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Enhancing Li⁺ Ion Transport via Dynamic Coupling With Borohydride Reorientation in Li₆PS₅X Argyrodites

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ABSTRACT

All-solid-state batteries employing solid electrolytes offer improved safety and thermal stability compared to conventional lithium-ion batteries. Among various solid electrolytes, Li-argyrodites are particularly attractive due to their high ionic conductivity and favorable mechanical properties. In this study, we investigate the effect of borohydride (BH₄[−]) substitution on the structure and Li⁺ ion dynamics of Li-argyrodites (Li₆PS₅X, X = Cl[−], BH₄[−]) using solid-state NMR, pulsed field gradient NMR, and ab initio molecular dynamics to clarify the underlying mechanism of conductivity enhancement. We show that BH₄[−] occupancy at both non-bridging sulfur sites (Wyckoff 4a and 4d) promotes Li⁺ transport by inducing cage-size uniformity, which reduces energetic mismatch between interconnected Li⁺ cages and enables continuous, long-range inter-cage diffusion. Moreover, BH₄[−] reorientation at these sites is strongly coupled to Li⁺ transport, facilitating long-range diffusion via a paddle-wheel-like mechanism, whereas PS₄^{3−} reorientation does not significantly contribute to Li⁺ ion mobility. Finally, we demonstrate that strong interfacial contact and efficient Li⁺ exchange at the cathode–electrolyte interphase are critical for optimizing solid electrolytes and achieving high-performance all-solid-state batteries. Our findings elucidate the structural and dynamic origins of conductivity enhancement and provide design principles for advanced solid electrolytes.

1 | Introduction

Driven by global efforts toward carbon neutrality, lithium-ion batteries (LIBs) have become essential for electric vehicles and energy storage systems due to their high gravimetric and volumetric energy densities [1]. However, safety concerns associated with flammable liquid electrolytes in conventional LIBs have motivated growing interest in all-solid-state batteries (ASSBs) using solid electrolytes (SEs), which offer improved safety and

thermal stability [2–7]. Moreover, by acting as both electrolyte and separator, SEs can suppress dendrite growth, increase energy density, and render ASSBs attractive for high-power energy storage applications [8, 9]. ASSBs demand materials with high ionic conductivity and high chemical and electrochemical stability. Sulfide-based SEs are particularly promising due to their soft mechanical properties, good processability, and significantly enhanced ionic conductivities at room temperatures [10, 11]. In unsubstituted argyrodites Li₇PS₆, non-bridging S^{2−} ions occupy

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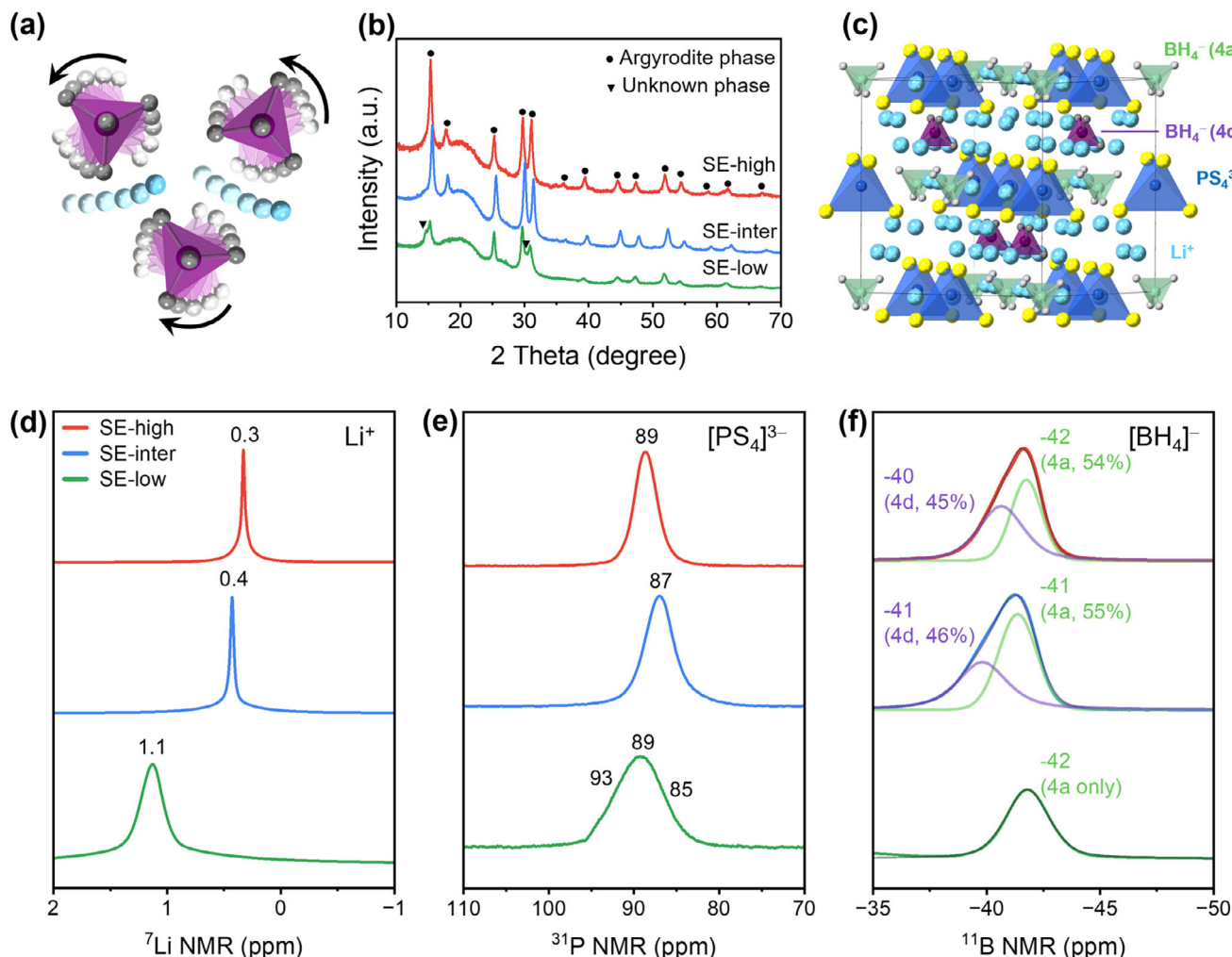


FIGURE 1 | Structural characterization by MAS NMR spectroscopy: (a) Schematic illustration of the coupling between polyanion rotation and Li^+ ion migration. (b) XRD patterns. (c) Crystal structure of the argyrodite $\text{Li}_5\text{PS}_4(\text{BH}_4)_2$ with BH_4^- occupancy at the 4a and 4d sites marked in different colors. (d) ^7Li , (e) ^{31}P , and (f) ^{11}B MAS NMR spectra of SE-high (red), SE-inter (blue), and SE-low (green).

