Li-Ion Diffusion in Nanoconfined LiBH₄-LiI/Al₂O₃: From 2D Bulk Transport to 3D Long-Range Interfacial Dynamics

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ABSTRACT: Solid electrolytes based on LiBH₄ receive much attention because of their high ionic conductivity, electrochemical robustness, and low interfacial resistance against Li metal. The highly conductive hexagonal modification of LiBH₄ can be stabilized via the incorporation of LiI. If the resulting LiBH₄-LiI is confined to the nanopores of an oxide, such as Al₂O₃, interface-engineered LiBH₄-LiI/Al₂O₃ is obtained that revealed promising properties as a solid electrolyte. The underlying principles of Li⁺ conduction in such a nanocomposite are, however, far from being understood completely. Here, we used broadband conductivity spectroscopy and ¹H, ⁷Li, ¹¹B, and ²⁷Al nuclear magnetic resonance (NMR) to study structural and dynamic features of nanoconfined LiBH₄-LiI/Al₂O₃. In particular, diffusion-induced ¹H, ⁷Li, and ¹¹B NMR spin–lattice relaxation measurements and ³Li-pulsed field gradient (PFG) NMR experiments were used to extract activation energies and diffusion coefficients. ²⁷Al magic angle spinning NMR revealed surface interactions of LiBH₄-LiI with pentacoordinated Al sites, and two-component ¹H NMR line shapes clearly revealed heterogeneous dynamic processes. These results show that interfacial regions have a determining influence on overall ionic transport (0.1 mS cm⁻¹ at 293 K). Importantly, electrical relaxation in the LiBH₄-LiI regions turned out to be fully homogenous. This view is supported by ⁷Li NMR results, which can be interpreted with an overall (averaged) spin ensemble subjected to uniform dipolar magnetic and quadrupolar electric interactions. Finally, broadband conductivity spectroscopy gives strong evidence for 2D ionic transport in the LiBH₄-LiI bulk regions which we observed over a dynamic range of 8 orders of magnitude. Macroscopic diffusion coefficients from PFG NMR agree with those estimated from measurements of ionic conductivity and nuclear spin relaxation. The resulting 3D ionic transport in nanoconfined LiBH₄-LiI/Al₂O₃ is characterized by an activation energy of 0.43 eV.

KEYWORDS: lithium borohydride, nanoconfinement, electrolytes, dynamics, conductivity, NMR

1. INTRODUCTION

The increase of anthropogenic CO₂ in the atmosphere is responsible for the global warming observed; this warming is generally known as the greenhouse effect. Burning of fossil fuels belongs to one of the main sources of energy-related CO₂ emissions. Cutting our dependency on hydrocarbons, such as coal, fuel oil, or natural gas, and finding alternatives to convert energy, e.g., from solar or wind power, to electricity is one of the most important challenges that humans need to face within the 21st century. As electricity from solar power is generated from a nondispicable source of energy and, thus, highly intermittent, we have to develop high-performance and sustainable energy storage devices that are connected to the electricity grid in a mainly decentralized way. Secondary batteries, which either use Li⁺ or Na⁺ ions as ionic charge carriers, are suitable devices for this purpose. While Na-based batteries are envisaged to play a pivotal role in stationary energy storage, Li⁺-ion batteries offering both considerably higher energy densities and higher power densities are the devices of choice for automotive applications. Currently, these systems use flammable, aprotic liquid electrolytes. To increase both safety and longevity, solid electrolytes attracted great attention. Highly conducting solids, that is, polymers or ceramics, are at the heart of all-solid-state systems as they ensure the facile transport of the ions between the two compartments of a battery, viz., the anode and cathode.

Over the last years, many ceramic materials that show ionic conductivities with values reaching or even exceeding a benchmark of 1 mS cm⁻¹ have been presented. Each material, regardless of whether being an oxide, sulfide, thio phosphate, or hydride, has its own advantages and disadvantages with respect to, for example, electrochemical stability, interfacial resistance, chemical robustness, synthesis costs, and sustainability.

Highly conducting anion-substituted hydrides based on lithium borohydride (LiBH₄) especially when prepared in nanostructured forms that benefit from interfacial properties belong to the core group of sustainable materials composed of elements with high natural abundance. Quite recently, some of...
us reported on enhanced ion dynamics in nanoconfined LiBH4−LiI.11 Nanoco

...d of (i) substitutions of iodide anions for the BH4− units and (ii) spatial confinement resulted in a composite material with promising ion conductivities at room temperature. The underlying transport mechanism in this interface-controlled or surface-dominated material remains, however, unclear. Here, we used time domain and magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy to shed light on both structural features and ion dynamics in nanoconfined LiBH4−LiI.

Numerous publications, which appeared over the last decades, pointed out that various NMR techniques represent crucial and powerful analysis methods also in metal hydrides research. Already in 1987, Jarrett et al.12 used solid-state 1H NMR to identify bridging and terminal metal hydride sites. In LiZn2(BD4)3, 11B MAS NMR and multiple quantum MAS NMR helped identify four different boron sites in the [Zn2(BD4)3]2− anion.13 Furthermore, 1H, 7Li, and 11B NMR, including spin–lattice relaxation rate measurements in particular, were used to characterize the translational and rotational dynamics in this compound.14

Before complex metal hydrides received considerable attention from the battery research community, lithium borohydride, LiBH4, and its relatives were intensively investigated as hydrogen storage materials.15–18 NMR played a central role in characterizing both local structures and ion dynamics.19,20 As an example, Mg(BH4)2(NH2BH3)2, that is, a metal borohydride–ammonia borane complex, was proposed as a good candidate for hydrogen storage. Results from 11B MAS NMR were compared with those from DFT calculations to validate the crystal structure.21 It turned out that the excellent hydrogen-sorption properties found could be further enhanced by synthesizing composites with nanocafolds.22–24 Gutowska et al.25 used solid-state 11B NMR to underline their hypothesis that nanoconfinement of the complex metal hydrides decreases the temperature for hydrogen release from ammonia borane together with an increase in hydrogen purity. Conradi and co-workers26,27 presented an elegant NMR-based study using 1H NMR and 7Li NMR on LiBH4 and LiBH4 confined in carbon aerogel. They observed pronounced changes in Li mobility when going from bulk materials to nanoconfined samples.

Nanococonfined is, in general, an elegant approach to increase the room-temperature conductivity of LiBH4.28–31 Bulk LiBH4 undergoes a reversible structural change at approximately Tp = 110 °C and changes from the highly conductive hexagonal phase to the poorly conductive orthorhombic phase.32 The scaffolds of the nanococonfined complex hydrides are ionic insulators. In such conductor/insulator composites,33–37 enhanced ion transport along the heterointerfaces can occur due to both structural disorder and/or space charge effects.38,41–43

The first NMR studies on LiBH4, which was confined in silica, were realized in 2012 by Kentgens and co-workers.44 In the following years, solid-state NMR, especially 7Li NMR, proved itself as a powerful technique to study Li diffusion in these compounds that were envisaged as solid electrolytes for Li batteries.45–51 Quite recently, the same group46 reported on the phase behavior and Li ion dynamics of nanococonfined LiBH4 in silica. Furthermore, the second approach to increase ionic conductivity, which is anion substitution with, e.g., LiI (vide supra), was successfully studied via solid-state NMR.47,48 As mentioned above, replacing [BH4]− partly by halogen anions such as I− stabilizes the highly conducting hexagonal phase of LiBH4 at room temperature.

