Conductor–Insulator Interfaces in Solid Electrolytes: A Design Strategy to Enhance Li-Ion Dynamics in Nanoconfined LiBH$_4$/Al$_2$O$_3$

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ABSTRACT: Synthesizing Li-ion-conducting solid electrolytes with application-relevant properties for new energy storage devices is a challenging task that relies on a few design principles to tune ionic conductivity. When starting with originally poor ionic compounds, in many cases, a combination of several strategies, such as doping or substitution, is needed to achieve sufficiently high ionic conductivities. For nanostructured materials, the introduction of conductor–insulator interfacial regions represents another important design strategy. Unfortunately, for most of the two-phase nanostructured ceramics studied so far, the lower limiting conductivity values needed for applications could not be reached. Here, we show that in nanoconfined LiBH$_4$/Al$_2$O$_3$ prepared by melt infiltration, a percolating network of fast conductor–insulator Li$^+$ diffusion pathways could be realized. These heterocontacts provide regions with extremely rapid $^7$Li NMR spin fluctuations giving direct evidence for very fast Li$^+$ jump processes in both nanoconfined LiBH$_4$/Al$_2$O$_3$ and LiBH$_4$/Li/I/Al$_2$O$_3$. Compared to the nanocrystalline, Al$_2$O$_3$-free reference system LiBH$_4$/Li/I, nanoconfinement leads to a strongly enhanced recovery of the $^7$Li NMR longitudinal magnetization. The fact that almost no difference is seen between LiBH$_4$/Li/I/Al$_2$O$_3$ and LiBH$_4$/Li/I/Al$_2$O$_3$ unequivocally reveals that the overall $^7$Li NMR spin-lattice relaxation rates are solely controlled by the spin fluctuations near or in the conductor–insulator interfacial regions. Thus, the conductor–insulator nanoeffect, which in the ideal case relies on a percolation network of space charge regions, is independent of the choice of the bulk crystal structure of LiBH$_4$, either being orthorhombic (LiBH$_4$/Al$_2$O$_3$) or hexagonal (LiBH$_4$/Li/I/Al$_2$O$_3$). $^7$Li (and $^1$H) NMR shows that rapid local interfacial Li-ion dynamics is corroborated by rather small activation energies on the order of only 0.1 eV. In addition, the LiI-stabilized layer-structured form of LiBH$_4$ guarantees fast two-dimensional (2D) bulk ion dynamics and contributes to facilitating fast long-range ion transport.

INTRODUCTION

Hydride-based solids attracted great attention as promising electrolytes for lithium-ion batteries due to their compatibility with Li metal and their mechanical robustness. While Li$^+$-ion transport in polycrystalline oxide-type electrolytes may suffer from large grain-boundary resistances, such regions do not hinder long-range ion transport in the mechanically softer hydrides.

The most prominent model hydride is LiBH$_4$, whose hexagonal modification, which is stable above $T_{ph} = 110$ °C, shows high conductivities in the mS cm$^{-1}$ range. The corresponding orthorhombic form, being the favorable crystal structure below $T_{ph}$ is, however, a rather poor ion conductor, likely because of much higher defect formation energies. While ultraslow Li$^+$ ion exchange in orthorhombic LiBH$_4$ is assumed to take place in three dimensions (Figure 1), for layer-structured LiBH$_4$, a two-dimensional (2D) conduction mechanism prevails (Figure 1), as has been shown by both frequency-dependent $^7$Li NMR spin-lattice relaxation (SLR) measurements and calculations. This 2D diffusion behavior is illustrated in Figure 1 using bond valence site energy estimations.

Two approaches have been established and presented in the literature that successfully enhance the room-temperature ionic conductivity of LiBH$_4$ by several orders of magnitude, viz, (i) nanoconfinement of LiBH$_4$ in insulating oxides and (ii) and partial cationic and especially anionic substitution of the BH$_4$ units with halogen ions like I$^-$, Br$^-$, or Cl$^-$. It is strongly anticipated that these two approaches lead to fundamentally
different diffusion mechanisms. While anion substitution in LiBH₄-LiX (X = I, Br, Cl) stabilizes the highly conductive hexagonal phase at much lower temperatures than Tₚ,t,15 through nanoconfinement, a large fraction of Li⁺-ion conductor−(ionic)insulator interfacial regions are introduced, which are suggested to be responsible for increased long-range ion transport. A definite proof of the latter concept or effect is, however, still missing for the LiBH₄/Al₂O₃ composites. For LiBH₄/SiO₂ nanocomposites, the important role of surface groups has been discussed recently.16,17

