and cation off-stoichiometry are found to favorably introduce intrinsic disorder, facilitating local deviation from the expected cation population. Lattice expansion likewise has a positive effect by aiding anion reorientations that are critical for conduction. Implications for engineering polyboranes for improved ionic conductivity are discussed.

Recently a class of polyborane salts has emerged as highly promising solid electrolyte candidates due to their exceptional Li and Na conductivities that can approach or even exceed 0.1 S cm⁻¹ at room temperature. Initially investigated as stable byproducts in hydrogen storage chemistries, these compounds are typically alkali salts of closo-borane molecular species such as B_{12}H_{12}^{2−} or B_{10}H_{10}^{2−} that form anion sublattices of various crystallographic symmetries. The pseudoaromatic character of the closo-borane “cages” leads to high thermal and electrochemical stability as well as an ability to form ionically conductive salts. A rapid increase in ionic conductivity results from a first-order phase transition to a disordered cation sublattice, with the transition temperature and resulting conductivity dependent on the anion and cation species. Despite advances that have driven the superionic transition to lower temperatures, such as carbon doping, alloying, and synthesis variations, many questions remain regarding the origins of these successes in terms of the fundamental mechanisms that drive ionic conductivity. This lack of understanding has impeded the adoption of a more rational design approach, motivating the need for more detailed and systematic investigations that properly leverage the rich diversity of this materials class toward commercial viability. To this end, we perform extensive ab initio molecular dynamics (AIMD) simulations within an automated high-throughput scheme to broadly explore conductivity trends in polyborane superionic conductors. Our studies offer new mechanistic understanding and guidance for future optimization of ionic conductivity in polyborane-based solid electrolytes.

AIMD simulations were run on (√2 × √2 × 1) supercells within the canonical (NVT) ensemble using the Quantum Espresso code and the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional (see Supporting Information and Figure S1 for details). In Figure 1a, we show the computed activation energy barriers for bulk stoichiometric compounds of Li⁺ and Na⁺ cation combinations with B_{12}H_{12}^{2−}, B_{10}H_{10}^{2−}, and...
Figure 1 (a) Activation energies for cation diffusivity in Li and Na close-(carbo)boranes computed from Arrhenius plots of AIMD simulations (see Figure S2 in the Supporting Information). The symmetries of the anion centers are colored with red, green, blue, and orange for derivatives of fcc, bcc, orthorhombic, and monoclinic structures, respectively. (b) Schematic of one material in panel a, fcc Li,B₁₂H₁₂ in the low-temperature α phase. Motifs adopting the different anion species shown at right (B₁₀H₁₀⁻², CB₁₁H₁₂⁻, and CB₉H₁₀⁻) were also considered.

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their carborane analogs CB₁₁H₁₂⁻ and CB₉H₁₀⁻ in various crystal structures. As discussed in the Supporting Information, we estimate that the PBE barriers are within ~10–15% of those obtained using more accurate hybrid functionals; nevertheless, trends should be robustly predicted. Collectively, the tested systems encompass the primary polyborane compositions with known superionic behavior. Full Arrhenius plots for temperatures from 400 to 900 K can be found in Figure S2 in the Supporting Information; at lower temperatures (≤500 K) where experimental data are available, the computed diffusion coefficients in Figure S2 generally follow trends consistent with published observations, with the carboranes as the most conductive, B₁₀H₁₀ compounds more conductive than B₁₂H₂⁰, and Na salts more conductive than Li salts. Figure 1b shows one representative structure (fcc α-Li,B₁₂H₁₂) among the systems we studied, along with a schematic of the various anion chemistries we tested.

Significantly, the results of Figure 1 demonstrate no clear pattern connecting the point-group symmetry of the anions to cation mobility, as has been suggested in other superionic systems. Many structural variants of the Na and Li close-boranes exhibit high ionic conductivity, with no clear preference for one symmetry over another; accordingly, crystal structure alone is insufficient as a descriptor for low-barrier conductivity. In certain cases (particularly the mixed-cation alloy LiNaB₁₁H₁₂) our results also identify fairly large uncertainties in the determination of the activation energy barriers (see Supporting Information for details). While some sampling error is present in the computation of the diffusion coefficients, the primary origin of the uncertainty is non-Arrhenius behavior, as signaled by deviations from linearity in the Arrhenius plot (Figure S2). Such non-Arrhenius behavior has been suggested as a common feature in superionic systems, and its relevance will be discussed further below.

