NMR Study of LiBH₄ with C₆₀

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LiBH₄ doped with 1.6 mol % well-dispersed C₆₀ is studied with solid-state nuclear magnetic resonance (NMR).
Variable-temperature hydrogen NMR shows large changes between the data upon first heating and after
exposure to 300 °C. After heating, a large fraction on the order of 50% of the hydrogen signal appears in a
motionally narrowed peak, similar to a previous report of LiBH₄ in a porous carbon aerogel nanoscaffold.
Magic-angle spinning (MAS) NMR of ¹³C in a ¹³C-enriched sample finds the C₆₀ has reacted already in the
as-mixed (unheated) material. Dehydriding and rehydriding result in further ¹³C spectral changes, with nearly
all intensity being found in a broad peak corresponding to aromatic carbons. It thus appears that the previously
reported improved dehydriding and rehydriding kinetics of this material at least partially result from in situ
formation of a carbon framework. The method may offer a new route to dispersal of hydrides in carbon
support structures.

Introduction

Solid-state systems offer a possible route to on-board hydrogen fuel storage for transportation applications. Interstitial
metallic hydrides generally have inadequate weight fractions of hydrogen, so research has focused on ionic (e.g., MgH₂) and
complex (e.g., LiBH₄) hydrides involving one or more light-weight metal atoms. However, unlike the metallic hydrides,¹
the ionic and complex hydrides show very slow hydrogen diffusion. This is one cause of the observed slow kinetics of
their dehydriding and rehydriding reactions.

Mechanical activation (ball-milling) often results in improved kinetics by reducing the crystallite grain and overall particle
sizes. The fundamental equation

\[ \bar{r}^2 = 6Dt \]

relates the mean-squared displacement \( \bar{r}^2 \) to the diffusion time \( t \) and diffusivity \( D \).² Thus, smaller grain and particle sizes (for
example, following ball-milling) result in much smaller hydrogen diffusion times. In addition, some nanostructured materials,
including some hydrides, have a substantial fraction of atoms with an enhanced diffusivity \( D \), further decreasing the diffusion time.³

However, this kinetic improvement can be reduced or eliminated by grain and particle growth due to repeated
dehydrider/rehydrate cycling.⁴ Thus, much interest has been directed toward hydrides contained in supporting structures with
nanometer scale dimensions (nanoscaffolds). The scaffold serves to direct or control the growth of hydride grains within its pores.⁵
An example relevant to the present work is LiBH₄ that is wicked into a porous carbon aerogel structure, resulting in greatly
improved reaction kinetics and somewhat improved cycling.⁶ Hydrogen NMR shows that this system contains a substantial
fraction of mobile hydrogen (as BH₄ anions) already at room temperature,⁷ while bulk LiBH₄ does not display motional
narrowing of hydrogen until around 175 °C.⁸

A recent report examined the hydrogen reaction kinetics of LiBH₄ with C₆₀.⁹ The C₆₀ was well dispersed by incorporating
it with LiBH₄ in tetrahydrofuran (THF) solvent and then drying. The dehydriding temperature was 80 °C lower than that in bulk
LiBH₄, and the composite also showed the ability to cycle at least three times at the 4 wt % hydrogen level.

We show here that the LiBH₄ with C₆₀ material forms a carbon framework upon first heating, with definite breakdown
of the C₆₀ structure and likely polymerization. The changes are evident in static ¹H and ¹³C NMR and ¹³C MAS NMR.

Experimental Methods

As described elsewhere,⁹ fullerene (C₆₀; 98%, Sigma-Aldrich) was combined with LiBH₄ (Albemarle) in anhydrous THF
(99.9%). The C₆₀ concentration was 1.6 mol % relative to LiBH₄, approximately 0.54 g of C₆₀ for each gram of LiBH₄. After the
solution was stirred for 1 h, the solvent was removed and the dark brown powder sample collected. This sample preparation
was done at Savannah River National Laboratory (SRNL).