Despite the various studies,26,28–31,46 the role of the surface of the pore walls and complex hydride is not completely clear yet. A reaction or at least an interaction of the surface groups of the porous supports (Al2O3 or SiO2) with the metal hydride could be the key factor to explain the origin of the significant increase in ionic conduction upon nanoconfine

ment. Most of these studies deal with silica supports. It was, however, shown that the surface groups in alumina beneficially affected ion diffusion too.56 Similar effects were found with other oxides such as MgO, CaO, TiO2, and ZrO2.49 These surface groups can, in ideal cases, be identified via 7Al MAS NMR. Besides the well-known NMR signals for octahedrally and tetrahedrally coordinated Al in nanostructured γ-Al2O3, another signal shows up. In terms of chemical shift values, this signal is located between these two main signals and points to pentacoordinated alumina near the surface regions.50–52 Such sites might be involved in ion transport in nanoconfined, anion-stabilized LiBH4−LiI/Al2O3.

In our recent study on this system,11 we shed light on the correlation between morphology and Li-ion conductivity by means of X-ray diffraction, diffuse reflectance infrared Fourier transform spectra, N2 physisorption, and scanning electron microscopy. Impedance spectroscopy was used to characterize long-range ion transport in the nanoconfined composite. The present paper is aimed at giving insights into the mechanisms of Li+ diffusion in LiBH4−LiI/Al2O3. For this purpose, we used solid-state NMR techniques including variable-temperature 1H, 7Li, and 11B spin–lattice relaxation measurements and 7Li pulsed-field gradient (PFG) experiments to study ion dynamics on different length scales. We compare our results with transport parameters extracted from broadband conductivity measurements and electrical module spectroscopy. Structural features of the sample were probed by 1H, 6Li, 7Li, and 27Al MAS NMR. Taken together, we show that nuclear spin relaxation, PFG NMR, and electrical relaxation provide consistent diffusion coefficients characterizing long-range ion dynamics. Via the combination of these techniques, we were able to study ion transport in the nanoconfined ion conductor over a dynamic range of 6−8 orders of magnitude.

2. EXPERIMENTAL SECTION

2.1. Preparation of the LiBH4−LiI/Al2O3 Electrolyte. Lithium boron hydride (LiBH4 with a purity of 95%, Sigma Aldrich) and lithium iodide (LiI, 98%, Sigma Aldrich) were thoroughly mixed for several minutes in a ceramic mortar. The molar ratio LiBH4/LiI was 80:20. A sufficient amount of physical mixture was added to the porous support material, alumina (Al2O3, Sasol Puralox SCCa-5/200, see ref 11 for detail), to fill the pores by 130%. The pore size was determined by N2 physisorption and turned out to be 8.7 nm.11 The extra 30% was added to enable interconnectivity between the insulating alumina particles. The calculation was done after the specific pore volume has been determined via N2 physisorption. To finally obtain the melt-infiltrated alumina product, the mixture was filled in a quartz reactor and placed inside a stainless-steel high-pressure autoclave (Parr). After applying a pressure of 50 bar H2, the sample was heated to \( \theta = 295 \) °C with a heating rate of approximately 3 °C min\(^{-1}\). During a dwell time of 30 min, LiBH4 and LiI built a solid solution and infiltrate the pores of the alumina support.55 For a more detailed description, we refer to our recent study,11 which also includes the characterization of the reference samples LiBH4−LiI, i.e., a sample without alumina.
six-fold Al species, we also recognize pentacoordinated Al centers, [AlO5]. Most likely, as this signal does not show up in the spectra of LiBH4/LiI/Al2O3, we assume that six-fold coordinated surface species [AlO5X] (X = I, BH4−) are present.

To acquire the spectra, we used a Bruker Avance III 500 spectrometer that was connected to a 7.0 Tesla cryomagnet yielding the following resonance frequencies for the nuclei under investigation: 300.00 MHz (1H), 73.58 MHz (6Li), 160.42 MHz (11B), and 130.29 MHz (27Al). LiBH4/LiI/Al2O3 was re-sealed in Duran tubes for the 7Li and 1H experiments, and in quartz tubes for the 11B experiments, respectively. The rotors were carefully filled portion by portion with the powder sample, which was pressed by hand after each filling step to prepare a dense-packed rotor. Various reference samples such as LiBH4, Al2O3, LiBH4-LiI, and LiBH4/Al2O3 were also investigated to interpret the results of the nanocoated composite LiBH4-LiI/Al2O3 obtained via 1H, 6Li, 11B, and 27Al MAS NMR. To acquire the spectra, we used a Bruker Avance III 500 spectrometer that was connected to an 11.4 Tesla cryomagnet. This magnet field corresponds to the following resonance frequencies: 500.00 MHz (1H), 73.58 MHz (6Li), 160.42 MHz (11B), and 130.29 MHz (27Al). The MAS probe was operated at a spinning speed of 25 kHz. The temperature of the bearing gas was set to approximately 300 °C.

Pulse lengths, delay times, and number of scans of the time-domain free induction decays (FIDs) against the waiting time (t) were acquired with the spin-lock technique at a locking frequency of 20 kHz. The spin-lock period was varied such that it takes values ϑ = 30 °C. Spectra were recorded with a single-pulse excitation sequence. Pulse lengths, delay times, and number of scans for each spectrum are listed in Table S1. Free induction decays were Fourier transformed to obtain spectra without any further manipulation except for zero- and rst-order phase correction.

Figure 1. (a) 1H, 6Li, 11B, and 27Al MAS NMR spectra of LiBH4-LiI/Al2O3. The NMR spectra are compared with those of LiBH4, LiBH4-LiI, LiBH4/Al2O3, and Al2O3, respectively. The spinning speed was 25 kHz. (b) 6Li MAS NMR spectra, for LiBH4/Al2O3 a line composed of two spectral components is observed. (c) 11B MAS NMR spectra, which also show a two-component line shape for the nanoconﬁned samples. (d) 27Al MAS NMR spectra of Al2O3, besides lines attributable to four- and six-fold Al species, we also recognize pentacoordinated Al centers, [AlO5]. Most likely, as this signal does not show up in the spectra of LiBH4/Al2O3 and LiBH4-LiI/Al2O3 we assume that six-fold coordinated surface species [AlO5X] (X = I, BH4−) have been formed.

2.2. Nuclear Magnetic Resonance. Samples for MAS NMR measurements were filled in Bruker MAS rotors (ZrO2) with a diameter of 2.5 mm and a length of 1 cm. The rotors were carefully filled portion by portion with the powder sample, which was pressed by hand after each filling step to prepare a dense-packed rotor. Various reference samples such as LiBH4, Al2O3, LiBH4-LiI, and LiBH4/Al2O3 were also investigated to interpret the results of the nanocoated composite LiBH4-LiI/Al2O3 obtained via 1H, 6Li, 11B, and 27Al MAS NMR. To acquire the spectra, we used a Bruker Avance III 500 spectrometer that was connected to an 11.4 Tesla cryomagnet. This magnet field corresponds to the following resonance frequencies: 300.00 MHz (1H), 73.58 MHz (6Li), 160.42 MHz (11B), and 130.29 MHz (27Al). The MAS probe was operated at a spinning speed of 25 kHz. The temperature of the bearing gas was set to approximately 300 °C. Spectra were recorded with a single-pulse excitation sequence. Pulse lengths, delay times, and number of scans for each spectrum are listed in Table S1. Free induction decays were Fourier transformed to obtain spectra without any further manipulation except for zero- and rst-order phase correction.

Information about ion dynamics, i.e., activation energies $\tau_1$, jump rates $\tau_1^{-1}$, was collected under static, that is, under non-MAS conditions with a Bruker Avance III 300 spectrometer. The spectrometer was connected to a 7.0 Tesla cryomagnet yielding the following resonance frequencies for the nuclei under investigation: 300.00 MHz (1H), 116.59 MHz (6Li), and 96.25 MHz (11B). LiBH4-LiI/Al2O3 was re-sealed in Duran tubes for the 6Li and 1H measurements and in quartz tubes for the 11B experiments, respectively. The samples were placed in a commercially available probe head (Bruker) designed to be operated at temperatures $\theta$ as high as 300 °C; the probe was equipped with a ceramic sample chamber and a type T thermocouple to monitor the temperature which we adjusted with a stream of nitrogen gas that passed a heater beneath the sample chamber. The heater was connected to a Eurotherm temperature controller. We varied the temperature for the measurements of longitudinal NMR spin–lattice relaxation (SLR) rates $R_L$ (1/T1) and for the measurement of the spin-lock rates $R_{\rho}$ (1/Tρ) from $-100$ °C to 160 °C.