the 4a and 4d sites. By substituting S^{2-} with halide anions, $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) exhibit significantly enhanced conductivities up to $10 \text{ mS}\cdot\text{cm}^{-1}$, comparable to those of liquid electrolytes [12–17]. $\text{Li}_6\text{PS}_5\text{X}$ possesses a cubic crystal structure (space group $F\bar{4}3m$), where P^{5+} and S^{2-} occupy the 4b and 16e Wyckoff sites, forming $[\text{PS}_4]^{3-}$ tetrahedra [18, 19]. $\text{Li}_6\text{PS}_5\text{I}$ exhibits anion ordering between S^{2-} occupying the 4d sites and I^- occupying the 4a sites, due to the size mismatch (S^{2-} : $1.84 \text{ \AA}$, I^- : $2.16 \text{ \AA}$), which results in relatively low conductivity. In contrast, $\text{Li}_6\text{PS}_5\text{Br}$ and $\text{Li}_6\text{PS}_5\text{Cl}$ show disordered anion distributions at the 4a/4d sites owing to the similar ionic radii (Br^- : $1.95 \text{ \AA}$, Cl^- : $1.81 \text{ \AA}$), leading to higher conductivity [18, 20]. Moreover, substitution of mixed halide (Br^- and Cl^-) or polyanion, such as SO_4^{2-} , PO_4^{3-} , SiS_4^{4-} , and BH_4^- , further enhance the ionic conductivities [21, 22]. Structural features such as Li^+ and anion site disorder, anion polarizability, and lattice size and distortions have been suggested to affect the ionic conductivity of $\text{Li}_6\text{PS}_5\text{X}$ [12, 23–26]. However, the role of polyanion substitution remains controversial. The paddle-wheel mechanism has been proposed for Li_2SO_4 , Na_3PO_4 , and Li_3PS_4 , in which rotational disorder of anions coincides with high cationic conductivity (Figure 1a) [27–30]. In contrast, based on molecular dynamic simulations,

Sun et al. have suggested that the increased conductivity of BH_4^- substituted argyrodite does not result from the rotation or vibration of the BH_4^- group, but rather from the weaker electrostatic interaction between the Li^+ and BH_4^- groups [31]. To understand mechanisms influencing Li^+ migration in SEs, it is crucial to investigate ion dynamics across a wide range of time and length scales, from the microscopic to the macroscopic.

In our earlier work, we reported that co-substitution of BH_4^- ($r = 2.03 \text{ \AA}$) and Cl^- into argyrodites enhances ionic conductivity with good cycling performance [32]. A systematic compositional study ($\text{Li}_3\text{PS}_4 + x\text{LiBH}_4 + 0.5\text{LiCl}$) showed that the conductivity increases with BH_4^- content, with a maximum at $x = 2.0$ [32]. Here, we elucidate the mechanism of conductivity enhancement induced by BH_4^- substitution. Based on previous compositional variation studies, three representative samples were selected for this work to examine the correlation between Li^+ diffusion and BH_4^- dynamics: SE-high, with BH_4^- occupying both 4a and 4d sites and exhibiting the highest conductivity; SE-inter, with BH_4^- at both sites but lower occupancy and intermediate conductivity; and SE-low, with BH_4^- only at the 4a site and the lowest conductivity [32, 33]. We employed solid-state NMR,

TABLE 1 | Sample characteristics.

Sample label	Molar ratio of LiBH ₄ : LiCl ^a	Ionic conductivity, σ (mS·cm ⁻¹)	Lattice parameter, <i>a</i> (Å) ^b	BH ₄ ⁻ site occupancy ^c
SE-high	2: 0.5	16.4	9.9636	4a (0.614) / 4d (0.535)
SE-inter	1.25: 0.75	7.9	9.9085	4a (0.380) / 4d (0.309)
SE-low	2.5: 0	0.7	10.0034	4a (0.36)

^aThese values represent the molar ratio of LiBH₄: LiCl added during the synthesis. Based on the Rietveld refinement of the XRD data (see Tables S1–S3), the stoichiometries are estimated as Li_{5.35}PS_{4.35}(BH₄)_{1.15}Cl_{0.5} for SE-high, Li_{5.56}PS_{4.56}(BH₄)_{0.69}Cl_{0.75} for SE-inter, and Li_{6.64}PS_{5.64}(BH₄)_{0.36} for SE-low.

^bLattice parameter and site occupancy were obtained from Rietveld refinement using the *F*43*m* (No. 216) space group (Tables S1–S3) [32, 33].

which probes fast motional processes (micro- to nanosecond timescale) occurring on a microscopic length scale, and pulsed field gradient (PFG) NMR, which measures long-range transport motion [34–37]. First-principles calculations were performed to gain theoretical insights into Li⁺ diffusion. The structural stability of argyrodites and cathode electrolyte interphase (CEI) were monitored by ex situ NMR of cycled samples. Overall, our study on the correlation between the structure and dynamics of argyrodites provides not only important design principles for new ion conductors but also a fundamental understanding of diffusion and reorientational motions of ions.

2 | Results and Discussion

2.1 | Structural Characterization

To study the effect of structural features on Li⁺ translational motion, three argyrodites of Li_{7-x-y}PS_{6-x-y}(BH₄)_xCl_y were investigated, displaying different conductivities and anion distributions (Table 1) [32, 33]. These samples are labeled SE-high, SE-inter, and SE-low according to their ionic conductivities, which range from 17 to 0.7 mS·cm⁻¹. XRD results confirm that all samples contain only argyrodite-type phases (Figure 1b). Rietveld refinement indicates that the lattice parameter increases with substituted BH₄⁻ content and that Cl⁻ occupies both the 4a and 4d sites, consistent with previous Li₆PS₅Cl reports (Tables S1–S3) [37]. For SE-high and SE-inter, the BH₄⁻ anion occupies both the 4a and 4d sites (Figure 1c) [32], whereas in SE-low, the BH₄⁻ anion is located only at the 4a site [33].

The local environments of Li⁺, PS₄³⁻, and BH₄⁻ were investigated using ⁷Li, ³¹P, and ¹¹B magic angle spinning (MAS) NMR spectroscopy. The ⁷Li NMR spectra (Figure 1d) of SE-high and SE-inter exhibit a single narrow signal near 0.3 ppm, indicative of rapid Li⁺ motion. The ⁷Li signal of SE-low appears at 1.1 ppm with a broader linewidth, implying decreased electrostatic interaction between Li⁺ and the anion framework, as well as reduced Li⁺ mobility, which aligns with its low ionic conductivity [19]. ³¹P MAS NMR is sensitive to the types of anion substitution, anion ordering, and distribution at the 4a and 4d sites, as well as Li cation ordering [18, 20–22, 32, 33, 37]. Previously, ³¹P NMR signals of PS₄³⁻ unit were observed at ≈84, ≈90, ≈92, and ≈96 ppm for Li₆PS₅X with X = Cl⁻, BH₄⁻, Br⁻, and I⁻, respectively [18, 20–22, 32, 33, 37]. In particular, Li₆PS₅I exhibits a sharp ³¹P signal due to the fully ordered structure between I⁻ at the 4a sites and S²⁻ at the 4d sites [18, 20]. The ³¹P NMR spectra of SE-high and

SE-inter (Figure 1e) show a single, broad, Gaussian-like peak centered at 87–89 ppm, corresponding to isolated PS₄³⁻ tetrahedra surrounded by randomly distributed S²⁻, Cl⁻, and BH₄⁻ over the 4a and 4d sites. SE-low exhibits an even broader overlapping ³¹P NMR signal, indicating increased structural disorder (Supporting Information S1: Note S1). This is consistent with the reduced crystallinity and higher defect density in SE-low, as indicated by the broad XRD peaks. The ¹¹B MAS NMR spectra (Figure 1f) provide additional structural information, including BH₄⁻ site occupancy. For SE-high and SE-inter, asymmetric ¹¹B NMR signals are observed, which can be deconvoluted into distinct peaks corresponding to BH₄⁻ occupancy at the 4a (–42 ppm) and 4d (–41 ppm) sites. The relative occupancy ratio of BH₄⁻ at the 4d/4a sites is approximately 0.84 [32]. In contrast, SE-low yields a single symmetric ¹¹B signal at –42 ppm, indicating BH₄⁻ occupancy only at the 4a site [33]. These are consistent with XRD refinement results shown in Table 1.