In general, heterocontacts between two different phases, viz., an ion conductor and an insulating phase, or even between two (mixed) conductors, may generate a percolation network of space charge regions with enhanced charge carrier mobility. The most prominent two-phase system is composed of alternating layers of F⁻-ion-conducting BaF₂ and CaF₂ with thicknesses of 9 nm, which were grown by molecular beam epitaxy.18 The foundations of space charge zones in such nanostructured artificial ion conductors were laid by Maier,19−22 explaining such nontrivial size effects that rely on overlapping space charge zones. CuBr/Al₂O₃(TiO₂) composites, as studied by Knauth and co-workers,23 belong to another group of such composites that show enhanced electrical conductivity.24,25

In the case of Li-ion conductors, Liang observed increased ionic conductivities in samples of LiI/Al₂O₃.26 Later, for the nanocrystalline system LiₓO/YₓO₃ (X = B, Al), similar effects27,28 were observed by 'Li NMR SLR rate measurements.29,30 Although enhanced Li⁺ diffusivity was probed, the resulting conductivities28 could not reach any practical benchmark needed to realize all-solid-state batteries equipped with ceramic electrolytes.

This situation is, however, different for nanoconfined LiBH₄-LiI/Al₂O₃ and LiBH₄/Al₂O₃, both showing ionic conductivities in the order of 10⁻⁴ S cm⁻¹,31 which is by more than a factor of 100 higher than in orthorhombic LiBH₄.13 To understand the synthetic approaches and their impact on overall ionic transport, the role of the conductor−insulator interface in achieving such high conductivities needs to be studied in detail. Preferably, such studies should include spectroscopic methods22 being sensitive to local Li⁺ hopping processes in or near these interfacial areas. Here, we used ⁷Li NMR spectroscopy to quantify the effect of the conductor−insulator interfacial regions in nanoconfined LiBH₄-LiI/Al₂O₃ and LiBH₄/Al₂O₃ prepared by melt infiltration. Although a recent ²⁷Al NMR study in our labs suggested that (unsaturated) penta-coordinated Al centers near the Al₂O₃ surface regions are involved in creating a defect-rich LiBH₄/Al₂O₃ interface,33

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Figure 1. (a, b) Crystal structure of orthorhombic LiBH₄ slightly different viewing direction as indicated by the axes drawn. The topology of possible ion-migration paths, as estimated via the SoftBV software tool and the bond valence pathway analyzer (see text), turned out to be interrupted rather than interconnected, mirroring the poor ionic conductivity of this phase. (c−e) Crystal structure of layered, hexagonal LiBH₄ for which the Li⁺ ions preferentially diffuse in two dimensions. (d) View along the c-axis in both directions to visualize the next-neighbor Li⁺ jump processes on a hexagonal lattice. (e) When jumping between regularly occupied sites, the ions temporarily occupy an intermediate position (IM). The saddle points connecting IM with the regular sites are marked with Sd and represent the points of the highest energy along the migration path.
The ultimate proof via $^7\text{Li}$ NMR SLR measurements is still missing. In the present study, we directly compared the $^7\text{Li}$ (and $^1\text{H}$) NMR response of longitudinal SLR of LiBH$_4$(-LiI)/Al$_2$O$_3$ with those of bulk LiBH$_4$ and LiI-stabilized LiBH$_4$. We observed a tremendous effect of the insulator Al$_2$O$_3$ on $^7\text{Li}$ NMR SLR, which is directly proportional to the diffusive motions of the Li$^+$ ions, clearly showing the superior role of conductor–insulator regions in solid electrolytes with nanometer-sized dimensions. Only in such samples, the volume fraction of these regions is large enough to have a dominant effect on overall ion transport properties.

**Methods and Characterization.** The composite electrolytes investigated here, i.e., LiBH$_4$/Al$_2$O$_3$ and LiBH$_4$-LiI/Al$_2$O$_3$, were prepared via melt infiltration; LiBH$_4$-LiI served as a reference compound. A detailed description of the corresponding procedure$^{34}$ as well as of the preparation and characterization of the composites$^{31}$ can be found elsewhere as the same samples were used for earlier studies. Ionic substitution was realized in a molar ratio of 80:20 (LiBH$_4$/LiI). The samples were kept at 295 °C for 30 min under 50 bar H$_2$ pressure in a stainless steel high-pressure autoclave (Parr). The average diameter of the pores in Al$_2$O$_3$ is in the order of 10 nm.$^{31}$ As mentioned above, at room temperature, bulk LiBH$_4$ crystallizes with orthorhombic structure and transforms into its hexagonal phase at temperatures higher than 110 °C; the corresponding X-ray diffraction patterns are shown in Figure S1. Here, results from differential scanning calorimetry (DSC), see Figure S2, reveal that the corresponding signal of LiBH$_4$/Al$_2$O$_3$ splits into two peaks at 103 °C and 114 °C; the signals are significantly decreased compared to the expected one of bulk LiBH$_4$ which was found at 117 °C. We do not observe any diagnostic DSC signals pointing to a phase change in LiBH$_4$-LiI/Al$_2$O$_3$ as for LiBH$_4$-LiI, the hexagonal modification is stabilized by the introduction of LiI already at lower temperatures. For the sake of completeness, LiBH$_4$-LiI shows a slight endothermic signal at −19 °C. The thermal behavior of LiBH$_4$/Al$_2$O$_3$ is useful when interpreting the diffusion-induced $^7\text{Li}$ NMR data, which were collected as follows.