The so-called saturation recovery pulse sequence was used to record the 1/T1 rates in the laboratory frame of reference: a comb of closely spaced $\pi/2$ pulses destroys any longitudinal magnetization $M_0$. The subsequent recovery curve of $M_0$, see the Supporting Information (Figure S1), is obtained by plotting the area under the free induction decays (FIDs) against the waiting time $t_w$. To parametrize the transients $M_0(t_w)$, stretched exponential fits were used, $M_0(t_w) \propto 1 - \exp(-(t_w/T_\rho)^\gamma)$ with $0 < \gamma \leq 1$. Rotating-frame 1H NMR SLR$p$ rates were acquired with the spin-lock technique at a locking frequency of 20 kHz. The spin-lock period $t_{lock}$ was varied such that it takes values from 10 μs to 1 s. Worth noting, it is crucial to ensure full longitudinal relaxation between each spin-lock scan. This is realized by paying attention to a recycle delay of $5 \times T_1$. Again, stretched exponential fits were used to analyze the transversal transients, $M_0(t_{lock})$: $M_0(t_{lock}) \propto \exp(-(t_{lock}/T_{\rho}^\phi)^\phi)$ with $0 < \phi \leq 1$, see Figure S1, and obtain the $R_{\rho}$ rates (1/Tρ). All sample-preparation steps for MAS NMR and static NMR were carried out under a protective argon (Ar) atmosphere. Pulse lengths, delay times, and number of scans of the time-domain experiments are summarized in Table S1 also.

PFG diffusion-ordered spectroscopy (DOSY) NMR was conducted using a 300 MHz Varian direct drive spectrometer and Doty Scientific
closed-bore gradient probe capable of producing gradients of up to 1200 G cm\(^{-1}\). The sample was packed under the Ar atmosphere into high-throughput NMR tubes (Wilmad) with a 5 mm outer diameter and sealed with tight-fitting caps and Paraflm. \(^7\)Li NMR experiments were then conducted to determine the relaxation and diffusion properties of the sample at different temperatures. For further information on the PFG DOSY experiment, we refer to the Supporting Information section. Results were fit using the Stejskal–Tanner equation for stimulated echo pulse sequences with square pulses, see Figure S2 and the Supporting Information for details.

Transverse relaxation times \(T_2\) were measured at three temperatures, viz., at 25, 60, and 90 °C using a Hahn–Echo pulse sequence with variable delays; corresponding transients are shown in Figure S3. At 25 °C, the spin–spin relaxation time was 500 \(\mu\)s. At 60 and 90 °C, \(T_2\) increased, however, to 2.7 and 4.9 ms, respectively. \(T_2\) was approximated to be on the order of hundreds of milliseconds at all temperatures based on sample saturation observation at shorter delays between single-pulse experiments. In fact, independent measurements of \(T_2\) yielded \(T_2 = 590\) ms at 60 °C (116.59 MHz) and \(T_2 = 510\) ms at \(\theta = 100\) °C. This circumstance enabled sufficiently long diffusion times in \(^7\)Li-stimulated echo DOSY experiments and the measurement of diffusion coefficients on the order of \(10^{-11}\) \(m^2\) s\(^{-1}\).\(^\text{2..3. Impedance Spectroscopy.}\) For the impedance spectroscopy measurements, a sample of LiBH\(_4\)-LiI/Al\(_2\)O\(_3\) was pelletized with a load of 0.5 tons. The final two pellets (5 mm in diameter) were sputtered on both sides with gold. The Au layers (100 nm in thickness) acted as ion-blocking electrodes. The sample was placed in an active ZGS sample cell (Novocontrol), which was connected to a Concept 80 broadband impedance spectrometer (Novocontrol) using an Alpha-A analyzer. The cell was continuously flushed with a stream of freshly evaporated nitrogen to avoid any contamination or reaction with moisture. The sample was placed between two gold-sputtered spacer electrodes and a spring to ensure a sufficiently long contact throughout the measurements. We corrected the measured impedance for the cell stray and spacer capacity, which depends on the dimensions of the electrodes and the sample pellet itself. Conductivity isotherms were recorded at temperatures \(\theta\) ranging from \(-50\) to \(100\) °C in a frequency range of 10 MHz to 10 mHz.

A second pellet of the same batch was used to carry out variable-temperature impedance measurements but at fixed frequencies of 100 Hz and 100 kHz (\(-140\) to 160 °C, in steps of 5 °C). We analyzed the resistivity in the form of \(M'/\omega\) where \(M'\) is the imaginary part of the complex electric modulus, and \(\omega\) denotes the angular frequency. Such a plot reveals peaks being similar to those seen in \(^7\)Li NMR spin–lattice relaxation.

3. RESULTS AND DISCUSSION

3.1. Structural Elucidation. High-resolution (MAS) NMR was used to observe structural changes of the different LiBH\(_4\)-based composites. \(^1\)H, \(^7\)Li, \(^11\)B, and \(^27\)Al MAS NMR spectra are shown in Figure 1. Intensities are given in arbitrary units; the spectra are scaled such that it is easier to differentiate between the distinct spectral contributions. The \(^1\)H MAS NMR spectrum (Figure 1a) of LiBH\(_4\)-LiI/Al\(_2\)O\(_3\) reveals a main signal that is very similar to that of the LiBH\(_4\)-LiI sample. The spectra of the samples without LiI are shifted toward lower parts per million (ppm) values, that is, these lines are upfield or shielded. Obviously, because halides have a higher electronegativity than the borohydride anion, \(^1\)H in the direct neighborhood of I experiences, on average, a reduced electron density at its site, and it is therefore less magnetically shielded. Consequently, the corresponding lines appear in the downfield region, i.e., they are shifted toward the direction of positive ppm values. Interestingly, nanocofiguration of LiBH\(_4\) (or LiBH\(_4\)-LiI) in Al\(_2\)O\(_3\) did not lead to a shift on the ppm scale of the corresponding NMR lines.

The small signal at more positive ppm values (isotopic shift \(\delta_{iso} = -11.5\) ppm, see Figure 1a) might be attributed to an \(H\)-containing impurity phase. This signal is anticipated to be related to the 95% purity of the sample. The same holds for the tiny line located at \(-14\) ppm (see arrow), which we also assign to a slight amount of impurities in pristine LiBH\(_4\).\(^\text{4..5.}\) Most likely, these lines arise from compounds such as LiB\(_2\)H\(_7\) or LiB\(_2\)H\(_{12}\). Alternatively, it has been suggested, at least for LiBH\(_4\)/SiO\(_2\), that this line would be attributed to trapped H\(_2\), which is released as a result of a surface reaction between BH\(_4\)\(^-\) and the silanol groups at the surface of the oxide.\(^\text{45..55}\)

Compared to \(^1\)H, \(^6\)Li MAS NMR revealed more distinct changes when going from LiBH\(_4\) to the final anion-stabilized nanocomposite, see Figure 1b. Coarse-grained LiBH\(_4\) shows a signal at approximately \(\delta_{iso} = -1.35\) ppm, the \(^6\)Li NMR spectra are referenced to an aqueous solution of LiCl (0 ppm, crystalline lithium acetate served as a secondary reference). If in contact with Al\(_2\)O\(_3\), we see that more than approximately 50% of the Li ions, as estimated via deconvolution of the spectrum with Gaussian functions, experiences an NMR line shift toward positive ppm values. The original line, being reduced in intensity, is still seen. This feature reveals the important effect of Al\(_2\)O\(_3\) and its surface groups on the \(^6\)Li NMR signal of the composite.