2.2 | Dynamics on a Microscopic Scale by Solid-State NMR Spectroscopy

To investigate the local dynamics of the systems, we used static NMR lineshape analysis and spin-lattice relaxation (SLR) time (*T*₁) measurements at various temperatures. Static NMR showed narrow lineshapes without any anisotropy features even at 220 K, suggesting that rapid Li⁺ hopping and reorientation of PS₄³⁻ and BH₄⁻ already occur even at such low temperatures (Figures S1–S3) [20, 37].

Relaxation time, particularly *T*₁ measurement, is a powerful tool for probing local dynamics on the micro- to nanosecond timescale, enabling characterization of Li⁺ ion hopping and polyanion motion separately [34, 38, 39]. The influence of local motion on long-range dynamics was examined through analysis of the ⁷Li, ³¹P, and ¹¹B SLR rates (≡1/*T*₁) over a range of temperatures (Figure 2a–c). First, Li⁺ jump processes of the three samples were compared by the ⁷Li SLR rates. Plots of ln(1/*T*₁) versus inverse temperature show that the ⁷Li SLR rates increase with temperature and pass through well-defined maxima, which are characteristic of the diffusion-induced relaxation. At *T*_{max} where the SLR rate maxima appear, the motional correlation rate (*τ*_c⁻¹) can be estimated from the Larmor frequency (*ω*_L) since *ω*_L *τ*_c ≈ 1, providing insight into the dynamics [40]. For SE-high, *τ*_c⁻¹ is roughly 1.5 × 10⁹ s⁻¹ at *T*_{max} = 322 K. Using the Nernst-Einstein equation (Supporting Information S1: Note S2), *σ* of 15 mS cm⁻¹ is estimated, which is in good agreement with the measured

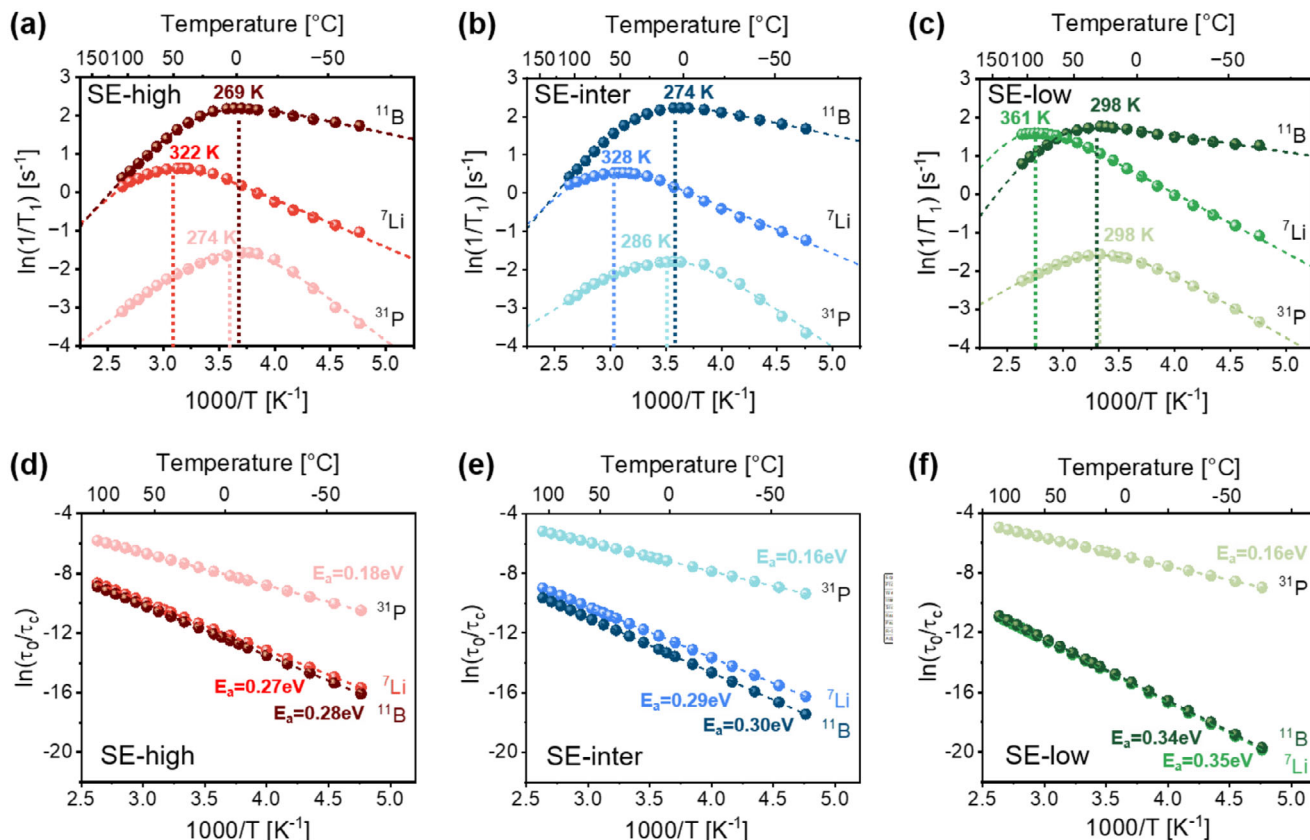


FIGURE 2 | Dynamics on a microscopic scale by solid-state NMR spectroscopy: Logarithmic plots of the ${}^7\text{Li}$, ${}^{31}\text{P}$, and ${}^{11}\text{B}$ SLR rates ($1/T_1$) as a function of inverse temperature for (a) SE-high, (b) SE-inter, and (c) SE-low. Normalized correlation rates of the motional processes derived from ${}^7\text{Li}$, ${}^{31}\text{P}$, and ${}^{11}\text{B}$ SLR data for (d) SE-high, (e) SE-inter, and (f) SE-low.

conductivity [35]. As the conductivities of the samples increase, T_{max} shifts toward lower temperatures, that is, SE-low > SE-inter > SE-high, suggesting an increase in Li^+ dynamics [41]. In particular, T_{max} of SE-low is significantly higher than those of SE-high and SE-inter, in line with the conductivity of SE-low being ten times smaller than the other two samples. The ${}^{31}\text{P}$ and ${}^{11}\text{B}$ SLR rate peaks occur at significantly lower temperatures than the ${}^7\text{Li}$ SLR rate peak, suggesting faster spin fluctuations sensed by ${}^{31}\text{P}$ and ${}^{11}\text{B}$ compared to ${}^7\text{Li}$ (Figure 2a–c). The concurrent shift of the ${}^7\text{Li}$, ${}^{31}\text{P}$, and ${}^{11}\text{B}$ SLR maxima toward lower temperatures with increasing conductivity suggests that Li^+ translational motion and $\text{PS}_4^{3-}/\text{BH}_4^-$ reorientation may be influenced by similar mechanisms or structural factors.