To further investigate mechanisms and elucidate observed trends in Figure 1, we ran a series of AIMD “experiments” on Li₂B₁₂H₁₂ designed to isolate the effects of stoichiometry, volume, and relevant chemical modifications. Given the structural and chemical similarities between the polyboranes, qualitative conclusions should be generalizable across the compounds in Figure 1. In the low-temperature α phase of Li₂B₁₂H₁₂, the B₁₂H₁₂⁻ anions occupy an fcc arrangement with the Li sublattice ordered. The superionic transition to the high-temperature β phase at 628 K retains the fcc anion symmetry but is accompanied by an 8.7% volume expansion and orientational disordering of the B₁₂H₁₂⁻ units. The similar fcc structures of α-Li₂B₁₂H₁₂ and β-Li₂B₁₂H₁₂ allow decoupling from the effects of crystal symmetry.

The tested perturbations can be grouped into five general classes (Figure 2): cation off-stoichiometry via lithium vacancies (Vᵢ⁻ Li), or interstitials (Li⁺); aliovalent anion substitution by CB₁₁H₁₂⁻ (C⁺) or B₁₂H₁₁⁻ (V⁺); isovalent anion substitution by B₁₀H₁₀⁻² ((B₁₀H₁₀)₁(B₁₂H₁₂)⁻); hydrogen interstitials (H⁺ and H⁻); and volume expansion from the α phase to the β phase. Charge compensation of C⁺ by defect pairing with V⁺ or V⁻ was also included. All substitutions were considered in the dilute limit. Cation alloying (LiNaB₁₁H₁₂ in Figure 1) can be considered a sixth general class of perturbation.

Calculated diffusion coefficients at 800 K are shown in Figure 2a. This temperature maximized statistics while preserving the lower temperature mechanisms (higher temperatures often exhibited an increased activation barrier, similar to other superionic conductors). We also consider a discrete statistics-based jump analysis of the AIMD trajectories to supplement the diffusion constants (Figure 2b). This approach provides an alternative description that overcomes shortcomings in typical Brownian motion-based analyses. To understand the behavior at other temperatures, we also include the activation energy barriers extracted from the Arrhenius plots (Figure 2c). At 800 K, each of the perturbations influences the calculated Li diffusivity, increasing D as much as several fold relative to the pure α-Li₂B₁₂H₁₂ reference. Indeed, several of these strategies have been previously demonstrated to enhance conduction, including C doping and anion alloying. From the discrete jump analysis (Figure 2b), we find that not only does the total Li jump frequency increase but so does the relative proportion of “mobile” jumps that contribute to Li conduction (proceeding to another unique site without returning to the original site; see the Supporting Information).

Interestingly, the activation barrier trends (Figure 2c)—generally a better predictor of low-temperature behavior—do not necessarily follow the trends in the diffusion coefficients at 800 K (Figure 2b). Accordingly, a significant role is played by prefactors at higher temperature, which exhibit anomalously broad disparity; such anomalous prefactor behavior has been discussed in the context of other superionic systems. Moreover, the uncertainties in the Arrhenius fits are often very large, particularly for higher-barrier processes (α-Li₂B₁₂H₁₂ and the defect pair complexes). This again points to non-Arrhenius behavior because the statistical quality of the diffusion coefficients (Figure 2a) is reasonable. Because the data in
Figure 2. Trends in Li+ diffusivity in Li1.5B12H12 upon perturbations to stoichiometry and composition. (a) Diffusion constants at 800 K calculated from the mean-squared displacement; (b) associated frequency of discrete jumps; and (c) barriers computed from temperature-dependent Arrhenius plots. See the text for definitions of the labels. In panel b, the size of the bars denotes the total frequency of jump events, with the fraction of “mobile” jumps indicated in blue. Standard-error uncertainties for the linear fits are shown in panels a and c.

Figure 2c derive from linear Arrhenius fits over all simulated temperatures for which diffusion was observed, the quantitative accuracy of the barriers should not be overemphasized.

Several of the perturbations in Figure 2 can be interpreted as introducing symmetry-breaking extrinsic disorder into the crystal. Li off-stoichiometry (e.g., via aliovalent doping) prevents cation ordering25 (B10H10)B12H12, the barrier is much higher (>773 meV) because fluctuations first require formation of pairs of overpopulated and underpopulated local complexes. However, subsequent diffusion may proceed with a far lower barrier once these pairs are unbound, which explains why moderate diffusivity is nonetheless observed in Figure 2a,b. As further confirmation of this interpretation, we estimated the separation barrier in the system by computing the binding energy between the constituent defect pairs. The value of ∼400 meV matches the difference between the calculated Li diffusion barrier (955 meV) and that of individual CB− or VLi+ defects (541–543 meV). The proposed multibarrier nature also explains the larger non-Arrhenius behavior of the high-barrier complexes. While H4− does not complex with the closo-borane anions, we propose that the low barrier arises from competition with B12H12− anions for nearby Li+, which can catalyze cation density fluctuations.