All samples were transported under nitrogen or argon. At Washington University (WU), samples were stored in an N₂
glovebag and loaded into 6 mm outer diameter (o.d.), 20 cm
long alumina ceramic tubes for $^1$H NMR. The ceramic tubes were sealed with O-ring sealing caps. Alumina was used instead of glass to avoid the reaction of molten LiBH$_4$ with silica.$^{10}$ For $^7$Li measurements, samples were sealed into short fused silica tubes and the temperature was kept at least 25 °C below the nominal melting point (270 °C). At the California Institute of Technology (Caltech), where MAS NMR was performed, samples were stored in an argon glovebox and loaded into 4 mm o.d. zirconia rotors. The rotors were sealed with tight Kel-F caps, and dry N$_2$ gas was used for spinning.

Variable-temperature hydrogen NMR was performed at WU in a field of 2.0 T, corresponding to 85.03 MHz. Hydrogen line shapes were obtained from the Fourier transformation of free induction decays (FIDs), after application of short (1–2 μs) rf pulses to reduce spectral distortion. Correction of the FIDs for receiver dead time has been described elsewhere.$^{11}$ The relaxation time $T_1$ was determined by the saturate–wait–inspect method, with saturation by 20 π/2 rf pulses for $^1$H NMR. A superconducting 7.04 T magnet was used for variable-temperature $^7$Li work at a frequency of 116.46 MHz. The Li spins were saturated through rf field inhomogeneity using a 200 μs rf pulse.

Samples that were dehydrided and rehydrided were processed at SRNL. Samples were dehydrided by heating the sample to 350 °C at 1 bar of H$_2$ and rehydrided by heating to 250 °C at 110 bar of H$_2$ for 12 h. For all of this work, a Sievert’s apparatus (HyEnergy PCT Pro 2000) was used.

For MAS NMR $^{13}$C and $^{11}$B measurements at Caltech, a Bruker DSX-500 spectrometer with an 11.7 T field, so at 125.72 and 160.42 MHz, respectively, was used. All measurements were at room temperature. The purpose of high-resolution NMR was identification of the chemical changes in the sample upon mixing of the C$_{60}$ and LiBH$_4$ and after subsequent dehydriding, rehydriding, or heating with minimal hydrogen release. The typical MAS spinning frequency was 15 kHz. The $^{13}$C work was facilitated by the higher signal-to-noise ratio provided by a sample made with C$_{60}$ with enhanced $^{13}$C content (20%–30% of the carbons were $^{13}$C). The $^{13}$C-enriched C$_{60}$ was purchased from MER Corp.

Results and Discussion

Hydrogen NMR. Static (not MAS) NMR spectra of hydrogen in LiBH$_4$ with C$_{60}$ appear in Figure 1. The spectra of Figure 1a were taken upon increasing the temperature with as-mixed material (previously heated only to 60 °C for solvent removal); the spectra in Figure 1b are for material after 1 h of exposure to 300 °C in a sealed tube (above the nominal melting point of bulk (pure) LiBH$_4$, 270 °C).$^{12}$ Comparing the spectra at 22 °C, we see that the heat treatment results in a strong motionally narrowed component. The heat-treated sample has a more intense narrow component at 80 °C, as a fraction of total spectral area, than does the as-mixed sample at 150 °C. We note that measurements on additional samples demonstrate that some spectral changes on first heating occur already by 150 °C. Once a sample is exposed to 300 °C, no further changes in the hydrogen spectra occur, though we restricted our operations to $T \leq 300$ °C to avoid substantial hydrogen evolution and possible sample tube rupture.

To confirm that the narrow peak in the heat-treated sample is due to motional narrowing, line shapes from +22 to −100 °C were measured, as in Figure 1b. The amplitude of the narrow component decreases rapidly to −50 °C. From −50 to −100 °C, only a small narrow central pip remains on top of the broad BH$_4$ resonance. The pip is believed to be the signal of a small amount of trapped H$_2$ gas.$^{13}$

We also prepared one sample with extra effort to remove the last vestiges of THF solvent. This heat-treated material’s hydrogen spectra were nearly identical to those of the less carefully dried material of Figure 1b. Thus, residual THF solvent is not important here.