Variable-temperature $^7\text{Li}$ (and $^1\text{H}$) NMR $1/T_1$ SLR rates were measured with a Bruker Avance III 300 spectrometer that is connected to a 7-Tesla cryomagnet. The corresponding Larmor frequencies were 116 MHz for $^7\text{Li}$ and 300 MHz for $^1\text{H}$. All samples were smoothly hand-pressed in Duran tubes under protective atmosphere and sealed. Relaxation rates were determined at temperatures ranging from −100 to 200 °C with an increment of usually 20 °C. In the region of the diffusion-induced rate peaks, additional $^7\text{Li}$ NMR $1/T_1$ rates were recorded every 10 or 5 °C. The laboratory-frame $^7\text{Li}$ (and $^1\text{H}$) NMR $1/T_1$ rates were acquired with the well-known saturation recovery pulse sequence; depending on temperature, the 90° pulse length (200 W) varied from 2.5 to 2.9 µs ($^7\text{Li}$) and from 1.1 to 3.3 µs ($^1\text{H}$). Usually four to eight scans were accumulated to obtain a single free induction decay. For a detailed description of the pulse programs used and for a discussion of the procedure employed to parameterize the longitudinal NMR transients (partly displayed in Figure S3), we refer to our previous study.$^{33}$

We also performed bond valence site energy estimations combined with a bond valence pathway analyzer using the softBV software tool developed by Adams and co-workers.$^{35,36}$ We took the structural information from published synchrotron X-ray powder diffraction data.$^{37}$ The softBV software executes a structure plausibility check, calculates surface energies, and gives information about the positions of interstitial sites and saddle points, as well as the topology.
and dimensionality of ion-migration paths and the respective migration barriers.\textsuperscript{5,36} For the calculations, Li\textsuperscript{+} was chosen as the mobile ion and the grid resolution was set to 0.1 Å. Pros and cons of the approach via softBV are discussed elsewhere.\textsuperscript{36} For the visualization of the data, we used the VESTA software package.\textsuperscript{38}

**RESULTS AND DISCUSSION**

**NMR Spin-Lattice Relaxation: Li-Ion Translational Dynamics and Rotational Jumps of the Polyanions.** As mentioned above, LiBH\textsubscript{4} crystallizes either with orthorhombic or with hexagonal symmetry. At temperatures lower than \( T_{pt} = 110 \) °C, the poorly conducting orthorhombic modification is present (see Figure 1). In ortho-LiBH\textsubscript{4}, the \(^7\text{Li} NMR spin-lattice relaxation rates indirectly sense the rapid rotational BH\textsubscript{4}\textsuperscript{−} dynamics rather than \(^7\text{Li}^\text{translational diffusion} (see Figure 2a). Thus, at temperatures below \( T_{pt} \), the \(^7\text{Li} NMR rates pass through two rate peaks that mirror the two distinct rotational jump processes of the BH\textsubscript{4}\textsuperscript{−} polyanions (see Figure 2a), which shows the \(^7\text{Li} NMR SLR rates of coarse-grained, that is, microcrystalline LiBH\textsubscript{4}. The broad rate maximum located at 220 K is composed of two individual rate peaks, which are represented by dotted lines and labeled P1 and P2 in Figure 2a. These rate peaks were analyzed in detail by both NMR\textsuperscript{9,39,40} and quasi-elastic and inelastic neutron scattering elsewhere.\textsuperscript{42} Additionally, the mobility of boron atoms is discussed elsewhere.\textsuperscript{43}

Above \( T_{pt} \), the overall \(^7\text{Li} NMR response in bulk LiBH\textsubscript{4} is governed by rapid Li\textsuperscript{+} (translational) jump processes in the layer-structured form of LiBH\textsubscript{4}. This dynamic process, which is 2D in nature as is illustrated in Figure 1, produces a single rate peak that points to an activation energy of 0.5 eV. In general, diffusion-induced \(^7\text{Li} NMR rate peaks appear if the motional correlation rate 1/\( \tau_c \), which is expected within a factor of ca. 2 to be identical with the jump rate 1/\( \tau \), reaches the order of the (angular) Larmor frequency of \( \omega_0 \).\textsuperscript{32} At the temperature where the peak appears, the condition \( \omega_c \approx 1 \) is fulfilled.\textsuperscript{43} A symmetric rate peak is only obtained for uncorrelated and isotropic (three-dimensional, 3D) diffusion. In many cases, a structural disorder combined with Coulomb interactions results in asymmetric NMR peaks whose low-T flank shows a lower slope than that characterizing the flank on the high-T side.\textsuperscript{43} Moreover, while the slope in the high-T regime is characteristic for long-range ion diffusion, the low-T flank of the peak is sensitive to short range, that is, local diffusion processes.\textsuperscript{11}