The connection between local cation density fluctuations and diffusivity is explored further in Figure 3. In this example based on α-Li1.5B12H12 at 800 K, Li+ records periods of relatively low and relatively high diffusivity (Figure 3a), the latter of which results from rapid, highly correlated motion of multiple nearby cations that is also reflected in the average internal energy (Figure 3b). Figure 3c shows how these highly diffusive periods (e.g., < 10 ps and 35–55 ps) follow initial increases in the momentary fraction of Li+ ions that deviate from expected local stoichiometry, determined by tracking the occupation of volume-filling polyhedra in the fcc lattice with respect to the mean stoichiometric value (see Supporting Information for details). (d) Distribution of coordination numbers n of Li+ around B12H12−, with the distance cutoff chosen such that <n> = 4. The data represent a portion of the AIMD trajectory for α-Li1.5B12H12 at 800 K. In panels a and b, black lines are running averages over the full data (gray).
landscape. We hypothesize that this frustration may result from an incompatibility between the symmetry and local occupancy of the cation sites, which will be explored in a future publication. Local cation density fluctuations may also be interpreted from a liquid-like viewpoint, as in Figure 3d where a wide distribution of first-shell coordination numbers around anions is apparent. The breadth of this distribution is directly related to the shape of the potential well, implying higher anions is apparent. The breadth of this distribution is directly related to the shape of the potential well, implying higher

Although arguments based on local disorder explain much of the data in Figure 2, they cannot account for the very different barriers for the α and β phases. Because both phases feature an fcc anion arrangement, once the mobile cations become thermally disordered, the key remaining difference lies in their volumes. To explore this effect, we scanned over a much larger range of volumes for Li₂B₁₂H₁₂ at 800 K. Consistent with Figure 2, we find that increasing the volume of the α phase generally enhances conduction, whereas decreasing it slows conduction. However, the diffusivity surprisingly saturates at larger volumes (Figure 4a). The associated jump frequencies (Figure 4b) and activation barriers (Figure 4c) further suggest that diffusion actually reaches a maximum before declining at larger volumes. Up to the volume of the β phase, the trend is well-fitted by a linear increase in cation diffusivity. Extrapolation suggests a maximum conductivity at 800 K would be reached after 17% volume expansion relative to the α phase. When we run a similar analysis at different temperatures (Figure S3), the maximum diffusivity is reached at lower volumes at higher temperatures and vice versa. Interestingly, the diffusivity and volume of the LiNaB₁₂H₁₂ alloy from Figure 1 fit the linear trend reasonably well (open circle in Figure 4a), which suggests that the most important influence of Na⁺ alloying for enhanced Li⁺ diffusion lies in the volume increase associated with the larger cation.

For conventional single-barrier vacancy diffusion, increasing the lattice parameter might be expected to lead to a lower barrier for Li⁺ jumping, as it reduces cation repulsion and lessens the lattice distortion required to accommodate the diffusing ion. Alternatively, given the large mass difference between the anions and diffusing cations, one might instead consider cation exploration of an energy landscape that is fixed on the time scale of the diffusive processes. In this case, a larger lattice volume should similarly enhance diffusion by increasing the channel size for Knudsen-type processes. However, neither of these explanations can account for the saturation of conductivity at large volumes. A third compelling possibility that explicitly considers the complex dynamics of the material is that volume increases facilitate anion rotation, which, in turn, enhances diffusivity. This connection has been previously suggested based on comparisons between nuclear magnetic resonance-derived anion rotational frequencies and conductivity in Li₂B₁₂H₁₂ upon transitioning to the high-temperature superionic β phase. Anion rotation was likewise found to be important in a recent computational study on Na₂B₁₀H₁₀.

To analyze B₁₂H₁₂⁻ rotation, we define an angular autocorrelation function \( \phi(t) = \langle \hat{\mathbf{r}}(t) \cdot \hat{\mathbf{r}}(0) \rangle \), where \( \hat{\mathbf{r}} \) is the unit vector from the anion center of mass to a constituent boron atom. Figure 5a shows the decay of \( \phi(t) \) as a function of volume, which at short times measures the anion rotation rate within a rigid-body approximation. Whereas the smallest volume \( V = 0.95V_\alpha \) shows no rotation at all, slow rotation starts at \( V = V_\beta \) and accelerates with volume before saturating at the highest volumes. This trend matches extremely well with the trend in diffusivities in Figure 4; diffusion begins to manifest around \( V = V_\alpha \) once rotation is activated before saturating at higher volumes \( (V = 1.20V_\alpha) \) when the anion rotation rate approaches the unconstrained limit. Figure 5b,c shows the corresponding cation density isosurfaces for the α and β phases, from which the transition from slow to fast diffusion as anion rotation becomes activated is clear.