The hydrogen spectra were decomposed into a sum of two lines, one narrow and one broad. We note that narrowing requires motion that is rapid compared to $10^{-5}$ s. The fraction of the total spectral area of the narrow component is equal to the fraction of rapidly moving hydrogen nuclear spins. This fraction is presented in Figure 2, for both as-mixed and 300 °C heat-treated material. Clearly, heat treatment greatly increases the fraction of mobile hydrogen. According to previous work in bulk LiBH$_4$, this signal represents intact mobile BH$_4$ anions.$^8$
For the heat-treated material, the narrow component is well described by a Lorentzian line shape. The fwhm line width (full width at half-maximum intensity) falls from 1400 Hz at 22 °C to 600 Hz at 100 °C; further heating to 225 °C yields a little more narrowing, to 400 Hz width. We note that these widths are approximate (±20%) because of uncertainties in the spectral decomposition process. The broad component is approximately Gaussian; its width is relatively independent of temperature to 150 °C and then narrows at higher temperatures. The broad component line width closely follows the line width of bulk LiBH₄.

The two-component spectra of Figure 1b are similar to previously obtained results on LiBH₄ in a porous carbon aerogel polymer, a nanoscaffold with a mean pore size of 13 or 26 nm. There, a superposition of narrow and broad components was also observed. In particular, we note the appearances of the spectra here in Figure 1b are strikingly similar to those for LiBH₄ in aerogel in Figure 1 of ref 7. The aerogel nanoscaffold directs crystallite growth and imposes nanometer dimensions on the crystallites. The aerogel data imply the borohydride ions near the crystallite edges are more mobile and result in the motionally narrowed peak; the anions in the crystallite cores are immobile and result in the broad resonance. The broad component line width closely follows the line width of bulk LiBH₄.

Small grain sizes of the LiBH₄ in the heat-treated structure are also suggested by the hydrogen T₁ data of Figure 3. Wherever the narrow component was sufficiently large, separate T₁ values are reported for the broad (B) and narrow (N) components; T₁ for bulk LiBH₄ is also presented. For the bulk and as-mixed samples, a discontinuity in T₁ occurs near 113 °C, signaling the solid–solid phase transition there (the high-temperature phase exhibits BH₄ orientational disorder and rapid diffusion of lithium cations). By contrast, T₁ of both broad and narrow components is continuous in this temperature range after heat treatment at 300 °C. Evidently, the transition is suppressed or is at least broadened by the interaction with or confinement by the carbon framework. Related behavior was observed in solid solutions of LiBH₄ with lithium halides and in LiBH₄ in aerogel.

**Lithium NMR.** Figure 4 presents ⁷Li spectra. At 22 °C, the spectrum of the as-mixed LiBH₄ with C₆₀ is very similar to that of bulk LiBH₄. At 150 °C, the quadrupolar satellite features at ±9 kHz are broadened (so less tall) after heating, compared to those of the as-mixed material.
The present narrowing is motional in origin is evident by further line narrowing with increasing temperature. In Figure 4, at 150 °C, the sharp quadrupolar satellite cusps are much less prominent in the heat-treated material, similar to the broadened satellite features of LiBH₄ in aerogel at 100 and 200 °C.⁷ While not shown here, the ⁷Li T₁ is also continuous through the phase transition in the heat-treated material, but not in the as-mixed material. It thus appears that the framework that forms upon heat treatment serves (i) to interfere with the solid—solid transition, so that the ⁷Li is mobile and considerably narrowed as in C₆₀ (as evidenced by their high positive shift), with a small broadening the satellite features.

The central transition line at 150 °C in the heat-treated material is also broader than it is for the as-mixed material. This could indicate that some of the LiBH₄ is actually within the carbon framework itself (rather than inside larger porous spaces) and that the framework is interfering with free motion. Alternatively, some of the lithium could be interacting with carbon without any closely interacting hydrogen. MAS and CPMAS NMR data on ⁶Li (not shown) suggest that some small fraction of the lithium is acting as suggested in the latter statement. No LiH peak was detected by the ⁶Li NMR measurements.