To gain deeper understanding into the motional processes in these structurally complex systems, we analyzed the temperature dependence of the SLR rate using a modified Bloembergen–Purcell–Pound (BPP) theory [40]:

$$\frac{1}{T_1} \approx \frac{\tau_c}{1 + (\omega_L \tau_c)^\beta} \quad (1)$$

where ω_L is the Larmor frequency, τ_c the correlation time, and β the asymmetry parameter representing the degree of motional correlation ($1 < \beta \leq 2$). For a thermally activated process, the temperature dependence of τ_c^{-1} is given by an Arrhenius

equation:

$$\tau_c^{-1} = \tau_0^{-1} \times \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where E_a is the activation energy, R the gas constant, T the temperature (K), and τ_0^{-1} the pre-exponential factor. For three-dimensional diffusion, the SLR rate becomes independent of frequency in the high-temperature limit ($\omega_L \tau_c \ll 1$, $1/T_1 = \tau_c$), whereas the SLR rate exhibits frequency dependence in the low-temperature limit ($\omega_L \tau_c \gg 1$, $1/T_1 = (\omega_L)^{-\beta} (\tau_c)^{1-\beta}$). For uncorrelated isotropic motion following ideal BPP behavior, the SLR rate curve is symmetric ($\beta = 2$). By contrast, when the system undergoes correlated motion, the SLR curve becomes asymmetric and $1 < \beta < 2$. This correlated motion is often observed in glassy or amorphous ion conductors, where ions experience Coulombic interactions or structural disorder [35, 42].

From the BPP fitting of ${}^7\text{Li}$ SLR rate curves (Table 2), E_a of 0.27 and 0.29 eV were obtained for SE-high and SE-inter, respectively, which are smaller than those reported for $\text{Li}_6\text{PS}_5\text{Cl}$ (≈ 0.32 eV) [20, 43]. This suggests that additional anion substitution with BH_4^- enhances Li^+ mobility. The E_a increases in the order SE-high < SE-inter < SE-low, consistent with conductivity behavior. This parallel trend implies that the long-range ionic conduction observed in impedance spectroscopy is related to the Li^+ hopping probed by SLR. Asymmetry parameters of ≈ 1.4 imply that Li^+ hopping is governed by correlated motion. The ${}^{31}\text{P}$ SLR rates

TABLE 2 | Individual BPP fit results for ^7Li , ^{31}P , and ^{11}B spin-lattice relaxation rates ($1/T_1$).

Sample	^7Li				^{31}P				^{11}B			
	E_a (eV)	β	$\tau_0^{-1}(\text{s}^{-1})$	T_{max} (K)	E_a (eV)	β	$\tau_0^{-1}(\text{s}^{-1})$	T_{max} (K)	E_a (eV)	β	$\tau_0^{-1}(\text{s}^{-1})$	T_{max} (K)
SE-high	0.27	1.4	5.4×10^{13}	322	0.18	2	9.3×10^{12}	274	0.28	1.2	2.8×10^{14}	269
SE-inter	0.29	1.3	6.3×10^{13}	328	0.16	1.9	3.0×10^{12}	286	0.30	1.2	5.9×10^{14}	274
SE-low	0.35	1.4	20×10^{13}	361	0.16	1.8	1.7×10^{12}	298	0.34	1.1	6.1×10^{14}	298

exhibit nearly symmetric peak shapes ($\beta \approx 2$) with smaller E_a than those of ^7Li dynamics, whereas those from the ^{11}B SLR plots are comparable to those from the ^7Li curves. The normalized correlation rates (τ_0/τ_c) are plotted as a function of inverse temperatures in Figure 2d–f. Several intriguing observations can be made. First, the ^7Li pre-exponential factor (τ_0^{-1}) decreases (SE-low > SE-inter > SE-high) with increasing ionic conductivity (Table 2). Second, the ^7Li and ^{11}B pre-exponential factors follow similar trends across the samples (SE-low > SE-inter > SE-high), whereas the ^{31}P exhibits the opposite trend (SE-low < SE-inter < SE-high). Third, the normalized correlation rates for ^7Li and ^{11}B are nearly identical, indicating similar temperature dependence, while that of ^{31}P is larger and shows a distinct temperature dependence. Since $\tau_0^{-1} = \nu_{p,0} \exp(\Delta S/k_B)$, a decrease in τ_0^{-1} of ^7Li indicates a reduction in either phonon frequency ($\nu_{p,0}$) or the migration entropy (ΔS) [20]. This interpretation is reasonable given that SE-high possesses a more ordered structure. The inverse correlation between the ^7Li pre-exponential factor and the conductivity suggests that the enhanced conductivity does not originate from an increased frequency of local Li^+ hopping attempts or from increased disorder. Instead, it implies that Li^+ transport becomes more effective through assistance from additional enthalpic contributions. The similar normalized jump rates observed for ^7Li and ^{11}B indicate comparable activation energies for Li^+ translational motion and BH_4^- reorientation (Figure 2d–f). In contrast, ^{31}P exhibits distinct behavior, suggesting that PS_4^{3-} reorientation is governed by a different activation barrier or motional constraint. These observations are consistent with a paddle-wheel transport mechanism, in which anion reorientation promotes more efficient, correlated long-range Li^+ transport. Specifically, dynamic coupling between Li^+ hopping and BH_4^- reorientation is likely to promote Li^+ conduction in these SEs, whereas PS_4^{3-} reorientation does not significantly contribute to enhanced Li^+ transport [44–46]. Interestingly, the occupancy of BH_4^- at both the 4a and 4d sites appears crucial for dynamic coupling and enhanced Li^+ transport. Systems with BH_4^- occupying both the 4a and 4d sites show higher Li^+ mobility, while the system with BH_4^- only at the 4a site exhibits lower conductivity (Table 1). Previously, Wang et al. suggested that the full occupancy of the 4a/4d Wyckoff sites by BH_4^- is necessary for improved conductivity [21]. At this stage, the influence of local defects and substitution extent on conductivity cannot be ruled out.

2.3 | Structural and Dynamic Effects by First-Principles Calculations

To clarify the origin of the enhanced Li^+ conductivity upon BH_4^- substitution in Li-argyrodite, DFT-based ab initio molecular

dynamics (AIMD) simulations were carried out on simplified model systems. In these models, BH_4^- tetrahedra occupy both the 4a and 4d sites, enabling isolation of the intrinsic effect of BH_4^- on Li^+ transport without the influence of halide anions (Figure 3a). The directional nature of BH_4^- was accounted for by considering multiple orientational configurations, which capture distinct local structural environments (Figure S5) [47]. AIMD simulations were performed for each model over 500–900 K, and Li^+ ion conductivities were obtained from Arrhenius fits and extrapolated to 300 K (Figure 3b). The relative stabilities (E_{rel}) and corresponding conductivities of the four models are summarized in Table S5. Based on these results, the bulk ionic conductivity of $\text{Li}_5\text{PS}_4(\text{BH}_4)_2$ was estimated by a Boltzmann-weighted average over the four configurations (details in Supporting Information S1: Note S3) [48]. This approach captures both the thermodynamic populations of the configurations and their kinetic impact on Li^+ transport. It is therefore well suited to the present system, where multiple BH_4^- orientational configurations give rise to distinct energetics and Li^+ transport characteristics. To better align the AIMD-based prediction with experimental microstructure, we further applied a crystallinity correction introduced in the previous study (Figure S6) [48]. Given the bulky and orientational disorder associated with BH_4^- , we adopted a crystallinity fraction of $\chi_c = 60\%$. The corrected Li^+ ion conductivity, calculated using the formulation in Supporting Information S1: Note S4, is reported in Table S6. With this correction, the room-temperature conductivity was estimated to be $7.2 \text{ mS}\cdot\text{cm}^{-1}$, more than twice that of $\text{Li}_6\text{PS}_5\text{Cl}$ ($3.82 \text{ mS}\cdot\text{cm}^{-1}$) (Figure 3c, Table S7). Notably, this value is in excellent agreement with the experimental measurement ($7.0 \text{ mS}\cdot\text{cm}^{-1}$), supporting the reliability of our computational framework [47].