To further evidence the link between anion rotation and diffusion, we ran simulations at the volumes of the α and β phases in which the anion degrees of freedom were explicitly frozen. A sharp decrease of roughly three orders of magnitude in cation diffusion was observed with respect to the fully dynamical case (down to \( 1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \) for α and \( 2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \) for β). The necessity of B₁₂H₁₂⁻ anion dynamics for

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**Figure 4.** (a) Li diffusion coefficient at 800 K as a function of volume for strained Li₂B₁₂H₁₂ shown relative to the volume of the α phase. The solid lines are linear fits to the data before and after the saturation point at \( \sim 1.17V_\alpha \). Volumes of the α and β phases are shown as dotted vertical lines, and the hollow point represents the data for the LiNaB₁₂H₁₂ alloy. (b) Statistics of discrete Li jump events over the same volume range using ion. Alternatively, given the large mass difference between the anions and diffusing cations, one might instead consider cation exploration of an energy landscape that is fixed on the time scale of the diffusive processes. In this case, a larger lattice volume should similarly enhance diffusion by increasing the channel size for Knudsen-type processes. However, neither of these explanations can account for the saturation of conductivity at large volumes. A third compelling possibility that explicitly considers the complex dynamics of the material is that volume increases facilitate anion rotation, which, in turn, enhances diffusivity. This connection has been previously suggested based on comparisons between nuclear magnetic resonance-derived anion rotational frequencies and conductivity in Li₂B₁₂H₁₂ upon transitioning to the high-temperature superionic β phase. Anion rotation was likewise found to be important in a recent computational study on Na₂B₁₀H₁₀.

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Another strategy that emerges as particularly promising is strain engineering to accommodate faster anion rotation. The influence of strain explains why crystallite size reduction and disordering associated with ball milling has been effective at lowering the superionic transition temperature.12 Another solution may be substitution with very large cations that could be introduced at low concentrations to achieve significant volume expansion without appreciable loss of mobile cation carriers. This strategy has been experimentally successful by alloying with Na.14 Very large anions could also be considered; however, substitution with anions that lack rotational mobility may offset the benefits. At the same time, the saturation limit of the anion reorientation in Figures 4 and 5 suggests volume expansion can only be leveraged to a point (which is temperature-dependent). Because this limit is defined by the unconstrained rotation rate, one solution may be to decrease the anion mass or alter the moment of inertia for enhanced rotational mobility. Indeed, this may explain some of the benefits of substituting B12H12−2 with B10H10−2, because the ions are otherwise similarly sized.

In conclusion, we have used extensive ab initio molecular dynamics simulations to perform computational assessments of cation diffusivity in a wide variety of Li and Na closo-borane and carboborane salts as well as structurally and chemically modified variants thereof. The simulations reveal distinct patterns associated with the effects of lattice strain, anion chemical modification, and cation off-stoichiometry that can be used to rationalize prior experimental studies. Our work illustrates how computational “experiments” can be used to understand general trends in polyborane ionic conductors as well as to suggest general improvement strategies.

fast cation diffusion allows us to categorically reject a Knudsen-type fixed-anion diffusion scheme. Indeed, previous investigations of superionic conductors have suggested that processes that can provide dynamical fluctuations in the underlying energy landscape on time scales relevant to diffusion may be important for fast ion conduction.22,29

Overall, our results highlight potential strategies for engineering polyborane electrolytes with enhanced conductivity. The increase in cation diffusivity in Figure 2 resulting from dilute substitution of B12H12−2 with CB12H12− or associated charge-compensating cation defects (i.e., V Li−) is significant but less than that observed for full anion substitution of Li2B12H12 in Figure 1. (Some of these differences are likely attributable to structural changes upon full substitution.) Moreover, superionic phases are entropically stabilized, so it is reasonable to assume that faster conductivity should generally lower the superionic transition temperature. This strategy has already proven effective.3−6 However, the overall conductivity of the monovalent carboboranes must be balanced against a decreased concentration of available Li+ due to charge compensation. Accordingly, an optimal doping concentration should exist, which will depend on temperature. This situation also applies for alloying with other anions such as with B10H10− or CB6H10−. The low barrier for diffusion of complexes with excess or depleted Li+ not bound to a charge-compensating defect (Figure 2) suggests that diffusion may be enhanced at the interface with an electrode where cation depletion or accumulation may be introduced by space-charge effects.