Stabilizing the hexagonal phase of LiBH\textsubscript{4} by the incorporation of LiI leads to several changes of the overall \(^7\text{Li} NMR response (see Figure 2a). First, it shifts the phase transition toward lower temperatures. Consequently, the \(^7\text{Li} NMR 1/\( T_1 \) rates pass into the low-T flank of the rate peak, which characterizes translational Li\textsuperscript{+} dynamics already at temperatures equal to or larger than 340 K. In agreement with faster Li\textsuperscript{+} diffusion in LiBH\textsubscript{4}-LiI, the slope of the low-temperature flank of the rate peak yields an activation energy \( E_a \) of 0.36 eV (Figure 2a) instead of 0.5 eV for LiBH\textsubscript{4}.\textsuperscript{9} This comparison shows that LiI does not only stabilize the hexagonal form at lower \( T \) but also reduces the mean activation barrier for Li\textsuperscript{+} translational diffusion as it is seen by NMR (Figure 2a).

Apart from the change of the rates above \( T_{pt} \), we recognize that also the rotational jump processes change when going from microcrystalline LiBH\textsubscript{4} to nanocrystalline LiBH\textsubscript{4}-LiI. The overall, original maximum located at 220 K shifted toward a much lower temperature (Figure 2a), indicating an increase in the corresponding motional correlation rate sensed by the \(^7\text{Li} spins. We assume that this increase is a direct consequence of the expanded lattice through the incorporation of \( \text{I}^− \) having a larger radius than BH\textsubscript{4}−. A deconvolution of this response into two rate peaks turned out to be no longer possible; for the LiI-containing sample LiBH\textsubscript{4}-LiI, the former two rate peaks P1 and P2 (see above) merge into a much broader peak located at \( T \approx 190 \) K. Most likely, this change originates from a broader distribution of rotational jump rates in LiBH\textsubscript{4}-LiI. The shift toward lower temperatures agrees with a reduction of the activation energies \( E_a \) associated with the BH\textsubscript{4}− rotational jumps. Here, \( E_a \) decreases from 0.26 to 0.12 eV if we consider the high-T flank of the \(^7\text{Li NMR rate peaks just below } T_{pt} \) (see Figure 2a). The introduction of LiI does also reduce the overall NMR coupling constant determining the maximum rates at \( T = 190 \) K.

Figure 2b shows the NMR responses of the two nanoconfined samples, LiBH\textsubscript{4}-LiI/Al\textsubscript{2}O\textsubscript{3} and LiBH\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3}. Starting from low temperatures, we recognize that the rates evolve in a similar manner to those of LiBH\textsubscript{4} and LiBH\textsubscript{4}-LiI, respectively. However, especially for LiBH\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3}, without any LiI incorporated, we notice enhanced BH\textsubscript{4}− rotational dynamics compared to the microcrystalline reference sample LiBH\textsubscript{4} having no contact to any insulator phase. For LiBH\textsubscript{4}-LiI/Al\textsubscript{2}O\textsubscript{3} and LiBH\textsubscript{4}-LiI, the \(^7\text{Li response turned out to be rather similar, while variable-temperature } ^\text{1H NMR SLR measurements (Figure 2a) showed some subtle differences in this temperature regime (see the Supporting Information). As suggested by Figures 4 and 2b, rotational ion dynamics in or near the conductor–insulator interfacial regions are enhanced for LiBH\textsubscript{4}-LiI/Al\textsubscript{2}O\textsubscript{3} compared to those in the bulk regions of LiBH\textsubscript{4}.

Most importantly, the largest effect of the insulating phase on \(^7\text{Li NMR spin-lattice relaxation is seen at higher temperatures when Li}\textsuperscript{+} translational ion dynamics start to govern the spin fluctuations (Figure 2b). In contrast to the sample without any Al\textsubscript{2}O\textsubscript{3}, we clearly recognize that the \(^7\text{Li NMR rates start to increase at temperatures as low as 240 and 270 K, respectively. These temperatures are clearly lower than } T_{pt} = 340 \) K for LiBH\textsubscript{4}-LiI (see Figure 2a). At temperatures slightly above 270 K, we recognize that the LiI-free sample does almost show the same NMR SLR response as seen for LiBH\textsubscript{4}-LiI/Al\textsubscript{2}O\textsubscript{3}, which unequivocally reveals that the interface effect is the main reason for the longitudinal recovery of the magnetization mirroring Li\textsuperscript{+} diffusivity.