To rationalize the structural origin of this enhanced conductivity, we examine the uniformity of Li^+ cages surrounding the 4a and 4d sites (details in Supporting Information S1: Note S5). Previous studies on argyrodite electrolytes have established that minimizing the size mismatch between these cages reduces inter-cage diffusion barriers and facilitates long-range Li^+ transport. [48] In the BH_4^- substituted system, the Li^+ sublattice forms an interconnected cage framework (Figure S7), with the size difference between the 4a and 4d cages below $0.05 \text{ \AA}$ and a small statistical dispersion ($\text{STD} \leq 0.054 \text{ \AA}$; Table S8). Consistent with this structural uniformity, the Li^+ probability density reveals a highly connected diffusion network (Figure 3d), while the self-part van Hove correlation function shows long-range Li^+ displacements on short timescales (Figure 3e). These features collectively identify cage-size uniformity as a key static factor enabling fast Li^+ transport in $\text{Li}_5\text{PS}_4(\text{BH}_4)_2$.

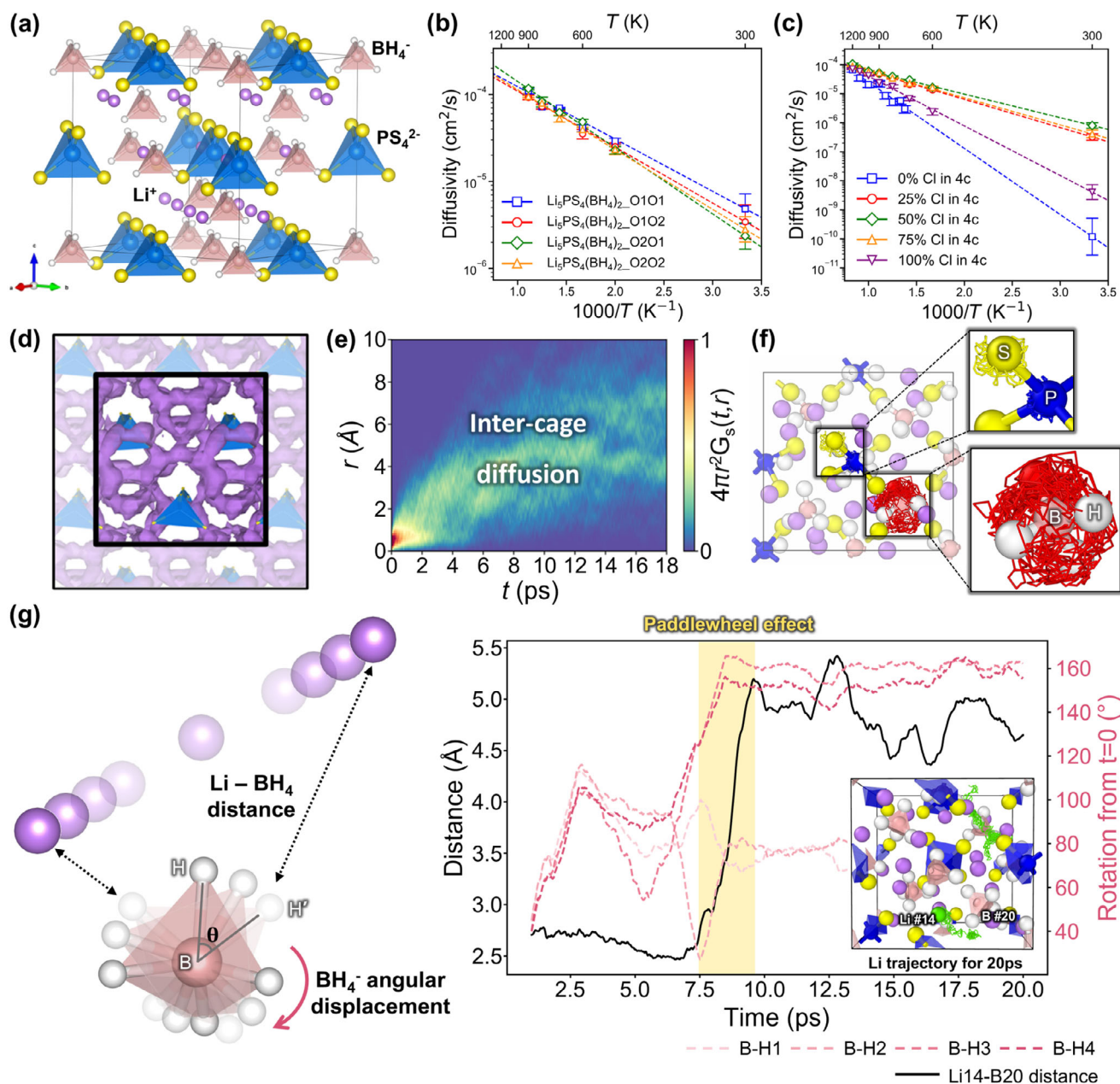


FIGURE 3 | Structural and dynamic effects by First-principles calculations: (a) Crystal structure of argyrodite $\text{Li}_5\text{PS}_4(\text{BH}_4)_2$ with BH_4^- tetrahedra occupying both 4a and 4d sites. Arrhenius plots of Li^+ ion diffusivities from AIMD simulations of (b) $\text{Li}_5\text{PS}_4(\text{BH}_4)_2$ (500–900 K) and (c) $\text{Li}_6\text{PS}_5\text{Cl}$ (600–1200 K) extrapolated to 300 K. Four structural models with different site-disorder configurations are compared. (Figure S5) (d) Isosurface of Li^+ ion probability density for $\text{Li}_5\text{PS}_4(\text{BH}_4)_2$. (e) Self part of the van Hove correlation indicating inter-cage diffusion. (f) Trajectories of a single H atom within a BH_4^- tetrahedron and P and S atoms in a PS_4^{3-} tetrahedron. (g) Definition of BH_4^- rotation angle (θ) and the $\text{Li}-\text{BH}_4$ distance and their time evolution. The selected $\text{Li}-\text{BH}_4$ distance (black, Li#14–B#20) and BH_4^- rotation angles (dashed red lines) referenced to $t = 0$. Distance and angle data are smoothed with an 1 ps moving average, and the shaded region highlights a time interval in which BH_4^- reorientation coincides with stepwise Li^+ hopping, consistent with a paddle-wheel-like transport behavior.