Figure 5. (a) Angular autocorrelation function φ(t) for Li2B12H12 at 800 K at the series of volumes shown in Figure 4. The inset records the time constant τ (in ps) from an exponential fit to φ(t) = exp(−t/τ). The saturation of the volume dependence of the anion rotation correlates with the saturation of the diffusivity in Figure 4. (b,c) Contour plots of the cation density isosurfaces at 800 K for volumes corresponding to the (b) α (preferred below the superionic transition) and (c) β (preferred above the superionic transition) phases. The cation density changes from well-defined site occupancy at the smaller α volume, where anion rotations are slow, to liquid-like superionic behavior at the larger β volume, where anion rotations are less constrained.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.6b00620.

Further computational details, structural information, full Arrhenius plots for the data in Figure 1, temperature dependence of the diffusivity for strained Li2B12H12, and details of the analysis of diffusivities and discrete jumps (including the definition of f in Figure 3).

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Notes
The authors declare no competing financial interest.

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Further computational details

Ab initio molecular dynamics simulations (AIMD) were performed using the Quantum Espresso code¹ using the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional,² a plane-wave cutoff of 30 Rydberg, and k-point sampling at the gamma point only. Our calculations adopted ultrasoft Rappe-Rabe-Kaxiras-Joannopoulos (rrkju) pseudopotentials³ downloaded from the Quantum Espresso website as part of the standard pseudopotential library.¹ The simulations employed the Car-Parrinello (CP) method⁴ with an effective elec-
Figure S1: (a) Evolution of the total internal energy (black) and the Car-Parrinello constant of motion (red) for a portion of an AIMD trajectory of Li$_2$B$_{12}$H$_{12}$ at 900 K. The dotted vertical lines indicate timesteps at which the electronic degrees of freedom were quenched to the Born-Oppenheimer surface (which shifts the constant of motion). (b) Corresponding evolution of the fictitious electronic kinetic energy (black, multiplied tenfold for easier viewing) and ionic kinetic energy (red).

electron mass of 400 au and a timestep of $\Delta t = 12$ au (0.29 fs). The mass of hydrogen was set to that of deuterium in order to facilitate a larger timestep. The canonical ($NVT$) ensemble was used, with Nosé-Hoover chains$^5$ to maintain the constant temperature, and with volumes fixed to zero-temperature atomic relaxations. Prior to the thermostated production runs, all calculations were thermalized to the specified temperature, then equilibrated within a microcanonical ensemble ($NVE$) for a minimum of 2 ps. Data was collected over a minimum of 50 ps, with longer simulations invoked for cases where statistical sampling was inadequate (i.e., at lower temperatures or for slower diffusing systems). To ensure that the electronic energy did not drift from the Born-Oppenheimer surface over the long CP trajectories, we performed Born-Oppenheimer steps every 0.5 ps using conjugate gradient minimization of the electronic degrees of freedom. Suitability of the choice of timestep was verified by com-
paring the dynamics of Li$_2$B$_{12}$H$_{12}$ with $\Delta t = 12$ au against short AIMD with $\Delta t = 6$ au. Figure S1 shows the conservation of the Car-Parrinello constant of motion against the total internal energy, as well as the evolution of the ionic and fictitious electronic kinetic energies.

All calculations were performed on $(\sqrt{2} \times \sqrt{2} \times 1)$ supercells generated from the optimized unit cells, which included 208 atoms for the Li$_2$B$_{12}$H$_{12}$ ($Pa\bar{3}$), LiNaB$_{12}$H$_{12}$ ($Pa\bar{3}$), and Na$_2$B$_{12}$H$_{12}$ supercells, and 176-atom supercells for Li$_2$B$_{10}$H$_{10}$ and Na$_2$B$_{10}$H$_{10}$ based on the high-temperature $Fm\bar{3}m$ phase, 200-atom supercells for the orthorhombic LiCB$_{12}$H$_{12}$ and NaCB$_{12}$H$_{12}$ phases, and 252-atom cells for the orthorhombic LiCB$_{9}$H$_{10}$ and NaCB$_{9}$H$_{10}$ phases. The perturbations considered for the Li$_2$B$_{12}$H$_{12}$, such as C$_B$, V$_H$ and (B$_{10}$H$_{10}$)$_{B12H12}$, consisted of a single anion substitution and corresponded to an effective concentration of 12.5% (1 out of 8 anions modified). Changes to the Li stoichiometry corresponded to deviations of 6.25% from the 16 Li included in the pristine Li$_2$B$_{12}$H$_{12}$ supercell.