Here, this effect turned out to be much larger than that seen for LiBH\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} composites that were earlier prepared by (high-energy) ball milling.\textsuperscript{15} Melt infiltration leaves behind a defective LiBH\textsubscript{4} phase, and we assume tight conductor–insulator contacts. The nanoconfined samples provide a large fraction of these heterocontacts. Our comparative NMR results clearly show that the interfacial regions play a dominant role in explaining enhanced ion dynamics in the nanoconfined samples regardless of whether LiI is present or not. The latter finding is supported by recent calculations revealing that the poor ion transport in orthorhombic LiBH\textsubscript{4} originates from very high defect formation energies.\textsuperscript{7} The LiBH\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3} zones are, however, expected to be rich in defects, thus facilitating ion transport.\textsuperscript{33} A similar effect has been described very recently by first-principles calculations for the interface in LiBH\textsubscript{4}/Mo\textsubscript{2}S\textsubscript{3} composites.\textsuperscript{44} Importantly, in LiBH\textsubscript{4}/SiO\textsubscript{2} composites, the role of surface groups should not be underestimated.\textsuperscript{16,17} Surface
effects are also important for LiBH₄/Al₂O₃ as has been shown quite recently by ²⁷Al NMR,⁴⁶ penta-coordinated Al centers Al⁴⁺ get saturated while generating Al⁵⁺BH₄⁻−Li⁺, forming a defect-rich zone with vacant or interstitial Li⁺ sites. The same mechanism has also been proposed by some of us for the recently studied LiF/Al₂O₃ nanocrystalline composites.⁴⁶

Up to 330 K, the ⁷Li NMR rates of the two nanoconfined Al₂O₃-containing samples (see Figure 2b) follow linear behavior. The associated activation energies turn out to be rather low and take values in the order of only 0.1 eV. This average value mirrors a flat potential landscape and is even lower than that of nanocrystalline LiBH₄ (0.18 eV) prepared by ball milling.⁴⁶ Values in the order of 0.07 eV were also recently studied by ⁷Li NMR, while NMR spin-lattice relaxation rates, especially when probed in the temperature regime of the low-T flank of the given 1/T₁(1/T) rate peak, are sensitive to the elementary hopping processes, NMR line shapes, which are governed by spin-spin-relaxation rates, can be used to probe Li⁺ transport on longer length scales. To see whether and to which extent the conductor–insulator effect does also affect the corresponding ⁷Li NMR lines, we recorded variable-temperature spectra of the reference sample LiBH₄-LiI (see Figure 3a) and the two nanoconfined samples (see Figure 3b,c).

Figure 3a shows the ⁷Li NMR lines of nanocrystalline LiBH₄-LiI. Starting from a broad signal at 173 K, which reveals sluggish Li⁺ translational ion dynamics in the bulk regions, the line undergoes heterogeneous motional narrowing upon heating. At temperatures above 294 K, a narrow line superimposes the broader Gaussian-shaped main signal. We attribute the narrowed line to Li⁺ ions in the interfacial regions of this nanocrystalline sample. These regions offer fast Li⁺ diffusion pathways as has recently been shown for nanocrystalline, orthorhombic LiBH₄.⁴⁶ The line recorded at 433 K reflects Li⁺-ion dynamics in hexagonal LiBH₄-LiI. At this temperature, all Li⁺ ions take part in rapid exchange processes. The quadrupolar satellite signals seen at ±8 kHz represent the 90° singularities of the powder pattern that is diagnostic for
this sample. In general, quadrupole intensities mirror the interaction between the electric quadrupolar moment of the $^7$Li nucleus (spin-quantum number $I = 3/2$) with a nonvanishing electric field gradient (EFG) at the nuclear site. This interaction alters the Zeeman levels such that for $I = 3/2$, four inequivalent levels are generated that depend on the crystallite orientation in the external magnetic field. Assuming an (averaged) axially symmetric EFG at the nuclear sites, the corresponding quadrupolar coupling constant $C_q$ of the powder sample is given by $C_q \approx 32$ kHz.

Nanoconfinement, i.e., the introduction of conductor–insulator interfacial regions, ensures that (heterogeneous) motional narrowing does already set in at temperatures lower than 250 K. This temperature agrees with the temperature at which the $^7$Li NMR rates start to increase. Satellite singularities come into the picture at 313 K. Already at 294 K, approximately 50% of the Li$^+$ ions in LiBH$_4$-LiI/Al$_2$O$_3$ (see Figure 3b) have access to fast diffusion pathways as is indicated by the ratio of the area fractions of the broad and the narrow NMR lines. For LiBH$_4$/Al$_2$O$_3$, the area fraction of the narrow line amounts to ca. 30% at 294 K (see Figure 3c).