Adding LiI to LiBH\(_4\) broadens the LiBH\(_4\) signal and shifts its center of gravity slightly to less negative ppm values; the NMR line of LiBH\(_4\)-LiI appears at ca. \(-1.3\) ppm (Figure 1b). Broadening of the line might be explained by site disorder introduced. For LiBH\(_4\)-LiI/Al\(_2\)O\(_3\), a single line is seen at \(\delta_{iso} = -1\) ppm (see Figure 1b). This line and its position can be explained by two-accumulating effects. Obviously, the Li ions in nanocofigured LiBH\(_4\)-LiI/Al\(_2\)O\(_3\) experience a magnetic environment, which is similar but not identical with that in LiBH\(_4\) or LiBH\(_4\)-LiI. As indicated by the line of LiBH\(_4\)/Al\(_2\)O\(_3\), a large amount of Li\(^+\) ions is influenced by the presence of Al\(_2\)O\(_3\). For LiBH\(_4\)-LiI/Al\(_2\)O\(_3\) this feature is even more pronounced. Second, as has been seen in a recent study,\(^\text{11..}\) \(^6\)Li ishanced by two-accumulating effects. Obviously, the Li ions in nanocofigured LiBH\(_4\)-LiI/Al\(_2\)O\(_3\) experience a magnetic environment, which is similar but not identical with that in LiBH\(_4\) or LiBH\(_4\)-LiI. As indicated by the line of LiBH\(_4\)/Al\(_2\)O\(_3\), a large amount of Li\(^+\) ions is influenced by the presence of Al\(_2\)O\(_3\). For LiBH\(_4\)-LiI/Al\(_2\)O\(_3\) this feature is even more pronounced. Second, as has been seen in a recent study,\(^\text{11..}\) compared to both LiBH\(_4\)-Al\(_2\)O\(_3\) and LiBH\(_4\)-LiI, ion dynamics, and thus the Li\(^+\) exchange rate, is noticeably higher in the nanocofigured composite. Hence, at room temperature, and above, the line already represents a motionally narrowed signal with the Li\(^+\) ions experiencing a magnetically homogeneous matrix (see also below). This view is supported by variable-temperature \(^7\)Li NMR line shape measurements revealing, from a dynamic point of view, a single, motionally narrowed central line. Moreover, the \(^7\)Li NMR lines do only reveal a single-electric quadrupole pattern pointing to an ensemble of Li ions experiencing the same electric field gradient. This observation is in line with a magnetically homogeneous environment to which the single \(^6\)Li MAS NMR line points.

For \(^{11}\)B, we observed a single line for LiBH\(_4\) the same is true for the line belonging to LiBH\(_4\)-LiI, which is shifted toward lower ppm values (see Figure 1c). The spectra were referenced to LiBH\(_4\) whose signal shows up at \(-41\) ppm when referenced to BF\(_3\)O(CH\(_2\)CH\(_3\))\(_3\) (0 ppm), see Hwang et al.\(^\text{56..}\) While for the nanocofigured samples, single lines are seen; those of the nanocofigured samples reveal two spectral components. For LiBH\(_4\)-LiI/Al\(_2\)O\(_3\), we see that the original line, assigned to LiBH\(_4\), is slightly shifted toward the position of the line of LiBH\(_4\)-LiI. In addition, a shoulder appeared that is also visible in the spectrum of LiBH\(_4\)/Al\(_2\)O\(_3\) (Figure 1c). Most likely, \(^{11}\)B

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senses the presence of Al$_2$O$_3$ causing this extra line in NMR spectroscopy.

Finally, we used $^{27}$Al NMR spectroscopy to visualize any unsaturated Al centers near or at the surface regions of the alumina scaffold, see Figure 1d. Indeed, pure Al$_2$O$_3$, which is here present in its $\gamma$-modification, produces a $^{27}$Al MAS NMR spectrum that is not only composed of the signals reflecting six- and four-fold-coordinated Al species, see the signals at 9 ppm and at ca. 65 ppm, but is also including a line at approximately 30 ppm (Figure 1d). Although the intensity of the line is low, we are certain that it represents unsaturated pentacoordinated Al ions near the surface of the oxide.\(^{36,52}\)

The generation of such pentacoordinated sites has been studied for nanocrystalline $\gamma$-Al$_2$O$_3$\(^{52}\) which can be prepared by high-energy ball-milling. These sites can be saturated if foreign anions, such as F$^-$ anions from CaF$_2$ or LiF, are offered.\(^{36,52}\) As a consequence, the signal disappears since [AlO$_5$F] will give rise to NMR lines with chemical shifts highly comparable to that of [AlO$_5$]. Indeed, this phenomenon is also seen in the present case, see Figure 1d. For both LiBH$_4$/Al$_2$O$_3$ and LiBH$_4$-LiI/Al$_2$O$_3$ we observe only the main signals reflecting [AlO$_5$] and [AlO$_4$]. This comparison shows that, at least to a certain degree, the anions $\Gamma^-$ and BH$_4^-$ interact with the [AlO$_5$] surface groups, which serve as anchoring points for these anions. In nanocomposites of LiF/Al$_2$O$_3$, this interaction influences Li$^+$ transport, as Li$^+$ is assumed to be electrostatically bound to the [AlO$_5$F] sites.\(^{36}\) The complex [AlO$_5$F]$^-$ Li$^+$ leaves behind Li$^+$ vacancies being necessary for the other Li$^+$ ions to perform hopping processes in the vicinity of the surface regions. Such a surface-controlled diffusion mechanism might be a universal feature of conductor/insulator composites with $\gamma$-Al$_2$O$_3$ equipped with unsaturated species in interfacial regions. As in the case of LiF/Al$_2$O$_3$\(^{36}\) or LiI/Al$_2$O$_3$\(^{37}\) percolating surface pathways would give rise to enhanced long-range Li ion transport. Here, also, hydroxyl surface groups might strongly influence Li$^+$ interfacial ionic transport as has been suggested by us recently.\(^{11}\)

Importantly, the asymmetry of the NMR signal belonging to [AlO$_5$] (and [AlO$_4$]) showing a tail in the direction of low chemical shift values serves as a classical indication of disordering. As LiBH$_4$-LiI (and LiBH$_4$ without LiI) infiltrates the pores of the oxide support, we attribute disordering to the generation of strain and polyhedra distortions experienced by the Al species on or near the surface of the oxide.\(^{27}\) $^{27}$Al multiquantum MAS NMR might be helpful to characterize this effect in future studies.