The sensitivity of the obtained activation energies with respect to the choice of the PBE functional was also checked against results obtained with the Heyd-Scuseria-Ernzerhof (HSE) screened hybrid functional using the VASP code. As full dynamics with the hybrid functional are too computationally demanding, we assessed the static barrier of $V^{-}_{\text{Li}}$ migration for $\alpha$-Li$_2$B$_{12}$H$_{12}$ using the climbing nudged elastic band (cNEB) method for when a Li jump event directly correlated with the rotation of a B$_{12}$H$_{12}$ anion. Our calculated barrier with PBE was 0.56 eV, close to the 0.54 eV activation energy predicted from the dynamics. To assess the barrier with HSE, we fully relaxed the geometries obtained from the PBE cNEB calculations for the saddle point and the ground state configurations and compared their final energies. Our barrier calculated in this way was 0.49 eV using the PBE lattice constant, which was only slightly smaller than the barrier calculated using PBE. If instead the HSE lattice constant is used ($a=9.590$ Å), the respective barriers are 0.61 eV for PBE and 0.59 eV for HSE, indicative of the large sensitivity of the activation energy to the volume as evident from the results discussed in the main text. Nonetheless, we expect the trends in the calculated diffusivities across the different materials to hold despite the exact quantitative
differences between the barriers obtained with PBE versus a different level of theory.

**Structure information**

Details of the structures of all phases modeled and included in Fig. 1 of the main text are summarized in Table S1. The reported space groups represent the initial zero-temperature configurations prior to subsequent disordering of cation positions and anion orientations with increased temperature. The structures were derived from the included references. The corresponding experimental lattice constants are shown for comparison.

Table S1: Structural data for systems simulated in the main text.

<table>
<thead>
<tr>
<th>Material</th>
<th>Initialized space group</th>
<th>Lattice constant (Å)</th>
<th>Experimental value (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Li$<em>2$B$</em>{12}$H$_{12}$</td>
<td>Pa3</td>
<td>9.634</td>
<td>9.577 (300 K)$^{b,15}$</td>
</tr>
<tr>
<td>β-Li$<em>2$B$</em>{12}$H$_{12}$</td>
<td>Pa3</td>
<td>10.05</td>
<td>10.017 (355 K)$^6$</td>
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<tr>
<td>Na$<em>2$B$</em>{12}$H$_{12}$</td>
<td>$Im3m$</td>
<td>7.980</td>
<td>8.098 (675 K)$^7$</td>
</tr>
<tr>
<td>Na$<em>2$B$</em>{12}$H$_{12}$</td>
<td>$P2_1/c$</td>
<td>$a=7.056, b=10.601, c=7.296,$</td>
<td>$a=7.0306, b=10.6540, c=7.0093,$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta = 95.146^\circ$</td>
<td>$\beta = 94.676^\circ$ (300 K)$^{16}$</td>
</tr>
<tr>
<td>LiNaB$<em>{12}$H$</em>{12}$</td>
<td>Pa3</td>
<td>9.890</td>
<td>9.820 (300 K)$^8,17$</td>
</tr>
<tr>
<td>Na$<em>2$B$</em>{10}$H$_{10}$</td>
<td>$Fm3m$</td>
<td>9.870</td>
<td>9.843 (410 K)$^9$</td>
</tr>
<tr>
<td>Li$<em>2$B$</em>{10}$H$_{10}$</td>
<td>$Fm3m$</td>
<td>9.356</td>
<td>–</td>
</tr>
<tr>
<td>LiCB$<em>{11}$H$</em>{12}$</td>
<td>$Pca2_1$</td>
<td>$a=10.077, b=9.474, c=9.878$</td>
<td>$a=9.667, b=9.489, c=9.727$ (300 K)$^{10}$</td>
</tr>
<tr>
<td>NaCB$<em>{11}$H$</em>{12}$</td>
<td>$Pca2_1$</td>
<td>$a=9.782, b=9.625, c=10.093$</td>
<td>$a=9.782, b=9.625, c=10.093$ (300 K)$^{10}$</td>
</tr>
<tr>
<td>LiCB$<em>{9}$H$</em>{10}$</td>
<td>$Cme2_1$</td>
<td>$a=7.089, b=11.656, c=12.762$</td>
<td>$a=6.807, b=11.819, c=10.604$ (333 K)$^{11}$</td>
</tr>
<tr>
<td>NaCB$<em>{9}$H$</em>{10}$</td>
<td>$Cme2_1$</td>
<td>$a=9.782, b=9.625, c=10.093$</td>
<td>–</td>
</tr>
</tbody>
</table>

**Arrhenius Plots**

Full Arrhenius plots for the data in Fig. 1 of the main text are shown in Fig. S2.