Beyond static structural effects, we examined dynamic contributions to Li^+ mobility in $\text{Li}_5\text{PS}_4(\text{BH}_4)_2$. Recent studies have shown that PS_4^{3-} units in Li-argyrodites primarily exhibit vibrational motion rather than paddle-wheel-like rotations [49–53]. By contrast, rotational dynamics of BH_4^- tetrahedra have been reported in pseudohalide-substituted systems [31]. In those studies, however, the associated conductivity enhancement was mainly interpreted in terms of weakened $\text{Li}^+-\text{BH}_4^-$ electrostatic interactions, leaving the direct coupling between BH_4^- rotation

and Li^+ migration unresolved. Consistent with these reports, our AIMD trajectories show that PS_4^{3-} units remain vibrationally constrained, whereas BH_4^- tetrahedra undergo pronounced rotational reorientation on the simulation timescale (Figure 3f, Video S1). To quantify the impact of BH_4^- rotation on Li^+ transport, additional AIMD simulations were conducted in which the rotational degrees of freedom of BH_4^- were artificially constrained. Under these conditions, the Li^+ diffusivity is reduced by nearly half relative to the fully dynamic system (Table S9), underscoring

the critical role of BH_4^- rotational motion. Time-resolved analysis further reveals that BH_4^- reorientation events are temporally correlated with stepwise Li^+ hopping between neighboring cages (Figure 3g). This temporal coincidence indicates that BH_4^- units act in a paddle-wheel-like manner, transiently facilitating Li^+ hopping between adjacent cages. Additional statistical analysis further supports this interpretation, confirming that the observed correlation is not limited to a single illustrative event but represents a recurring dynamical feature of the system (Table S10 and Figure S8). Taken together, these results suggest that the exceptional ionic conductivity of $\text{Li}_5\text{PS}_4(\text{BH}_4)_2$ arises from the synergistic interplay between cage-size uniformity and dynamically active BH_4^- reorientation.

2.4 | Dynamics on a Macroscopic Scale by PFG NMR Spectroscopy

PFG NMR probes ionic diffusion on a macroscopic length scale and on the time scale of approximately seconds, providing information more directly related to ion conductivity [54–59]. Under the influence of a field gradient, the spin-echo signal intensity decays as a function of the diffusion coefficient (D), magnetogyric ratio (γ), gradient strength (g), gradient pulse duration (δ), and the time interval between two gradient pulses (diffusion time, Δ), according to the Stejskal-Tanner equation [36, 60]:

$$I = I_0 \exp(-DB), \quad B = \gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \quad (3)$$

A single exponential decay function can describe the signal attenuation if the system follows a normal diffusion process, complying with Fick's law, which is typically observed in low-concentration electrolytes for lithium-ion batteries. Any deviation from a single exponential decay curve indicates that the system displays anomalous diffusion (e.g., restricted diffusion) or there exists a distribution in the diffusivity across the sample volume involving different translation mobilities (e.g., multiphase diffusion) [35, 61]. For multiphase diffusion, Equation (3) is extended as a sum of individual motional processes:

$$I = I_0 \sum_k p_k \exp(-D_k B) \quad (4)$$

where p_k is the relative fraction of each motional component with diffusion coefficient D_k [61]. Such multiphase behavior in terms of mobility has been observed in polymers, gels, and porous materials [62, 63].

The Stejskal-Tanner plots of SE - high and SE - inter, presented as logarithm signal intensity versus gradient factor (B), show nonlinear behavior, indicating that multiple motional processes with different translational mobilities exist (Figure 4a, Figure S9) [35, 36, 61, 62]. All samples show Δ -dependence; that is, the diffusion coefficients decrease with the diffusion time and reach plateau at $\Delta \geq 50$ ms, indicating restricted or constrained diffusion [35, 61, 63, 64]. Through a stepwise least-squares fitting procedure at $\Delta = 50$ ms (Figure S10), two distinct motional processes with high and low diffusivities can be identified. We assign the fast and slow motional component to intragranular diffusion (within individual grains) and intergranular diffusion

(involving grain boundary crossing), respectively (Figure 4c) [65]. The diffusion coefficients of the fast and slow components, as well as the average diffusivities (taking into account the relative fraction of each component), are higher for SE-high than for SE-inter (Figure 4d, Table S11). Li^+ diffusion of SE-low is too slow to be measured at room temp. Activation energies for Li^+ diffusion (Figures S11–S15) follow the order: SE-high < SE-inter < SE-low (Figure 4e, Table S11), which agrees with the E_a from SLR analysis. This suggests that the long-range motion represented by diffusivity is linked to the local motion captured by solid-state NMR.

The anomalous diffusion with multiphase behavior can be attributed to the structural complexity of the argyrodites, containing grain boundaries and particle agglomerates. To verify our assignment of motional components, PFG NMR measurements were performed on pellet-pressed SE-high samples: one by cold-pressing at room temperature (SE-high-cp), as used for the impedance measurements, and the other by hot-pressing with sintering at 120°C (SE-high-hp). The pressed samples show an almost linear Stejskal-Tanner plot with minimal Δ -dependence and a significant increase in the diffusion coefficients for both the fast and slow components, as well as in the average values (Figure 4b,d, Figures S9–S10). Particularly interesting is that the fraction of the slow-diffusion component increases from 16% in the powder to 45% and 55% in the cold-pressed and hot-pressed samples, respectively (Figure 4d). This trend confirms that the fast and slow motional processes indeed correspond to intragranular and intergranular Li^+ diffusion, respectively, and demonstrates that pressing the argyrodite powders reinforces particle contact and reduces grain boundary resistance, thereby promoting intergranular Li^+ transport. The highest ionic conductivity of 26.1 $\text{mS}\cdot\text{cm}^{-1}$ was achieved for SE-high-hp. Our results demonstrate that simultaneous pressing and sintering form more intimate and continuous grain interfaces, enhancing Li^+ ion diffusivity. Consistent results were observed in the SEM (Figure 4f, Figure S16). Average displacement of Li^+ , estimated from $(2Dt)^{1/2}$, is ~ 0.9 μm for SE-high, comparable to the particle size distribution. The SE-high-hp reveals fused particles, supporting the reduced Δ -dependence and enhanced Li^+ ion diffusivity.

2.5 | Behavior at the Cathode and Electrolyte Interphase: Cycled Samples

As reported previously, an ASSB assembled with a SE-high, Li-In anode, and LiNbO_3 -coated NCM811 cathode showed good electrochemical performance, retaining 96% reversible discharge capacity after 100 cycles at a 1C rate and 30°C (Figure 5a) [32]. To investigate structural changes in SEs and the CEI formation during charging/discharging, ex situ MAS NMR spectra were compared at various states of charge during the second charging step (Figure 5b). Cells were assembled specially using LCO cathode because lower paramagnetism of LCO enables clear distinction between the ^7Li signals of the SE and the cathode. For the SE area (Figure 5c), ^7Li , ^{31}P , and ^{11}B MAS NMR spectra (Figure 5d, Figure S17a,b) show no significant changes during the charging process, indicating structural stability upon cycling. For the cathode area, two discrete ^7Li NMR signals are observed near 0.4 and -0.4 ppm (Figure 5e,f), corresponding to the SE-high