### 3.2. Impedance Spectroscopy and Resistivity Measurements at Fixed Frequency

Figure 2a includes selected conductivity isotherms of LiBH$_4$-LiI/Al$_2$O$_3$, which show the real part, $\sigma'$, of the complex conductivity as a function of frequency $\nu$. The isotherms are composed of three regimes. Regime I is caused by polarization effects appearing at sufficiently low frequencies and high DC conductivity values. DC conductivities $\sigma_{DC}$ can be read off from the frequency-independent plateau spanning, at $\theta = 20$ °C, a frequency range of six orders of magnitude (regime II). At this temperature, the ionic bulk conductivity $\sigma_{DC}$ is in the order of 0.1 mS cm$^{-1}$, see the horizontal arrow in Figure 2a. With increasing frequency, the DC plateau passes into regime III, which is the dispersive region being characteristic for correlated, forward-backward jump processes and electrical relaxation processes proceeding on a shorter length scale. This regime is best seen at low temperatures and high frequencies, see Figure 2a.
The DC plateau together with its dispersive regime produces a single depressed, i.e., non Debye, semicircle in the complex plane plot; two of these plots are exemplarily shown in Figure 3a. They show the imaginary part, $-Z''$, of the complex impedance as a function of the real part, $Z'$. Simulating the main electrical response with an equivalent circuit consisting of a resistor connected in parallel with a constant phase element, as shown in the inset of Figure 3a, yields a capacity of 6.5 pF, which lies in the expected range for values of bulk processes. Values in the order of 10 pF are also estimated for this electrical process if we take a look at the change of the real part of the complex capacitance $C'$ as a function of frequency, see the first step of the $C'(\nu)$ when coming from high frequencies, which is marked by the dashed lines drawn. In terms of $\varepsilon'$, which is the real part of the complex permittivity, this values corresponds to $\varepsilon'(\nu \to 0) \approx 80$, see the right axis of Figure 3b. The shape of the corresponding complex modulus $M''(\nu)$ is shown in Figure 3c. At $\vartheta = -50 \, ^\circ C$, the characteristic relaxation frequency reaches values in the order of $10^5 \, Hz$. In all three plots (Figure 3a–c), neglecting the effect of polarization of the ion blocking electrodes, a single electrical response characterizes the overall behavior. Hence, from the point of view of electrical relaxation, nanoconfined LiBH$_4$-LiI/Al$_2$O$_3$ behaves like a homogenous matrix. Considering the small pore size of 9 nm, see above, this result seems to be quite reasonable as the inner regions of the pores are expected to be affected by space charge or surface effects. Here, we cannot see distinct responses that exclusively reflects relaxation in or near

Figure 3. (a) Nyquist plots showing the electrical response of nanoconfined LiBH$_4$-LiI/Al$_2$O$_3$ as the location curve of $-Z''$ as a function of $Z'$ at two different temperatures, viz., recorded at 25 °C and $-50 \, ^\circ C$. The dashed lines show simulations of the semicircle with the equivalent circuit shown. The response at low frequencies reflects electrode polarization, see also (b). In contrast to the spike seen at 25 °C, the flat response of the location curve referring to $-50 \, ^\circ C$ (see arrow) might indicate the influence of interfacial electrical relaxation processes. (b) Real part of the capacitance as a function of frequency. The curves correspond to the conductivity isotherms shown in Figure 2a; the right axis shows the change of $\varepsilon'$ with frequency. (c) Modulus spectra of nanoconfined LiBH$_4$-LiI/Al$_2$O$_3$ recorded at the temperatures indicated.

Figure 4. (a) Full set of conductivity isotherms recorded at temperatures ranging from $-140$ to $160 \, ^\circ C$. The solid lines show power law fits revealing that the dispersive regime directly associated with the DC response has to be characterized by an exponent $p = 0.5$, which points to 2D ionic conduction. The DC response corresponds to the conductivities in the limit $\nu \to 0$ excluding polarization effects. At lower temperatures, the frequency dependence in the dispersive regime changes from $p = 1/2$ to $p = 1$ and further to $p = 2$. While $p = 1$ is consistent of nearly constant loss behavior of the imaginary part of the complex permittivity, $p = 2$ indicates the influences of phonons on $\sigma'$. (b) Change of the DC conductivity with temperature, plotted as $\log_{10}(\sigma_{DC}T)$ vs 1000/T. The position $\sigma_{DC}T$ of microcrystalline LiBH$_4$ (orthorhombic modification) is also shown; data reproduced with permission from ref 29. Copyright 2010 John Wiley and Sons.
This view on $\rho_c$ crossover from Figure 2b marks a kink (380 K) most likely showing the maximum is composed of two contributions. The arrow in related to each other via deviation of the Lorentzian-shaped peak log10(\beta relaxation time, and would be obtained. From symmetric behavior. For \(\beta\) (regime III in Figure 2a).

$T_{\text{depressed}}$, non Debye semicircle in the complex plot lines, because of sufficiently rapid Li\(^+\) exchange, do not point to strongly dynamically distinct Li ions. This dynamic homogeneity seen does also agree with the shape of the resistivity peaks recorded, see Figure 2b.

In Figure 2b, the change of the resistivity expressed as $M''$ divided by frequency $\omega$ is shown. $M''$ is the imaginary part of the electrical modulus. $\rho'_M = M''/\omega$ is given by $\rho'_M = \tau_p/(1 + (\tau_p \omega)^\beta)$ with $1 < \beta \leq 2$ where $\tau_p$ denotes the electrical relaxation time, and $\beta$ is a parameter that quantifies the deviation of the Lorentzian-shaped peak log10($\rho'_M$) versus $1/T$ from symmetric behavior. For $\beta = 2$, symmetric rate peaks would be obtained. $E_{\text{high}} = 0.39$ eV and $E_{\text{low}} = 0.23$ eV are related to each other via $E_{\text{low}} = (\beta - 1)E_{\text{high}}$ yielding $\beta \approx 1.6$. This view on $\rho'_M$ is comparable to that of NMR spin–lattice relaxation measurements, see below. The shape of the $\rho'_M(1/T)$ peak, which points to length-scale-dependent heterogeneous electrical relaxation, agrees with the observation of a depressed, non Debye semicircle in the complex plot $-Z''(Z')$ as well as with the dispersive signature of the conductivity isotherms $\sigma(\nu)$, which is seen at sufficiently low temperatures (regime III in Figure 2a).

Importantly, we notice that the shape of the $\rho'_M$ peaks near the maximum is composed of two contributions. The arrow in Figure 2b marks a kink (380 K) most likely showing the crossover from $\rho'_M$ values being influenced by regime III and those governed by regime II. The latter influence is seen at higher temperatures where $\rho'_M(1/T)$ follows an Arrhenius behavior with $E_a = 0.39$ eV. This activation energy agrees well with that of $\sigma_{\text{DC}}/T(1/T)$, see Figure 4b, characterizing long-range ion transport. $\rho'_M$ values recorded below 380 K, see the curve measured at 10 MHz, reveal a frequency-dependent behavior if we compare the resistivity values measured at 10 Hz with those recorded at 1.2 MHz, cf. the dashed lines drawn.

Such a dispersive behavior is here interpreted as a result of 2D ionic conduction in the interior regions of LiBH\(_4\)-LiI/Al\(_2\)O\(_3\).

The frequency dependence of the conductivity isotherms in regime III of Figure 2a supports this idea. They are composed of a dispersive regime that also points to low-dimensional ionic transport in LiBH\(_4\)-LiI/Al\(_2\)O\(_3\). In general, for hexagonal LiBH\(_4\), being stable at temperatures above 110 °C, 2D Li\(^+\) self-diffusion was proved by frequency-dependent $^7$Li and $^{11}$B NMR relaxation.\(^{57}\) If the hexagonal modification is, however, stabilized at sufficiently low temperatures, the dispersive regime of the $\sigma(\nu)$ becomes detectable, which should contain information about dimensionality effects. In Figure 4a, a full set of conductivity isotherms recorded over a much larger temperature range than that covered by Figure 2a is shown. For these variable-temperature $\sigma(\nu)$ measurements, we used a second, fresh pellet to probe regime III in detail. Although $\sigma_{\text{DC}}$ is somewhat lower for this pellet (0.05 mS cm\(^{-1}\) at 20 °C), the dispersive part is perfectly seen over a large frequency range. If it is approximated with Jonscher’s power law,\(^{58}\) $\sigma(\nu) \propto \nu^p$, we obtain $p = 0.5$. It has been shown earlier that an exponent $p$ of 1/2 is a valid argument pointing to 2D ionic conduction.\(^{59}\) For 3D ion transport, $p$ is expected to take values of 0.6–0.9, while 1D (channel-like) transport should result in $p < 0.4$.\(^{59}\)

Here, the idea of 2D ionic transport restricts to the LiBH\(_4\)-LiI regions of the sample. As mentioned above, at higher $T$, the resistivity values are mainly governed by $\sigma_{\text{DC}}$ rather than by $\sigma(\nu) \propto \nu^p$. Hence, we conclude that effectively 3D ionic conduction is established on a long-range length scale in LiBH\(_4\)-LiI/Al\(_2\)O\(_3\) while 2D ion transport is seen on a shorter-length scale.