As discussed earlier, a total coupling constant $C_q \approx 20$ kHz turned out to be clearly reduced compared to that of LiBH$_4$-LiI. Importantly, for LiBH$_4$/Al$_2$O$_3$, almost the same 50% lines. For LiBH$_4$/Al$_2$O$_3$, the area fraction of the narrow lines is approximately 50% of the Li$^+$ ions in LiBH$_4$-LiI/Al$_2$O$_3$ (see Figure 3b) have access to fast diffusion pathways as is indicated by the ratio of the area fractions of the broad and the narrow NMR lines. For LiBH$_4$/Al$_2$O$_3$, the area fraction of the narrow line amounts to ca. 30% at 294 K (see Figure 3c).

As discussed earlier, the overall coupling constant $C_q \approx 20$ kHz turned out to be clearly reduced compared to that of LiBH$_4$-LiI. Importantly, for LiBH$_4$/Al$_2$O$_3$, almost the same line shapes are detected as for the LiBH$_4$-LiI/Al$_2$O$_3$. Again, this result demonstrates the leading role of Al$_2$O$_3$ in governing the $^7$Li NMR signals. Motional narrowing is slightly shifted toward higher $T$, which is in excellent agreement with the temperature behavior of the $^7$Li NMR rates. The corresponding coupling constant $C_q \approx 23$ kHz of LiBH$_4$-LiI/Al$_2$O$_3$ resembles that of LiBH$_4$-LiI/Al$_2$O$_3$, see also the magnified spectrum recorded at 433 K (Figure 3c). It shows that nanoconfinement is also responsible for the electric quadrupole interactions and the majority of Li spins are subjected to in or near the conductor–insulator interfacial regions. As the pore size of Al$_2$O$_3$ is less than 10 nm, as has been reported earlier, the bulk regions, if confined to such small cages, are obviously also affected by the insulating surface regions.

The magnification of the spectrum recorded at 433 K (see Figure 3c) shows an additional pair of satellite regions, which we earlier ascribed to the Li ions farther away from the interface regions. The corresponding coupling constant of ca. 37 kHz agrees well with that which is obtained from the interface regions. The corresponding coupling constant of ca. 37 kHz agrees well with that which is obtained from the interface regions. Hence, NMR is able to reveal the different electrical interactions the spins are sensing in nanoconfined LiBH$_4$/Al$_2$O$_3$, with most of them being subjected to the insulator surface interactions and some residing in the smaller bulk areas. As mentioned above, this view is also corroborated by the NMR central lines shown in Figure 3.

Importantly, fast spin diffusion connecting the two spin reservoirs in the nanoconfined phases causes single exponential $^7$Li NMR $T_1$ magnetization transients; thus, a separation of the two spin ensembles, as it was possible earlier for high-energy ball-milled LiBH$_4$, is almost impossible if we use the longitudinal transients for this purpose (see Figure S2). Moreover, at a given temperature, the associated $1/T_1$ $^7$Li NMR rates of the fast and slowly decaying part of the underlying free induction decays do almost coincide. Hence, we conclude that for the nanometer-sized architecture in the conductor–insulator composites, rather efficient spin diffusion is present. Hence, from the point of view of SLR NMR, LiBH$_4$ in LiBH$_4$/Al$_2$O$_3$ appears as an almost homogeneous phase.

Noteworthy, while NMR is able to monitor the fast Li$^+$ exchange processes in the interfacial regions of the nanocomposites, it is, in the present case, less sensitive to long-range ion transport in LiBH$_4$-(LiI)/Al$_2$O$_3$. While the two samples LiBH$_4$-LiI/Al$_2$O$_3$ and LiBH$_4$/Al$_2$O$_3$ show almost the same $^7$Li NMR response, through-going ionic transport in LiBH$_4$-LiI/Al$_2$O$_3$ is easier (ca. $1.3 \times 10^{-4}$ S cm$^{-1}$ (298 K)) than in LiBH$_4$/Al$_2$O$_3$ (0.3 $\times 10^{-4}$ S cm$^{-1}$ (298 K)).

Most likely, this difference originates from the orthorhombic bulk regions in the latter compound that hinder Li$^+$ ion dynamics; see the schematic illustration in Figure 4 that summarizes the findings. A similar picture has been proposed for other dispersed ion conductors, such as nanocrystalline Li$_2$O/Al$_2$O$_3$ composites, whose heterogeneous transport properties were explained by the percolation concept. Here, for both compounds, the LiBH$_4$/Al$_2$O$_3$ interface (heterocontacts) provides fast Li$^+$ diffusion pathways. While at low temperatures Li$^+$ diffusion in the orthorhombic bulk regions of LiBH$_4$ in LiBH$_4$/Al$_2$O$_3$ is slow, and only enhanced at the LiBH$_4$/LiBH$_4$ homocontacts, anion substitution in LiBH$_4$-LiI/Al$_2$O$_3$ additionally ensures fast Li$^+$ self-diffusivity in the hexagonal bulk regions that do not benefit from interactions with the surface regions. Therefore, the combination of nanoconfinement and anion substitution enables facile, overall Li$^+$ long-range ion transport as it is necessary for, e.g., battery applications.