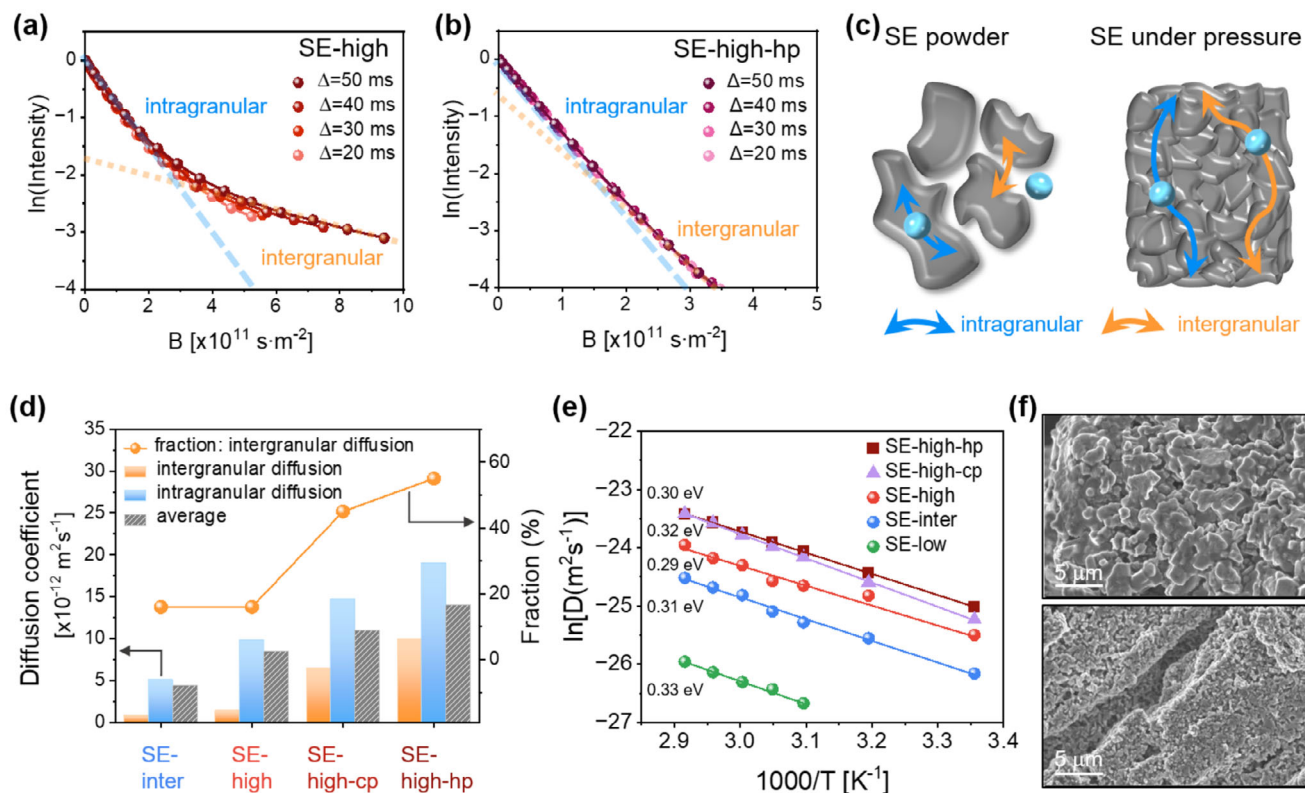


FIGURE 4 | Dynamics on a macroscopic scale by PFG NMR spectroscopy: Logarithmic plots of NMR signal intensities versus the gradient factor, B , obtained at 298 K with varying diffusion times (Δ) for (a) SE-high and (b) SE-high-hp. (c) Schematic illustration of Li⁺ diffusion occurring within the individual grain interior (intragranular diffusion) and involving grain boundary crossing (intergranular diffusion). (d) Comparison of diffusion coefficients and the fraction of intergranular diffusion. (e) Activation energies for Li⁺ diffusion derived from the temperature dependence of the diffusion coefficients. (f) Comparison of SEM images of SE-high (top) and SE-high-hp (bottom). For SE-high-hp, the hot-pressed pellet was fractured, and the image was taken from the cross-sectional side view.

electrolyte and the LCO cathode, respectively. As charging proceeds, the signal at -0.4 ppm disappears, and a new paramagnetic signal appears at a higher frequency, followed by a gradual shift toward ~ 100 ppm due to the oxidation of Co³⁺ to Co⁴⁺ at the cathode [66]. In addition, the ⁷Li NMR signal in the diamagnetic region (~ 0 ppm) exhibits a significant line broadening, with a gradual increase in linewidth as the states of charge increase (Figure 5f). This is in stark contrast to the SE area. The line broadening of the cathode area can be attributed to: (1) interactions with Co⁴⁺ and the enhanced bulk magnetic susceptibility; (2) formation of new species at the CEI; and (3) promoted exchange of Li⁺ ions. To identify the cause of the spectral changes, a ⁷Li-⁷Li two-dimensional (2D) exchange experiment (EXSY) was conducted on the 25% charged cathode area sample. 2D NMR enables the investigation of Li⁺ exchange between different sites and also improves spectral resolution. Along the diagonal, the paramagnetic LCO region (~ 60 ppm) exhibits a broad, homogeneous ⁷Li signal (Figure 5g). By contrast, the diamagnetic region (~ 0 ppm) shows a star-shaped signal, reflecting the high Li⁺ mobility in the argyrodite phase, which produces a Lorentzian lineshape and results in the characteristic star-shaped features upon 2D Fourier transformation. In the cross-sections along the F2 dimension (Figure 5h), the additional signals can be assigned to LiCl (-1.1 ppm; top slice) and to Li₂S and Li₃PS₄ (2.3 and 0.9 ppm, respectively; bottom slice); the corresponding reference spectra are shown in Figure S18. These species correspond to the

CEI formed after the first cycle. In addition, significant cross-peak intensities are observed, suggesting fast Li⁺ ion exchange between the SE, cathode, and CEI. Facile Li⁺ ion transport at the interface is known to be critical for solid-state battery performance, but, often degrades during cycling [67, 68]. Our results reveal that BH₄⁻-substituted argyrodites form a CEI that enables efficient Li⁺ ion transport across SE-CEI-cathode, thereby leading to stable cycling performance. Furthermore, the ¹¹B and ³¹P MAS NMR spectra of the cathode area display no noticeable changes (Figure S17c,d), indicating that the SE maintains its structural integrity with only minor CEI formation. Argyrodite-type SEs (Li₆PS₅Cl) are known to have a limited electrochemical stability window. It has been reported that at high potentials, Li₆PS₅Cl undergoes oxidative decomposition into Li₃PS₄, LiCl, S, and P₂S₅ during the charge cycle and subsequent reduction into Li₂S and Li₃P during the discharge cycle [69–73]. Our results demonstrate that the SSE based on the BH₄⁻-substituted argyrodite remains structurally stable during cycling, accompanied by the formation of a Li⁺-conducting CEI during the initial charge/discharge cycle. This formation of CEI products likely originates from the decomposition of a small fraction of the solid electrolyte at the immediate interface and appears to be self-limiting, thereby preserving the bulk of the electrolyte. This behavior is consistent with our previous report, in which cells employing the SE-high electrolyte exhibited improved cycling stability, suggesting the formation of a stable, passivating interphase [32].