To further analyze long-range ionic transport, we read off $\sigma_{\text{DC}}$ values from the isotherms presented in Figure 4a. In Figure 4b, the change of $\sigma_{\text{DC}}/T$ with 1/$T$ for pellet 2 is shown. In above ambient conditions, we see that the data points follow Arrhenius behavior with an activation energy of $E_a = 0.427$ eV. At approximately $\theta = -50$ °C, a slight curvature appears (see arrow) slightly reducing the ionic conductivity while almost
unchanging the activation energy. Thus, this change is mainly caused by a slight reduction of the pre-exponential factor $\sigma_0$ in $\sigma_{dc}(T) = \sigma_0 \exp\left(-E/(k_B T)\right)$ where $k_B$ denotes Boltzmann’s constant. The prefactor contains, among other quantities, the effective number of charge carriers, the attempt frequency, and an activation entropy term; thus, a range of factors can cause this slight difference. Below $-100$ °C, the values seem to be influenced by further conduction processes because $\sigma_{dc}(T)$ turned out to be higher than expected if the Arrhenius line, which is characterized by $E_a = 0.434$ eV, is extrapolated toward lower $T$, see Figure 4b. Likely, electronic conduction might influence the overall DC conductivity of such a nanostructured sample in this low-$T$ range. Most importantly, even up to temperatures well below ambient, we do not find strong indications that the material transforms from its hexagonal modification, stabilized by the incorporation of LiI, to the orthorhombic form. The latter, if present in a coarse-grained form or being in contact with Al$_2$O$_3$ in the sense of a dispersed stabilization of the hexagonal phase of LiBH$_4$-LiI nanocon. 3.3. 1H, 7Li, and 11B NMR Spin–Lattice Relaxation in LiBH$_4$-LiI/Al$_2$O$_3$. In Figure 5, the temperature behaviors of the NMR spin–lattice relaxation rates $1/\rho_1$ of $\text{LiBH}_4$, $\text{LiI}$, and $\text{LiBH}_4$-LiI$_2$/Al$_2$O$_3$ are shown. As nuclear spin relaxation is sensitive to both long-range and short-range ion dynamics, including translational processes, rotational motions, and even librations, we expect a wide range of activation energies probed by NMR. Indeed, the diffusion-induced rates, if analyzed in the frame of Arrhenius representations, yield a couple of different flanks pointing to activation energies ranging from 0.06 to 0.53 eV. A similar situation has been met for cation-disordered fluorides. 3.3.1. 1H NMR Spin–Lattice Relaxation. Starting with $1^H$ NMR, see Figure 5a, we see that, below 300 K, the laboratory-frame $1/\rho_1$ rates pass through a broad maximum. Most likely, this peak reflects rotational BH$_4$ motions as a very similar behavior has been documented for LiBH$_4$. The slight increase in $1/\rho_1$ above 300 K is attributed to either H-dynamics or localized Li$^+$ motions indirectly sensed by the $1^H$ probes or H-dynamics. The associated apparent activation energy of 0.06 eV points to correlated ionic motion proceeding on a local length scale. At even higher temperatures, one would expect the rate to pass through a diffusion-induced maximum. With decreasing Larmor frequency, this maximum would be shifted toward lower $T$. The corresponding peak $1/\rho_1(1/T)$ should occur at $T_{\text{max}}$ where the motional correlation rate $1/\tau_c$ reaches the angular Larmor frequency $\omega_0 = \nu_L \times 2\pi = 300 \text{ MHz} \times 2\pi$ fulfilling the relationship $\tau_c \omega_0 \approx 1$. $1/\tau_c$ is within a factor of 2 identical with the Li$^+$ jump rate, provided the peak is solely caused by Li$^+$-translational jumps. Replacing $\omega_0$ having values in the megahertz (MHz) range, by $\omega_0$, being the spin-lock frequency in the kilohertz (kHz) range, will shift this peak considerably toward lower $T$. As can be seen in the upper graph of Figure 5a, such a peak indeed appears at $T_{\text{max}} = 313$ K. This peak corresponds to a similar diffusion-induced peak seen in $^{11}$B NMR (333 K, Figure 5b), see below. The activation energy of the $^1$H NMR peak probes by $1/\rho_1$ is 0.16 eV. This value agrees with that from the $M^*/\omega$ analysis if we consider the low-$T$ flank of the $\rho_1^M(1/T)$ peak (0.21 eV, 100 kHz, see Figure 2b). We also observed that $1/\rho_1$ of $^1$H increases at temperatures lower than 200 K. At such low temperatures, the rate $1/\rho_1$ is expected to pass through another rate peak, which corresponds to the behavior of $1/\rho_1$ ($T_{\text{max}} = 200$ K), presumably characterizing fast rotational BH$_4^-$ dynamics.

Noteworthy, the $^1$H (spin-1/2) NMR rates shown in Figure 5a were extracted from magnetization transients that were constructed by analyzing the full area under the corresponding

**Figure 6.** (a) $^1$H NMR FIDs (300 MHz) of LiBH$_4$-LiI/Al$_2$O$_3$ measured at the temperatures indicated. The FIDS are composed of two contributions reflecting two $^1$H sub-ensembles that differ in spin–spin relaxation behavior. (b, c) Variable-temperature $^7$Li (116 MHz) and $^{11}$B NMR (96 MHz) spectra (173, 253, 294, 313, and 433 K) of nanoconfined LiBH$_4$-LiI$_2$/Al$_2$O$_3$. In the case of $^7$Li NMR, distinct satellite intensities show up at high temperatures.
Figure 7. (a) $^1$H NMR spectra of LiBH$_4$-LiI/Al$_2$O$_3$ being composed of two spectral components reflecting two dynamically distinct $^1$H spin ensembles. Dashed lines show deconvolutions of the spectra with Gaussian and Lorentzian functions. (b, c) $^7$Li and $^{11}$B spectra as in Figure 6 but shown in a stacked plot to highlight the Gaussian shape of the lines at low temperatures.

FIDs, see Figure 6a. The resulting transients show stretched exponential behavior, see Experimental Section. However, as can be seen in Figure 6a, we observed so-called two-component FIDs at temperatures above ambient. Such a two-component FID is composed of a slowly decaying part, which can be well separated from a fast-decaying contribution dominating the FID at short acquisition times. Consequently, Fourier transformation leads to $^1$H NMR spectra showing two contributions, as presented in Figure 7a.

The motionally narrowed contribution represents $^1$H spins sensing magnetic-dipolar fluctuations being fast on the NMR spectral time scale, i.e., the corresponding motional correlation greatly exceeds the rigid lattice line width (28 kHz at 173 K, see Figure 7a). With increasing temperature, the majority of the $^1$H spins benefit from this motional averaging process resulting in an overall line shape, which is mainly dominated by the narrow line. The change in area fraction $A_t$ of this line, on top of the broad one, is indicated in Figure 6a; $A_t$ reaches values as high as 64% at 433 K. At room temperature, approximately one third of the $^1$H spins participate in a rather fast dynamic process. In general, one would assign the narrow line to those $^1$H spins located in the interfacial regions. On the other hand, the two-component line shape could also originate from strongly heterogeneous dynamics of the whole spin ensemble, see below.