**CONCLUSIONS**

Using LiBH$_4$ and nanoconfined LiBH$_4$-LiI as model systems, we investigated the influence of conductor–insulator inter-
facial regions on the overall Li⁺ translational ion dynamics, which we sensed by 7Li NMR spin fluctuations. Al₂O₃ served as an insulating phase, that is, the phase usually blocking Li⁺-ion transport. As irregular diffusive motions trigger (longitudinal) 7Li NMR spin-lattice relaxation, with the help of variable-temperature measurements, activation energies and motional correlation rates can be probed.

While in nanoconfined LiBH₄-Lil rapid Li⁺ translational motions (0.36 eV) influence the 7Li NMR rates 1/T₁ at temperatures above 340 K, in the Al₂O₃-bear nanoconfined samples, a drastic change in overall NMR response is seen. For LiBH₄-Lil/Al₂O₃, the low-T flank of the corresponding diffusion-induced rate peak 1/T₁(1/T) is already seen at a temperature as low as 240 K, thus shifted by 100 K toward lower temperatures. Surprisingly, above 270 K, the same temperature as low onset temperatures and underpin the idea of a percolation network of fast diffusion pathways generated by the conductor–insulator interfacial regions.

7Li NMR line shape measurements corroborate the results from 7Li NMR relaxation and reveal, for both samples LiBH₄-Lil/Al₂O₃ and LiBH₄/Al₂O₃, an ensemble of mobile Li⁺ ions being subjected to rapid diffusive motions already at temperatures well below ambient. 7Li NMR quadrupole interactions seen in the spectra of nanoconfined LiBH₄/Al₂O₃ do reflect both bulk and interfacial regions, with the spins in the latter areas being highly mobile and benefiting from the interaction with the insulator surface. Our work highlights the importance of conductor–insulator interfacial regions in advanced solid electrolyte research. The clever introduction of such artificial interfaces, influencing ion dynamics by both structural disorder and space charge regions, represents an adjustable tool to manipulate overall (Li⁺) ion dynamics in solids with nanometer-sized dimensions.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c03789.

7Li and 1H NMR magnetization transients, 1H NMR rates, DSC curves, and XRD patterns (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Bachman, J. C.; Muy, S.; Grimaud, A.; Chang, H. H.; Pour, N.; Lux, S. F.; Paschos, O.; Maglia, F.; Luptar, S.; Lamp, P.; et al. Inorganic Solid-State Electrolytes for Lithium Batteries: Mechanisms and Properties Governing Ion Conduction. Chem. Rev. 2016, 116, 140–162.

(2) de Jongh, P. E.; Blanchard, D.; Matsuo, M.; Udovic, T. J.; Orimo, S. Complex Hydrides as Room-Temperature Solid Electrolytes for Rechargeable Batteries. Appl. Phys. A 2016, 122, No. 251.

(3) Gulino, V.; Brighi, M.; Murgia, F.; Ngene, P.; de Jongh, P.; Cerny, R.; Baricco, M. Room-Temperature Solid-State Lithium-Ion Battery Using a LiBH₄-MgO Composite Electrolyte. ACS Appl. Energy Mater. 2021, 4, 1228–1236.

(4) Thangadurai, V.; Narayanan, S.; Pinzaru, D. Garnet-Type Solid-State Fast Li Ion Conductors for Li Batteries: Critical Review. Chem. Soc. Rev. 2014, 43, 4714–4727.

(5) Manthiram, A.; Yu, X. W.; Wang, S. F. Lithium Battery Chemistries Enabled by Solid-State Electrolytes. Nat. Rev. Mater. 2017, 2, No. 16103.

(6) Matsuo, M.; Takamura, H.; Maekawa, H.; Li, H. W.; Orimo, S. Stabilization of Lithium Supercionic Conduction Phase and Enhance-
Conduction in Nanometre-Scale Planar Heterostructures. Experimental Results and Theoretical Models. Phys. Chem. Chem. Phys. 2003, 5, 2225–2231.

(30) Wilkening, M.; Indris, S.; Heitjans, P. Heterogeneous Lithium Diffusion in Nanocrystalline Li2O/Al2O3 Composites. Phys. Chem. Chem. Phys. 2003, 5, 2225–2231.

(31) Zettl, R.; de Kort, L.; Gombotz, M.; Wilkening, H. M. R.; de Jongh, P. E.; Ngene, P. Combined Effects of Anion Substitution and Nanoconfinement on the Ionic Conductivity of Li-Based Complex Hydrides. J. Phys. Chem. C 2020, 124, 2806–2816.

