

IV.A.1j Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

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Objectives

- Develop and demonstrate light-metal hydride systems that meet or exceed the 2010/2015 DOE goals for on-board hydrogen storage.
- Validate initial storage properties and reversibility in light element hydrides by providing identification of phases and reaction pathways.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The clearest representation of technical progress would probably be given by the maximum reversible fraction of the material systems investigated, with the relevant 2010 target listed in the MYRDDP as 4.5% reversible H₂ content by weight in the engineered

system. The material encapsulated in that system, obviously, must possess a higher content of H₂, perhaps in the 9-12% range. For several reasons, the Ca(BH₄)₂ system (theoretical 12 wt%) that was promising in prior years has shown several serious issues with its development. Turning to other systems as described below, some attention has been given to elucidating reaction processes and answering questions about capacities and charge/discharge rates (i.e., kinetics).

Accomplishments

- Via magic angle spinning – nuclear magnetic resonance (MAS-NMR) and thermo-volumetric methods, provided phase characterization, kinetics (i.e., diffusion behavior), and reversibility assessments in numerous systems (i.e., Mg-B-H, Ca-B-H + C-aerogel, Al-B-N-H).
- Investigated the effectiveness of specific additives (ScCl₃, TiF₃) on the desorption/absorption kinetics of the Mg(BH₄)₂ system by the use of MAS-NMR. Positive effects on the desorption kinetics were seen with 5 mol% of either additive, as well as an effect on the Mg(BH₄)₂ α to β phase transition and the production of borohydride (BH) intermediates.
- Determined that several pathways for boron products exist in the reaction pathways of hydrogen-metal BH systems. NMR is capable of determining the presence and activity of such products as MgB₂, MgB₁₂H₁₂ and amorphous boron “composites” within the Mg(BH₄)₂ system.
- Investigated the reactivity, capacity, and kinetic performance of the Al(BH₄)₃•2(NH₃) system. The total available H₂ capacity of this system has been shown to exceed 9% H₂ by mass at 330°C, with 7% available at 250°C.
- Continuing an Oak Ridge National Laboratory (ORNL)/Caltech/JPL study on the Al-B-N-H system, utilized ¹⁵N in the form of preparing labeled chemistries suitable for ¹⁵N NMR spectroscopy. Such detail proved necessary for elucidating the N-environments in the product, the precise chemical structure of which is still difficult to determine.



Introduction

Activities at JPL under the auspices of DOE's Metal Hydride Center of Excellence (MHCoe) are designed to contribute to the development of light-

metal hydride systems that meet or exceed the DOE/FreedomCAR technical targets for on-board reversible hydrogen storage. JPL performs in several different roles in the Center. The major portion of the effort at JPL is dedicated to validating initial storage properties (2010 target: >4.5 wt% reversible gravimetric, 28 g/l volumetric hydrogen capacity) of novel light element metal hydrides including destabilized hydride systems containing LiH, MgH₂, and LiBH₄, complex amide/imides, BHs, and AlH₃-based hydrides as well as other promising samples provided by many MHCoe partners; significant attention in the latter part of the project has been paid to the metal BHs with Mg, Ca, Sc, and Al cations, as well as dual-cation systems. Along the way, the fundamental role of the B₁₂H₁₂²⁻ anion and associated intermediate reaction pathways in preventing reversibility has been elucidated. Throughout, JPL has had a role within MHCoe to assess the reversibility and durability of the more promising hydrides during cycling.

In the course of these tasks, various solid-state NMR studies and other analytical techniques were used to assess promising “catalyzed” complex hydrides including alanates and BHs for their kinetics and reversibility to improve their practical hydrogen storage potentials. Such techniques have proven quite powerful for characterization of hydrogen and metal diffusion behaviors as well as critical phase transformation processes, often providing insight into chemical processes, configurations, and reaction pathways otherwise impossible to determine via other analytical spectroscopic methods.

Approach

JPL’s participation in the MHCoe continues as a widespread effort, involving all the individual projects within the Center scope. In the area of complex anionic materials, JPL continues to work closely with Sandia National Laboratories as an investigation into the Mg(BH₄)₂ system enters its final phases; metal BHs from ORNL and Ca(BH₄)₂ from United Technologies Research Center (UTRC) have also been part of JPL’s recent collaborative role.