To test whether these two spectral contributions with individual spin–spin relaxation times are also characterized by distinct $1/T_1$ rates, we analyzed parts of the underlying FIDs in the frame of a saturation recovery experiment. This procedure has been explained in detail elsewhere. Here, no difference in $1/T_1$ is observed between the rates obtained either by analyzing the full FID or the two differently decaying parts highlighted in Figure 7a. This finding points to fast-spin diffusion connecting the two $^1$H spin reservoirs with their distinct spin–spin relaxation behavior. Spin diffusion due to fast flip–flop processes results in a single, averaged spin–lattice relaxation behavior. It is, however, in contrast for $^1$H spin-lock $1/T_{1p}$. The circles in light green in Figure 5a show that it is possible to obtain two rates, which we call $1/T_{1p,fast}$ (0.11 eV) and $1/T_{1p,slow}$ (0.06 eV). The rates differ by a factor of 2 to 3, at most. Importantly, they follow nearly the same temperature behavior (0.09 eV) as seen for the mean rates $1/T_1$ in this $T$ range. Thus, spin-diffusion seems to be present too; however, it turns out to be less effective as in the case of $^1$H NMR spin–lattice relaxation characterized by the rate $1/T_1$.

3.3.2. $^7$Li and $^{11}$B NMR Spin–Lattice Relaxation. The $^7$Li and $^{11}$B NMR spin–lattice relaxation NMR rates $1/T_1$ and $1/T_{1p}$ are shown in Figure 5b, the evolution of the corresponding spectra with temperature is again presented in Figures 6 and 7. In contrast to $^1$H, the $^7$Li $1/T_1$ NMR rates do not reveal a strong influence of BH$_4^-$ rotations at low $T$. Rather, below 250 K, the rates are influenced by nondiffusive background relaxation. Above this temperature, they pass into a flank with an activation energy characterized by 0.11 eV. A slight curvature is seen at 340 K; above this temperature, $E_L$ reduces to 0.08 eV. As for $^1$H, we assign these low values of $E_L$ to short-range dynamics in nanoconfined LiBH$_4$-LiI/Al$_2$O$_3$. For comparison, in Figure 5b, the $^7$Li NMR rates of coarse-grained LiBH$_4$ are also included. While in hexagonal LiBH$_4$, present above $T_{pt} \approx 100 \, ^\circ C$, the rates are induced by Li$^+$ diffusion; below this temperature, they reflect BH$_4^-$ rotational dynamics. The $^7$Li NMR response of LiBH$_4$-LiI/Al$_2$O$_3$ turned out to be completely different to that seen for the source material showing that, from a dynamic point of view as seen by NMR, anion substitution and nanoconfinement have turned the ionic conductor into a completely different material.

$1/T_{1p}$ of $^7$Li reveals a more complex behavior compared to that observed for the corresponding $1/T_1$ rates, Figure 5b. A nondiffusion-induced background appeared below $T = 210$ K. Above this temperature, the rates, however, sharply increase. This increase is characterized by an activation energy of 0.53 eV, which is very similar to the activation energy extracted
from the \( \rho_0 T (1/T) \) peak in the high-\( T \) limit (0.57 eV, Figure 2b). Obviously, spin-lock \(^{7}\text{Li}\) NMR, if carried out at a locking frequency of 20 kHz, is able to sense long-range ion dynamics. The above-mentioned curvature seen in \( 1/T_i \) might correspond to the maximum in \( T_i \) seen at 243 K. At higher temperature than 243 K (Figure 2b), the behavior of \( 1/T_i \) can only be understood if we consider several relaxation rate peaks contributing to the overall response. Interestingly, the flank seen at high \( T \) is again characterized by an activation energy (0.15 eV, Figure 2b) that resembles those seen by \( 1/T_i \); it is also comparable to the values obtained from \(^{1}\text{H}\) NMR, see above.

Similar to \(^{1}\text{H}\) NMR, also, the FIDs of the \(^{7}\text{Li}\) nucleus are, at least to some extent, composed of several components if results above \( T = 230 \) K are regarded (not shown for the sake of brevity). The corresponding spectra are displayed in Figures 6b and 7b. As \(^{7}\text{Li}\) is a spin-3/2 nucleus,\(^{106}\) the sharply decaying part of its FID partly (or mainly) originates from electric quadrupole interactions, which are characteristic for \( \text{LiBH}_4 \) if present in its hexagonal modification. \(^{7}\text{Li}\) NMR spectra have been discussed in detail elsewhere;\(^{11}\) worth noting, at each temperature, the lines are to be characterized by a single, averaged quadrupole powder pattern with distinct 90° singularities appearing at a distance of \( \pm 5 \) kHz from the central line. They result in a quadrupole splitting of \( \Delta \approx 10 \) kHz (Figures 6b and 7b). Hence, also from the point of view of quadrupolar electric interactions, the Li ions belong a single ensemble with electrically equivalent spins. We do not see the original electrical powder patterns of \( \text{LiBH}_4 \) (\( \Delta \approx 18.5 \) kHz) or \( \text{LiBH}_4 \cdot \text{LiI} \) (\( \Delta \approx 18.6 \) kHz) any longer. In our earlier publication,\(^{11}\) we speculated that both the ions near the \( \text{Al}_2\text{O}_3 \) surface regions, possibly influenced by (residual) hydroxyl surface groups,\(^{11}\) and those farther away are subjected to a structurally stressed \( \text{LiBH}_4 \cdot \text{LiI} \) phase with high ionic conductivity. Space charge zones,\(^{34,41}\) high defect densities or increased structural disorder\(^{44}\) may characterize these inner, interfacially influenced regions leading to a magnetically and electrically homogeneous phase showing enhanced, but heterogeneous, ion dynamics.

The other part of the \(^{7}\text{Li}\) NMR FIDs, which forms the central NMR line after Fourier transformation, may also represent \(^{7}\text{Li}\) sub-ensembles differing in spin–spin-relaxation times. A clear separation as in the case of \(^{1}\text{H}\) NMR is, however, fraught with difficulties. Thus, we cannot precisely identify \(^{7}\text{Li}\) ions in the interfacial regions undergoing rapid exchange processes as those spins residing farther away from these regions are involved in rapid diffusion also. The same situation was met in \( \text{LiTiS}_2 \) for which structural disorder did not lead to a significant enhancement of \(^{7}\text{Li}\) dynamics. In layer-structured \( \text{TiS}_2 \), the mobility of \(^{7}\text{Li}\) is already rather high.\(^{67}\) Here, as in the case of \(^{1}\text{H}\) spin–lattice relaxation \( 1/T_i \), the different contributions to the \(^{7}\text{Li}\) FIDs undergo the same \(^{7}\text{Li}\) spin–lattice relaxation recovery. Again, we conclude that they belong to a magnetically homogeneous \( \text{Li} \) spin ensemble affected by rapid spin diffusion. Such an ensemble is also suggested by the thermally coalesced \(^{6}\text{Li}\) MAS NMR signal discussed above.

For comparison, this finding is in contrast for nanocrystalline, orthorhombic \( \text{LiBH}_4 \)-fast \( \text{Li}^+ \) ions (0.18 eV) were found that could separately be studied by \(^{7}\text{Li}\) NMR spin–lattice relaxation.\(^{38}\) A very similar result has been seen by \(^{7}\text{Li}\) NMR in \( \text{LiI}/\text{Al}_2\text{O}_3 \) mixtures investigated by Ardel et al.\(^{37}\) In such mixtures one \(^{7}\text{Li}\) site has been associated with surface or interface regions.