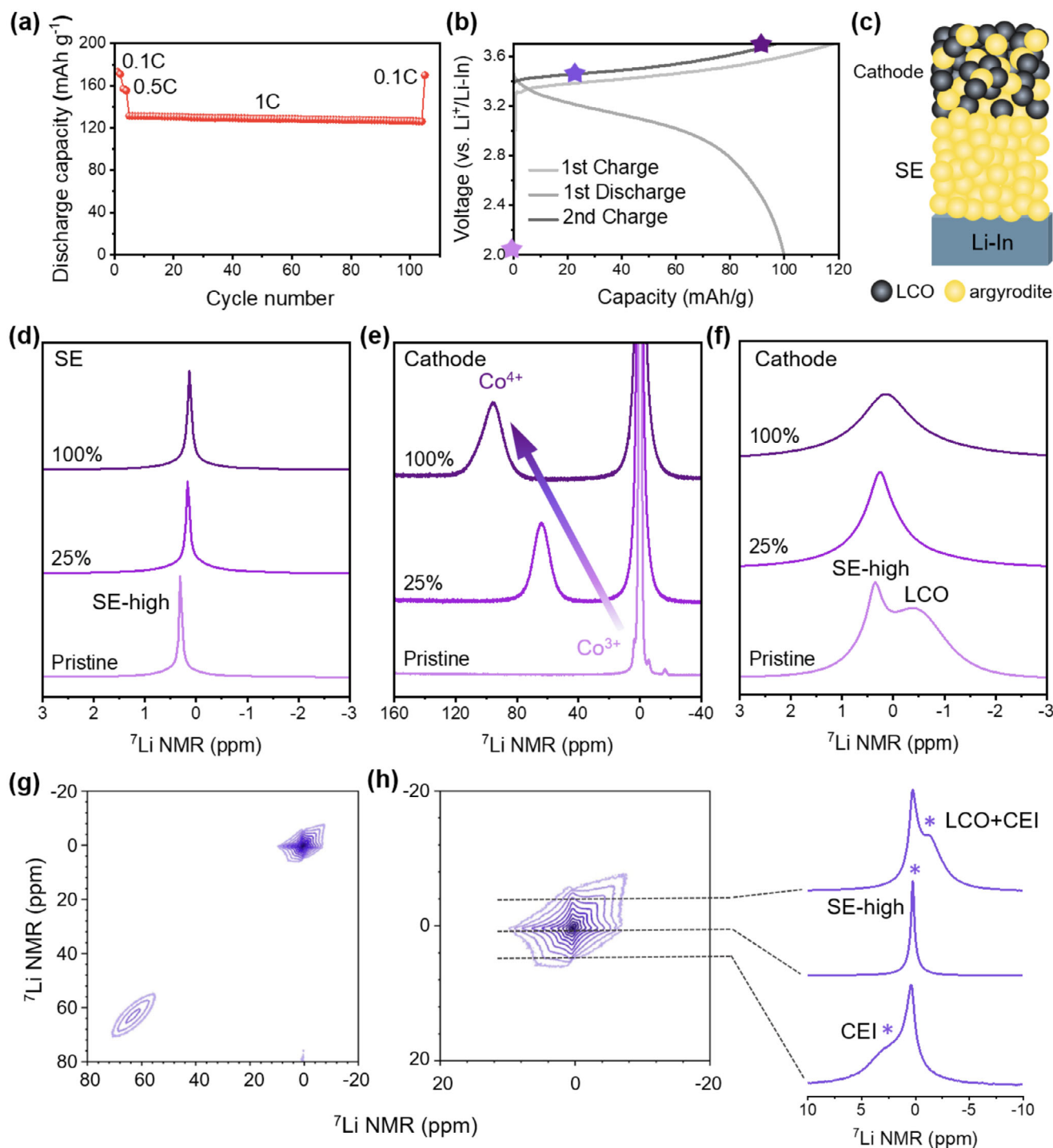


FIGURE 5 | Behavior at the cathode and electrolyte interphase: (a) Cycling performance of ASSB composed of NCM811 cathode/SE-high electrolyte/Li-In anode for 100 cycles at 1C rate and 30°C. Active material loading is 8 mg/cm². Cut-off voltage is between 2.0 and 3.7 V (versus Li⁺/Li-In). (b) Voltage profile of the ASSB composed of LCO cathode/SE-high electrolyte/Li-In anode designed for ex situ NMR measurements. Active material loading is 40.7 mg/cm² for a sufficient signal-to noise ratio in the NMR analysis. State of charge at which the cells were stopped for ex situ NMR measurements is marked with the star symbols. (c) Schematic of the ASSB configuration. Samples from the cathode area and the solid electrolyte (SE) area were separately extracted for subsequent NMR measurements. The cathode area contains both LCO and argyrodite (SE-high). (d) Ex situ ⁷Li MAS NMR spectra of the SE area at various states of charge. (e) Ex situ ⁷Li MAS NMR spectra of the cathode area at different states of charge. (f) Expanded view of (e), showing only the diamagnetic region. (g) ⁷Li-⁷Li magnetization exchange NMR spectrum of the cathode area at 25% state of charge. (h) Expanded view of (g), focusing on the diamagnetic region. Slices along the F2 dimension are displayed on the right-hand side of the 2D spectrum, with the positions of the diagonal signal indicated by asterisks on the slices.

3 | Conclusion

In this work, we studied the effects of BH_4^- substitution on the structure and Li^+ ion dynamics in argyrodite-type ($\text{Li}_6\text{PS}_5\text{X}$) solid-state electrolytes by using solid-state NMR spectroscopy and molecular dynamics simulations. MAS NMR distinguishes BH_4^- site occupancy at different crystallographic sites and reveals the extent of structural ordering in BH_4^- substituted argyrodites. Contrary to the conventional hypothesis that higher structural disorder leads to higher ionic conductivity, our results show that simultaneous BH_4^- occupancy at both the 4a and 4d sites is critical for achieving high Li^+ conductivity. This dual-site occupancy induces cage-size uniformity, reduces energetic mismatch between inter-connected Li^+ cages, and enables continuous, long-range Li^+ diffusion through the inter-cage network. Moreover, dynamic coupling between BH_4^- reorientation and Li^+ hopping further promotes Li^+ transport via paddle-wheel-like mechanism, highlighting the cooperative roles of site occupancy and anion dynamics in enhancing ionic conduction. In contrast, PS_4^{3-} reorientation plays a negligible role in Li^+ mobility. PFG NMR identifies Li^+ ion transport occurring within grains (intragranular diffusion) and involving grain boundary crossing (intergranular diffusion). The sample fabrication involving simultaneous thermal treatment and pellet pressing significantly improves microstructural connectivity and interfacial stabilization, thereby enhancing the bulk Li^+ ion diffusion. Finally, the formation of a $\text{Li}_2\text{S}/\text{LiCl}$ -based CEI during the initial cycling enables rapid Li^+ exchange between the cathode, CEI, and solid electrolytes, while maintaining the structural stability of the SE, thereby contributing to the excellent electrochemical performance of BH_4^- substituted argyrodites. Overall, our study provides crucial insights into the role of local polyanion dynamics in affecting long-range Li^+ ion transport. These findings offer valuable design principles for developing next-generation solid-state electrolytes with enhanced ionic conductivity and stable interfacial properties.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File 1: smll73722-sup-0001-SuppMat.pdf.

Supporting File 2: smll73722-sup-0002-VideoS1.trajectories of PS4 and BH4 polyhedra.mp4.