A comprehensive materials development and characterization project continues to be the central focus of JPL’s many roles in MHCoe. Of primary importance is the use of thermo-volumetric measurements to determine hydrogen storage capacities and equilibrium pressures on destabilized nanophase and complex metal hydrides. In addition, powder X-ray diffraction may be used at JPL to determine material compositions where applicable. In collaboration with the Solid-State NMR Facility at Caltech, MAS-NMR measurement techniques can be applied; these measurements are crucial for gaining an understanding of phase compositions and bonding characteristics in these material systems. Caltech also provides the capability for Raman

spectroscopy measurements for the elucidation of additional material characteristics; some of these, such as hydration state and bond parameters, are subtle and can provide good correlation with other techniques applied by the JPL-Caltech team.

Results

Under the guidance of MHCoe Project B (*Complex Anionic Materials*), JPL performed work relating to phase identification and reaction pathway discovery of various BHs. Samples of Ca(BH₄)₂ scaffolded with carbon aerogel were provided by partners at UTRC; these samples represented materials both as-made (38% by weight of the BH) and following several cycles of hydrogenation. JPL/Caltech were unable to determine a definitive effect on the use of C-aerogel as a scaffolding/encapsulation agent. In Figure 1, MAS-NMR shows the presence of the now familiar [B₁₂H₁₂]²⁻ intermediate as well as localized B-O bonding following several cycles of hydrogen absorption. Other than a partial peak shift, no improvement in performance was seen. It should be noted that the B-O bonding could be due to contamination of the parent sample by air.

Together with partners at Sandia National Laboratories, JPL/Caltech engaged in the study of the effects of various additives (ScCl₃, TiF₃) on the kinetics and reversibility of the Mg(BH₄)₂ system. Figure 2 shows a marked effect on the room-temperature stability of Mg(BH₄)₂, where an α to β phase transition is interpreted as a positive effect on reaction kinetics in this system due to the presence of the additives. Similarly, Figure 3 shows a high-temperature phase transition at 413 K, 40 K lower than the neat parent material; improved kinetics are a result. NMR has also elucidated the family of intermediates in this

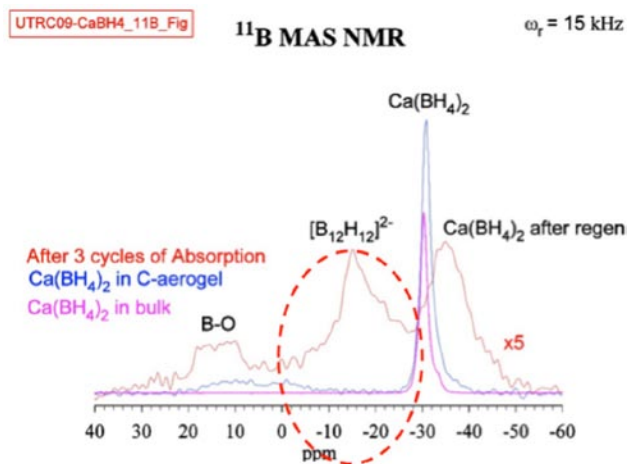


FIGURE 1. ¹¹B MAS NMR spectra illustrating the presence of the [B₁₂H₁₂]²⁻ intermediate as well as localized B-O bonding in the Ca(BH₄)₂ + C-aerogel system.

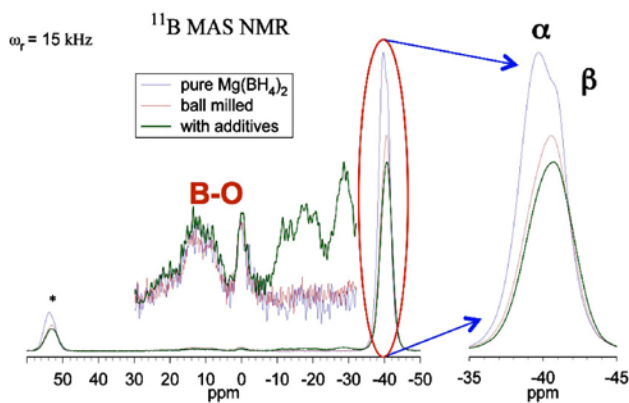


FIGURE 2. ^{11}B MAS NMR spectra showing the effect of additives (ScCl_3 , TiF_3) on $\text{Mg}(\text{BH}_4)_2$ after milling, specifically the peak shift illustrating the room temperature phase shift of the parent material. Similar evidence at temperature indicate a positive effect on the hydriding kinetics due to the presence of additives.