A separation, being similar to that discussed and carried out for \(^{1}\text{H}\) NMR, is only partly possible for the \(^{7}\text{Li}\) NMR spin-lock rates \( 1/T_i \). While \( 1/T_i \) slow \( \approx 1/T_i \) fast \( \approx 1/T_i \) reveal an even weaker temperature dependence than \( 1/T_i \) (0.11 eV vs 0.15 eV), see Figure 5b. Again, we interpret such low activation energies as a signature for fast, but localized, dynamic processes, which do not necessarily lead to long-range \(^{7}\text{Li}\) ion transport. Alternatively, they might reflect fast \(^{7}\text{Li}\) dynamic processes near the conductor/insulator interface,\(^{42}\) as also seen for nanocrystalline orthorhombic \( \text{LiBH}_4 \) (0.18 eV).\(^{38}\)

The \(^{11}\text{B}\) NMR spin–lattice relaxation rates, see Figure 5b, reveal two shallow NMR rate peaks. The one at lower \( T \) could again be assigned to rotational ion dynamics, while the exact origin of that seen at higher \( T \) remains unknown. In general, it is well known for \( \text{LiBH}_4 \) that the \( \text{BH}_4^- \) units undergo fast rotational motions. Moreover, also, the presence of translational ion dynamics has been suggested on the basis of \(^{11}\text{B}\) NMR.\(^{26,68}\) Interactions with the alumina scaffold might change this dynamic behavior of the anions. Here, in \(^{11}\text{B}\) spin-lock NMR, we observed a single peak located at \( T_{\text{max}} \approx 313 \) K; it might indeed be caused by a slower \( \text{Li} \) translational process indirectly seen by the \(^{11}\text{B}\) spins or by \( \text{BH}_4^- \) translational motions, which were suggested for \( \text{LiBH}_4 \).\(^{11}\) Interestingly, the activation energy extracted from the \(^{11}\text{B}\) \( 1/T_i (\text{s} 1/T_i) \) NMR is very similar to that seen by \( \sigma_{\text{DC}} (\text{f}) \); hence, this agreement supports the idea that, at least from a quantitative point of view, the peak is induced by \( \text{Li}^+ \)-hopping processes.\(^{12}\) \(^{11}\text{B}\) NMR spectra (spin-3/2) are shown in Figures 6c and 7c. A tiny line, which is marked by an asterisk in Figure 7c, points to a side phase that has already been discussed for \(^{1}\text{H}\) MAS NMR, see above. \(^{11}\text{B}\) NMR spectra are mainly governed by central lines that are flanked, at least at high temperatures, by satellite intensities. Alternatively, the broadband component could be interpreted as a signal arising from less mobile \( \text{BH}_4^- \) units.

3.4. Long-Range Ion Transport and Diffusion Coefficients as Probed by NMR and Electrical Measurements. NMR spin–lattice relaxation measurements reveal a rather complex picture of the magnetic fluctuations taking place in nanoconfined \( \text{LiBH}_4 \cdot \text{LiI}/\text{Al}_2\text{O}_3 \). Apart from rapid localized ion dynamics, a practical parameter being relevant for battery applications is the macroscopic (self-)diffusion coefficient \( D \) of the \( \text{Li} \) ions. Here, we took advantage of \(^{7}\text{Li}\) PFG NMR measurements to probe tracer diffusion coefficients \( D_{\text{PFG}} \) at two different temperatures, see the Arrhenius plot of Figure 8.

To compare the results from PFG NMR with those from conductivity spectroscopy, we used the Nernst–Einstein equation, \( D = (\sigma_{\text{DC}} k_\text{B} T)/(N q^2) \), to convert \( \sigma_{\text{DC}} \) into solid-state diffusion coefficients; in Figure 8, the results for the two pellets are included. Here, \( N \) is the charge carrier density, which we estimated to be approximately \( 1.8 \times 10^{27} \) m\(^{-3} \), \( q \) denotes the charge of the \( \text{Li}^+ \) ions. Here, we simply used the chemical formula of \( \text{LiBH}_4 \cdot \text{LiI}/\text{Al}_2\text{O}_3 \) and assumed that all \( \text{Li}^+ \) ions participate in diffusion. The effective number might be lower and should be related to the exact defect structure of the regions of nanocrystalline, orthorhombic \( \text{LiBH}_4 \)-fast \( \text{Li}^+ \) ions.
The resistivity peaks recorded. Indeed, as has been shown by both $^1$H, $^7$Li, and $^{11}$B NMR line shapes and NMR spin–lattice relaxation measurements quite complex, translational and rotational (and librational) dynamic processes are present including (strictly) localized events determined by much lower activation energies of only 0.06 eV.

4. SUMMARY AND CONCLUSIONS

Overall, long-range ionic transport in nanoconfined LiBH$_4$-Li/Al$_2$O$_3$ as probed by conductivity spectroscopy follows Arrhenius behavior (0.43 eV) over a dynamic range of almost 8 orders of magnitude. Solid-state diffusion coefficients estimated from conductivity values and variable-temperature resistivity data recorded at fixed frequency agree very well with those obtained from macroscopic $^7$Li PFG NMR. At room temperature, a diffusion coefficient of $3 \times 10^{-11}$ m$^2$ s$^{-1}$ was obtained. $^1$H, $^7$Li, and $^{11}$B NMR relaxation measurements revealed highly complex dynamics with a broad range of activation energies ranging from 0.06 to 0.57 eV.

Interfacial effects are seen by $^{27}$Al MAS NMR; most likely, pentacoordinated sites of the Al$_2$O$_3$ scaffold become saturated through the formation of Li$^+$$[\text{AlO}_5\text{I}]^−$ or Li$^+$$[\text{AlO}_5\text{H}]^−$ species; the participation of surface hydroxyl groups has to be considered also, as suggested recently. This view is supported by $^7$Li MAS and $^{11}$B MAS NMR, the latter reveals two B sites slightly differing in the magnetic environment. At least for $^1$H, the corresponding variable-temperature, two-component NMR line shapes showed H spins subjected to quite different spin−spin fluctuations. Most likely, they reflect spins near interfacial regions and spins farther away from the surface, that is, located in the LiBH$_4$-Li matrix. As shown by $^7$Li NMR line shapes and broadband conductivity spectroscopy, the Li spins participate in heterogeneous ion dynamics but; most likely, they belong to an electrically homogeneous ensemble. We speculate that interfacial effects also influence the inner regions of the nanometer-sized pores that are filled with LiBH$_4$-Li. This situation is usually met for nanostructured ion conductors dominated by space charge effects, which are termed artificial ion conductors. Specifically, the reaction with hydroxyl surface groups might play a crucial role too since insights into $^{27}$Al MAS NMR underpin this assumption.

Finally, the dispersive regions in conductivity spectra follows Jonscher’s power law with an exponent of $p = 1/2$. This result points to low-dimensional (2D) ionic transport in the layer-structured, hexagonal LiBH$_4$-Li regions. We were able to follow this 2D ion transport process down to temperatures as low as $-80$ °C. On the other hand, NMR and electric modulus spectroscopy carried out at sufficiently high temperatures reveal long-range 3D ion transport, likely involving fast ion conduction also along the interfacial conductor/insulator regions. While for many highly conducting layer-structured materials, grain boundaries may act as regions blocking ion transport; in the case of nanoconfined LiBH$_4$-Li/Al$_2$O$_3$, such limitations can be overcome by fast-conducting interfacial conductor/insulator regions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c10361.

NMR parameters; $^1$H, $^7$Li, and $^{11}$B NMR relaxation transients; and PFG NMR decay curves (PDF)
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https://pubs.acs.org/10.1021/acsami.0c10361

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Veronika Pregartner for her help with sample preparation with NMR and impedance spectroscopy measurements. R.Z. and H.M.R.W. thank the Austrian Federal Ministry for Science, Research and Economy and the Christian-Doppler Forschungsgesellschaft for financial support; further support by the FFG (The Austrian Research Promotion Agency) in the frame of the project Safe Battery is also acknowledged. R.Z. and H.M.R.W. thank the Austrian Federal Ministry for Science, Research and Economy and the Christian-Doppler Forschungsgesellschaft for financial support; further support by the FFG (The Austrian Research Promotion Agency) in the frame of the project Safe Battery is also acknowledged.

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