**Volume and Temperature Dependence of Diffusivity**

Calculated diffusion constants for strained Li$_2$B$_{12}$H$_{12}$ at 600 K, 700 K, 800 K, and 900 K are shown in Fig. S3. These data are analogous to the data presented in Fig. 4 of the main text. The data show a steeper dependence of diffusivity on volume and a systematic decrease in the saturation point with temperature.
Figure S2: Arrhenius plot of the calculated cation diffusivities for the Li and Na closo(carbo)boranes presented in Fig. 1 of the main text.
Figure S3: Volume scaling of diffusion constant for simulations of Li$_2$B$_{12}$H$_{12}$ at 600 K (red triangles), 700 K (green diamonds), 800 K (blue circles), and 900 K (navy squares). Volumes are scaled with respect to the volume of the α phase ($V_{\alpha}$).

**Analysis of Diffusivities and Discrete Jumps**

The diffusion constants were calculated via the Einstein relation $D = \lim_{t \to \infty} \frac{1}{6t} \langle MSD(t) \rangle$ from a linear fit of the slope of the cation mean-squared displacement (MSD) versus time over an intermediate time window. This procedure was repeated for independent time intervals of 5 to 10 ps to determine the average diffusion constant and associated standard error in Figs. 2 and 4 in the main text and illustrated in Fig. S4. MSD($t$) was computed by averaging over all available time windows of length $t$ (except for Fig. 3 of the main text). Activation energy barriers were computed with a linear fit to an Arrhenius relation using all diffusivities that pass a critical threshold of $1 \times 10^{-7}$ cm/s, since values below this threshold were assumed to have poor statistical convergence. The discrete jump analysis was performed using a molecular dynamics analysis package developed for the AiiDA software platform. We identified a jump event when a cation moved from one lattice site to another. We further classified these jumps as “mobile” if the cation accessed a third unique site without returning.
to its original site.

Figure S4: Ion-resolved mean-squared displacement (MSD) for α-Li$_2$B$_{12}$H$_{12}$ at 800 K based on different simulation times. Panels (a) and (b) show the results for the MSD obtained using windowed averaging over the first ∼50 ps and the full ∼80 ps of the simulation trajectory, respectively. Panel (c) shows the ion-resolved MSD for successive ranges of independent short-length simulation segments. Values for the diffusion constant and its associated uncertainty are obtained from the average and standard error of the slope of these segments. The dashed vertical lines indicate the region over which the slope was calculated in each case.

To formulate $f$ in Fig. 3 of the main text, we first divide each conventional $fcc$ anion unit cell into four equivalent volume-filling polyhedra (created from anion octahedra plus one quarter of each neighboring tetrahedron). Because stoichiometry requires that each polyhedron contains on average two cations, we monitor the cation occupancy $2 + n$ of these polyhedra and use the deviations $n$ to define an “activated” state $\phi^n$. Finally, we define $f = \frac{1}{N} \sum_i \left\{ \frac{1}{2} \sum_{n \neq 0} \phi^n(i) \right\}$, where the index $i$ runs over the $N$ available sites and the sum over $n$ accounts for all possible occupancy deviations. The factor of $1/2$ is included because each “activated” Li$^+$ contributes to a $(\phi^{-n} + \phi^{+n})$ pair.

Table S2 shows the values corresponding to the data for diffusivity and discrete jump statistics plotted in Figs. 2 and 4 of the main text. All perturbations are based on the low-temperature α phase. The diffusion constant is included as calculated from the mean-squared displacement over the entire length of the trajectory ($D$) with the correlation coefficient of the linear fit ($r^2$) and as averaged over independent time intervals of 5 to 10 ps are included for each calculation ($\bar{D}$), with the error expressed as twice the standard error over all the segments. The jump statistics reflect the values averaged over each Li atom in the simulation.
with the reported error taken as the standard deviation.

Table S2: Statistical analysis of the discrete jumps and diffusivities for Li$_2$B$_{12}$H$_{12}$ at 800 K.