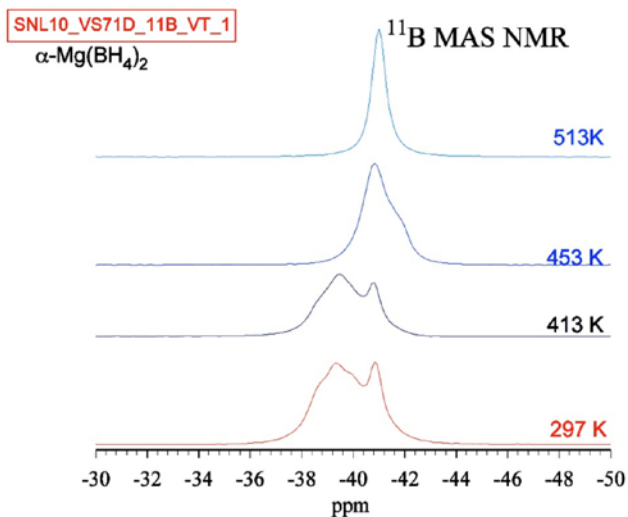


FIGURE 3. ^{11}B MAS NMR spectra of the $\text{Mg}(\text{BH}_4)_2$ system showing the high-temperature phase transition (peak shift) thought to be the indication of improved chemical kinetics due to the presence of additives.

system; Figure 4 suggests that the presence of additives in this system have differential effects on the possible intermediates.

JPL has continued to investigate novel Al-B-N-H chemistries with partner ORNL; during 2009-2010 the focus has been on the compound $\text{Al}(\text{BH}_4)_3 \cdot 2(\text{NH}_3)$, which was synthesized at ORNL using wet chemistry methods. This material was characterized using JPL's Sieverts' apparatus. For the purposes of NMR investigation, versions of this system were also synthesized in the form $\text{Al}(\text{BH}_4)_3 \cdot 2(^{15}\text{NH}_3)$, as the ^{15}N is a more NMR-active nucleus than the normal

	Chemical shift (ppm)	Relative quantity	
		no additives	with additives
MgB_2	97.3	0.25	0.21
Amorphous*	-11	0.04	0.23
$\text{MgB}_{12}\text{H}_{12}$	-15.5	0.05	0.07
$\text{Mg}(\text{BH}_4)_2$	-40.95	0.66	0.49

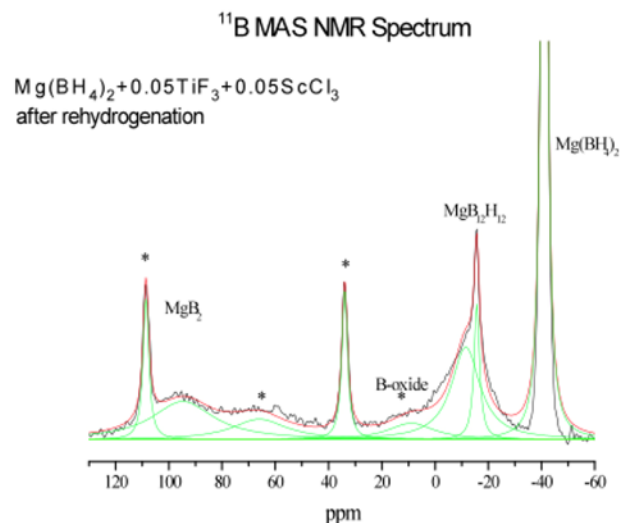


FIGURE 4. Summary the intermediate species present in the $\text{Mg}(\text{BH}_4)_2 + (\text{ScCl}_3, \text{TiF}_3)$ system, corresponding to the ^{11}B NMR spectra shown. The relative effect of the additives on different intermediates may be interpreted from the peak shifts.

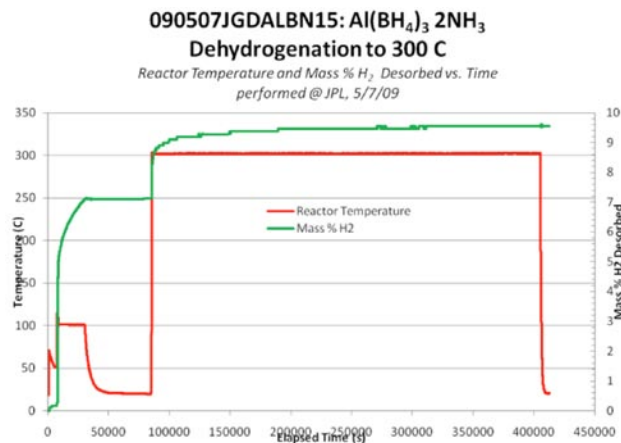


FIGURE 5. Experimental volumetric results from the desorption of $\text{Al}(\text{BH}_4)_3 \cdot 2(^{15}\text{NH}_3)$ system, showing a total available H_2 content in excess of 9% by mass.