Solvent Washing. A 260 mg sample of the postheated material was washed with THF, diethyl ether, and acetonitrile to remove the LiBH₄. The sample was 1.6 mol % C₆₀ and thus was composed of 91 mg of C₆₀, with the remainder as LiBH₄. The mass of the insoluble residue remaining after washing was 110 mg, slightly higher than would have been expected if all the LiBH₄ had been removed. The excess mass could be remaining solvent, or some of the LiBH₄ may have reacted with C₆₀, in support of the hypothesis in the previous paragraph.

MAS NMR. Samples of LiBH₄ with C₆₀ (with 20%–30% ¹³C content of the C₆₀) were examined by MAS NMR, using both ¹³C NMR (Figure 5a) and ¹¹B NMR (Figure 5b). Spinning sidebands in Figure 5a are marked with asterisks, including a shoulder near 160 ppm in the as-mixed spectrum that is a sideband from the 50 ppm peak. The as-mixed material shows a main ¹³C peak near 150 ppm, slightly up-frequency from the completely absent very sharp resonance of pure C₆₀ at 144 ppm, as well as an additional weaker peak near 50 ppm. Cross-polarization from hydrogen nuclear spins demonstrates that the 150 ppm carbons are relatively distant from any hydrogen atoms while each 50 ppm carbon has one or more bonded H atoms. This suggests primarily aromatic sp² carbon atoms, distorted as in C₆₀ (as evidenced by their high positive shift), with a small fraction, approximately 21%, of sp³ carbons with bonded H atoms.¹⁸ We remark that the reaction of C₆₀ has taken place prior to any heating beyond 60 °C for solvent removal.

After dehydriding and subsequent rehydriding, the primary carbon resonance is centered at 124 ppm with a broad width of about 35 ppm fwhm. The chemical shift of 124 ppm is more typical of planar aromatic carbon atoms, possibly indicating that the structure is no longer highly curved (nonplanar) as in C₆₀. (Typical carbon chemical shifts include 108–119 ppm for graphite, 120 ppm for solid benzene, 125 ppm for carbon nanotubes, and 144 ppm for C₆₀.)¹⁹ A very weak aliphatic (sp³) carbon peak is marked by Δ in Figure 5a. Material that is heated with minimal hydrogen release appears intermediate between the as-mixed and rehydrided samples. (b) MAS NMR ¹¹B spectra, relative to chemical shift reference BF₃–O(CH₂CH₃)₂. All peaks are from BH₄ anions. Small frequency shifts after dehydriding, rehydriding, or heating with minimal hydrogen release demonstrate the BH₄ anions are near enough to the framework to have an effect on the local field.

BH₄ resonance are apparent after the material is dehydrided, rehydrided, or heated without significant hydrogen release, indicating that shifts of the BH₄ groups are slightly affected by the proximity of BH₄ to the carbon framework.¹⁵

Conclusions

The hydrogen NMR spectrum of LiBH₄ with C₆₀ shows two components, a broad line from immobile BH₄ anions and a narrow resonance from rapidly moving ions. Heat treatment to 300 °C results in a much larger narrow component, approximately 36% of the total intensity already at 22 °C. By comparison with previous NMR of LiBH₄ in aerogel polymers,
the behavior suggests reaction of the C\textsubscript{60} to form a carbon framework, with definite breakdown of the C\textsubscript{60} structure and likely polymerization. In the heat-treated material, the solid–solid phase transition (113 °C in bulk LiBH\textsubscript{4}) is suppressed or broadened, as indicated by the continuous behavior of \textsuperscript{1}H and \textsuperscript{7}Li T\textsubscript{1} and by motional narrowing of \textsuperscript{7}Li at 22 °C. MAS NMR indicates that the C\textsubscript{60} reacts even before heating, and additional spectral changes after dehydriding and rehydriding support the formation of a framework during heating.

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**References and Notes**