(32) Verkuijlen, M. H. W.; Ngene, P.; de Kort, D. W.; Barré, C.; Nale, A.; van Eck, E. R. H.; van Bentum, P. J. M.; de Jongh, P. E.; Kentgens, A. P. M. Nanoconfined LiBH4 and Enhanced Mobility of Li+ and BH4− Studied by Solid-State NMR. J. Phys. Chem. C 2012, 116, 22169–22178.

(33) Zettl, R.; Gombotz, M.; Clarkson, D.; Greenbaum, S. G.; Ngene, P.; de Jongh, P. E.; Wilkening, H. M. R. Ion Diffusion in Nanoconfined LiBH4-LiBH4 and LiBH4/Al2O3: From 2D Bulk Transport to 3D Long-Range Interfacial Dynamics. ACS Appl. Mater. Interfaces 2020, 12, 38570–38583.

(34) Suwarno, S.; Ngene, P.; Nale, A.; Eggenhuisen, T. M.; Oschatz, M.; Emb, J. P.; Remho, A.; de Jongh, P. E. Confinement Effects for Lithium Borohydride: Comparing Silica and Carbon Scaffolds. J. Phys. Chem. C 2017, 121, 4197–4205.

(35) Wong, L. L.; Phuah, K. C.; Dai, R.; Chen, H.; Chew, W. S.; Adams, S. Bond Valence Pathway Analyzer—An Automatic Rapid Screening Tool for Fast Ion Conductors within softBV. Chem. Mater. 2021, 33, 625–641.

(36) Chen, H.; Wong, L. L.; Adams, S. SoftBV—A Software Tool for Screening the Materials Genome of Inorganic Fast Ion Conductors. Acta Crystallogr. Sect. B: Struct. Sci., Cryst. Eng. Mater. 2019, 75, 18–33.

(37) Soulé, J. P.; Renaudin, G.; Černý, R.; Yvon, K. Lithium Boro-Hydride LiBH4: I. Crystal Structure. J. Alloys Compd. 2002, 346, 200–205.

(38) Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. J. Appl. Crystallogr. 2011, 44, 1272–1276.

(39) Soloninin, A. V.; Skripov, A. V.; Buzlukov, A. L.; Stepanov, A. P. Nuclear Magnetic Resonance Study of Li and H Diffusion in the High-Temperature Solid Phase of LiBH4. J. Solid State Chem. 2009, 182, 2357–2361.

(40) Skripov, A. V.; Soloninin, A. V.; Filinchuk, Y.; Chernyshov, D. Nuclear Magnetic Resonance Study of the Rotational Motion and the Phase Transition in LiBH4. J. Phys. Chem. C 2008, 112, 18701–18705.

(41) Martelli, P.; Remhof, A.; Borgschulte, A.; Ackermann, R.; Strüsser, T.; Emb, J. P.; Ernst, M.; Matsuo, M.; Orimo, S.-I.; Züttel, A. Rotational Motion in LiBH4/Li Solid Solutions. J. Phys. Chem. A 2011, 115, 5329–5334.

(42) Corey, R. L.; Shane, D. T.; Bowman, R. C.; Conradi, M. S. Atomic Motions in LiBH4 by NMR. J. Phys. Chem. C 2008, 112, 18706–18710.

(43) Wilkening, M.; Heitjans, P. From Micro to Macro: Access to Long-Range Li+ Diffusion Parameters in Solids via Microscopic Li Spin-Arrangement Echo NMR Spectroscopy. Chem. Phys. Chem. 2012, 13, 53–65.

(44) Liu, Z.; Xiang, M.; Zhang, Y.; Shao, H.; Zhu, Y.; Guo, X.; Li, L.; Wang, H.; Liu, W. Lithium Migration Pathways at the Composite Interface of LiBH4 and Two-Dimensional MoS2 Enabling Superior Ionic Conductivity at Room Temperature. Phys. Chem. Chem. Phys. 2020, 22, 4096–4105.

(45) Breuer, S.; Pregartner, V.; Lunghammer, S.; Wilkening, H. M. R. Dispersed Solid Conductors: Fast Interface Li-Ion Dynamics in...
Nanostructured LiF and LiF:γ-Al₂O₃ Composites. *J. Phys. Chem. C* 2019, 123, 5222–5230.

(46) Breuer, S.; Uitz, M.; Wilkening, H. M. R. Rapid Li Ion Dynamics in the Interfacial Regions of Nanocrystalline Solids. *J. Phys. Chem. Lett.* 2018, 9, 2093–2097.

(47) Heitjans, P.; Wilkening, M. Ion Dynamics at Interfaces: Nuclear Magnetic Resonance Studies. *MRS Bull.* 2009, 34, 915–922.

(48) Roman, H. E.; Bunde, A.; Dieterich, W. Conductivity of Dispersed Ionic Conductors—a Percolation Model with 2 Critical Points. *Phys. Rev. B* 1986, 34, 3439–3445.