isotopic form. Several of these samples were reacted at ORNL and characterized using Caltech's NMR facilities. Figure 5 shows the results of the desorption of the as-made material at JPL in two steps, allowing

for intermediate NMR sampling; the total available H_2 content was greater than 9% by mass. Figure 6 shows the 1H and ^{11}B NMR spectra of the samples reacted at ORNL; ^{11}B MAS NMR of the samples show a trend similar to $Mg(BH_4)_2 \cdot 2(NH_3)$ cases where BH_4 units release hydrogen to form B-N-H polymeric species. Investigations of specific samples enriched with ^{15}N show two distinct NH_3 bonding environments as well as apparent B-N-H bonding activity at higher temperatures ($\sim 200^\circ C$), but more study is required to resolve these details. As also shown in Figure 7, there is the suggestion

of multiple Al bonding sites as well, suggesting perhaps a medium-range order to the material. Again, more study is desired. This material system continues to prove interesting, even though the formation of the dodecaborane intermediate still seems difficult to avoid.

Conclusions and Future Directions

As currently planned, this is the last year of record for JPL's participation in the MHCoe project. As the effort closes out, JPL plans to continue

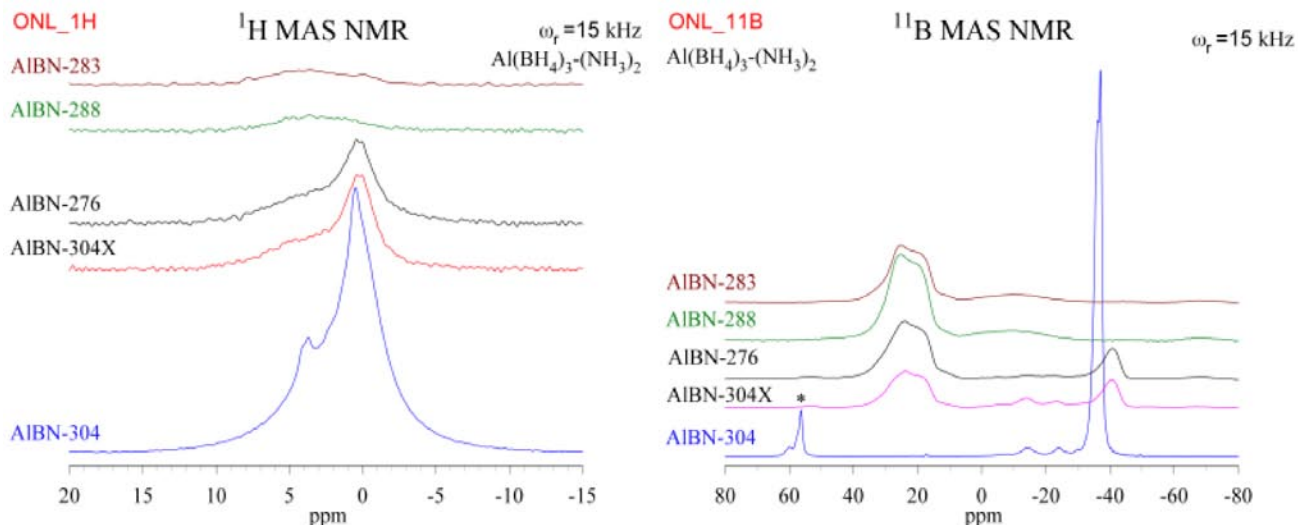


FIGURE 6. 1H and ^{11}B NMR spectra of the $Mg(BH_4)_2 \cdot 2(NH_3)$ samples reacted at ORNL. Boron peaks seen as broad powder pattern near at 10~35 ppm represents trigonal boron sites of such species. Peaks at -30 ~ 0 ppm range might be reaction intermediate. A broad resonance at -14 ppm is seen after the high temperature desorptions (AIBN-288, 283), and possible formation of dodecaborane ($B_{12}H_{12}$) can be speculated.