<table>
<thead>
<tr>
<th></th>
<th>$D$ (cm$^2$/s)</th>
<th>$r^2$</th>
<th>$\overline{D}$ (cm$^2$/s)</th>
<th>Total jump frequency (THz per Li)</th>
<th>Fraction of Mobile Jumps</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>2.45E-05</td>
<td>0.968</td>
<td>1.69E-05 ± 3.24E-06</td>
<td>3.21 ± 1.24</td>
<td>0.41 ± 0.06</td>
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<tr>
<td>V$x\times0.95$</td>
<td>4.08E-08</td>
<td>0.666</td>
<td>1.96E-07 ± 6.78E-08</td>
<td>1.08 ± 0.27</td>
<td>0.21 ± 0.09</td>
</tr>
<tr>
<td>V$x\times1.05$</td>
<td>6.24E-05</td>
<td>0.994</td>
<td>7.10E-05 ± 4.42E-06</td>
<td>6.05 ± 0.46</td>
<td>0.53 ± 0.03</td>
</tr>
<tr>
<td>$\beta$ (V$x\times1.13$)</td>
<td>1.24E-04</td>
<td>0.999</td>
<td>1.08E-04 ± 3.81E-06</td>
<td>6.64 ± 0.48</td>
<td>0.59 ± 0.04</td>
</tr>
<tr>
<td>V$x\times1.20$</td>
<td>1.49E-04</td>
<td>0.998</td>
<td>1.35E-04 ± 6.50E-06</td>
<td>6.75 ± 0.48</td>
<td>0.63 ± 0.04</td>
</tr>
<tr>
<td>V$x\times1.25$</td>
<td>1.29E-04</td>
<td>0.996</td>
<td>1.44E-04 ± 9.53E-06</td>
<td>6.30 ± 0.38</td>
<td>0.64 ± 0.03</td>
</tr>
<tr>
<td>V$x\times1.30$</td>
<td>1.15E-04</td>
<td>0.996</td>
<td>1.37E-04 ± 8.14E-06</td>
<td>6.30 ± 0.39</td>
<td>0.63 ± 0.04</td>
</tr>
<tr>
<td>V$x\times1.35$</td>
<td>1.29E-04</td>
<td>0.997</td>
<td>1.40E-04 ± 9.00E-06</td>
<td>5.96 ± 0.35</td>
<td>0.62 ± 0.03</td>
</tr>
<tr>
<td>C$_B^+$</td>
<td>2.83E-05</td>
<td>0.990</td>
<td>3.47E-05 ± 6.89E-06</td>
<td>4.23 ± 0.80</td>
<td>0.47 ± 0.04</td>
</tr>
<tr>
<td>(C$_B$ – V$_H$)$_0$</td>
<td>4.09E-05</td>
<td>0.997</td>
<td>3.88E-05 ± 7.96E-06</td>
<td>4.51 ± 0.71</td>
<td>0.48 ± 0.05</td>
</tr>
<tr>
<td>(C$<em>B$ – V$</em>{Li}$)$_0$</td>
<td>5.34E-05</td>
<td>0.989</td>
<td>6.75E-05 ± 5.52E-06</td>
<td>4.96 ± 0.46</td>
<td>0.52 ± 0.05</td>
</tr>
<tr>
<td>V$_H^-$</td>
<td>3.55E-05</td>
<td>0.997</td>
<td>3.40E-05 ± 3.66E-06</td>
<td>4.19 ± 0.59</td>
<td>0.47 ± 0.05</td>
</tr>
<tr>
<td>Li$_i^+$</td>
<td>5.11E-05</td>
<td>0.999</td>
<td>5.59E-05 ± 6.54E-06</td>
<td>4.75 ± 0.62</td>
<td>0.50 ± 0.05</td>
</tr>
<tr>
<td>V$_{Li}^-$</td>
<td>3.28E-05</td>
<td>0.991</td>
<td>3.78E-05 ± 4.03E-06</td>
<td>4.28 ± 1.01</td>
<td>0.48 ± 0.06</td>
</tr>
<tr>
<td>(B$<em>{10}H</em>{10}$)B$<em>{12}$H$</em>{12}$</td>
<td>5.42E-05</td>
<td>0.995</td>
<td>5.33E-05 ± 5.83E-06</td>
<td>5.07 ± 0.65</td>
<td>0.50 ± 0.04</td>
</tr>
</tbody>
</table>

Figure S3 shows the per-element mean-squared displacement (MSD) for $\alpha$-Li$_2$B$_{12}$H$_{12}$ at 800 K. The diffusion constant is related to the slope of the MSD by the Einstein relation and calculated from the linear fit between the range delimited by the dashed black lines. The length of the simulation included in the MSD analysis has a large effect on the quality of the fit as seen from the MSD in (a) and (b). This indicates that the diffusion events are inhomogeneous in time. To account for these effects we calculated the ion-resolved diffusion constants over a range of independent simulation length segments from 5 to 10 ps as illustrated in (c) for 8.5 ps. The deviation in the calculated diffusion constants by this method and the complementary discrete jump based analysis help quantify the cation diffusivities and associated uncertainties for systems that can exhibit highly spatially and temporally inhomogeneous conduction mechanisms.

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