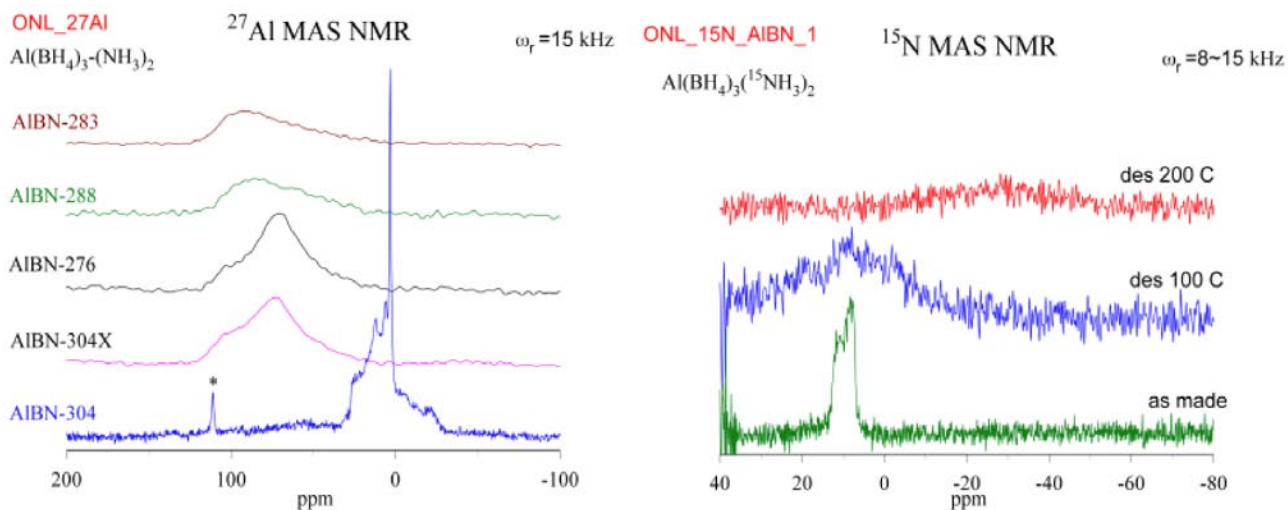


FIGURE 7. ^{27}Al MAS NMR of AIBN-304X and AIBN-276 show overlap of two broad resonances, one of them eventually disappeared when the desorption temperature was raised to $500^\circ C$. No clear spectral identification can be made at this time. Additionally, two distinct NH_3 sites are found for the as made $Al(BH_4)_3 \cdot 2(^{15}NH_3)$. A broad peak at -30 ppm is observed for B-N-H species when heated at $200^\circ C$, but further investigation is necessary to determine the N-environment.

certain specific lines of investigation while preparing closeout documentation and ensuring the archiving of information produced under this effort. Special attention will be given to feeding information to the Hydrogen Storage Engineering Center of Excellence, a parallel DOE project that also includes JPL.

FY 2010 Publications/Presentations

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3. C. Kim, S-J. Hwang, R.C. Bowman, Jr., J.W. Reiter, J.A. Zan, J.G. Kulleck, H. Kabbour[#], E.H. Majzoub, and V. Ozolins, "LiSc(BH₄)₄ as a Hydrogen Storage Material: Multinuclear High Resolution Solid State NMR and First-Principles Density Functional Theory Studies", *J. Phys. Chem. C*, 113 (22), 9956–9968, **2009**.
4. David Shane, David T. Shane, Robert L. Corey, Robert C. Bowman, Jr., Ragaiy Zidan, Ashley C. Stowe, Son-Jong Hwang, Chul Kim, and Mark S. Conradi, "NMR Studies of the Hydrogen Storage Compound NaMgH₃" *J. Phys. Chem. C* 2009, 113, 18414-18419.
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6. Son-Jong Hwang, John Vajo, Jason Zan, and Channing Ahn, "Suppressing the formation of stable intermediates in hydride destabilization reactions" Talk, APS, Portland, Mar. 2010.
7. V. Stavila, Son-Jong Hwang, R.J. Newhouse, M. Ulutagay-Kartin, W. Luo, J.G. Cordaro, T.J. Udovic, "Factors Affecting Hydrogen Release from Metal Borohydrides", Talk, Materials Challenges in Alternative and renewable Energy, Feb 21–24, 2010, Cocoa Beach, FL, USA.
8. Son-Jong Hwang, C. Ahn, J.W. Reiter, J.A. Zan, V. Stavila, J.J. Vajo, "Multinuclear High Resolution Solid State NMR Studies of Dodecaborate Intermediate of Borohydrides based Hydrogen Storage Systems" Talk, Materials Challenges in Alternative and renewable Energy, Feb 21–24, 2010, Cocoa Beach, FL, USA.
9. R.C. Bowman, Son-Jong Hwang, C. Kim, G.M. Brown, D.A. Knight, J. Zhao, J.W. Reiter, J.A. Zan, G.L. Soloveichik, S. Kniajanski, "Characterization Studies of Boron-Containing Compounds for Hydrogen Storage Applications, Invited talk, Materials Challenges in Alternative and renewable Energy, Feb 21–24, 2010, Cocoa Beach, FL, USA.