

IV.A.1n 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 Hydrogen, Fuel Cells and Infrastructure 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

Regarding the technical barriers addressed by JPL's activities within the Metal Hydride Center of Excellence (MHCoe), the best 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%) appeared to be a practical reality at the early part of the year, but with less than 6% reversible capacity on first absorb/desorb cycle – and less so after that – this material was shown to have serious issues. Still, as the only practically reversible borohydride in the MHCoe arsenal, much attention was given to its associated reaction paths.

Accomplishments

- Provided phase characterization, kinetics (i.e., diffusion behavior), and reversibility assessments via magic angle spinning nuclear magnetic resonance (MAS-NMR) in numerous systems (i.e., Li-Mg-B-H, Li-Sc-B-H, Li-B-Ca-Al-H, AlH₃, Li-Mg-Al-N-H).
- Determined the MB₁₂H₁₂ systems (M = Li, Mg, Ca) have unique affinities for water of hydration, presenting potential difficulty for manufacturing and distribution of these materials.
- Demonstrated the lack of destabilization in the Li₂B₁₂H₁₂ + MH₂ (M = Mg, Ca) system, in disagreement with theoretical predictions.
- Demonstrated the unique nature of NMR analysis in identifying the character of B-H bonding and reaction pathways in the metal-borohydride systems; this technique can distinguish amorphous/nanophase species that are not otherwise sensible via X-ray diffraction (XRD) or vibrational spectroscopy methods.
- As part of an Ohio State University (OSU)/Oak Ridge National Laboratory (ORNL)/Caltech/JPL team, discovered a new storage material, AlB₄H₁₁, giving initial capacity of 11% H₂ by weight.



Introduction

Activities at JPL under the auspices of DOE's 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, borohydrides, and AlH₃-based hydrides as well as other promising samples provided by many MHCoe partners; significant attention has been paid to the B₁₂H₁₂²⁻ system and associated reaction pathways. In addition, JPL has 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 borohydrides 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.

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 (SNL) towards an understanding of the characteristics of the Ca(BH₄)₂ system; borohydrides from OSU, ORNL, Caltech, General Electric, University of Hawaii (UH), and Savannah River National Laboratory have also been part of JPL's collaborative role. JPL has also actively participated in the discovery and characterization of destabilized Mg/Li/N systems in collaboration with Center partners UH, University of Utah (UU), the National Institute of Standards and Technology (NIST) and SNL.

A comprehensive materials development and characterization program continues to be the central focus of JPL's many roles in MHCoe. Of primary importance is the use of volumetric measurements to determine hydrogen storage capacities and equilibrium pressures on destabilized nanophase and complex metal hydrides. In addition, powder XRD 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

Project A

JPL's efforts within MHCoe Project A (Destabilized Hydrides) focused on the investigation of the possibility that the Li₂B₁₂H₁₂ system could be destabilized with the introduction of simple binary metal hydrides. The expectation of destabilization was provided by a theoretical development of these material systems, showing various reaction pathways in which the effect was predicted. In the resulting experiments at JPL and Caltech, Li₂B₁₂H₁₂ + MH₂ (M=Mg, Ca) which were reported to have favorable ΔH_{react} , appear to show a high kinetic barrier (Table 1).

TABLE 1. Li₂B₁₂H₁₂ + MH₂ Systems Investigated for Destabilization Effects

Reaction	Description
Li ₂ B ₁₂ H ₁₂	Desorbed 450°C,
Li ₂ B ₁₂ H ₁₂	Reabsorbed 450°C, 90 atm H ₂
Li ₂ B ₁₂ H ₁₂ + 6MgH ₂	Desorbed 400°C
Li ₂ B ₁₂ H ₁₂ + 6MgH ₂	Reabsorbed 300°C
Li ₂ B ₁₂ H ₁₂ + 2CaH ₂	Desorbed 400°C

In addition, Figure 1 shows that ¹¹B MAS-NMR results show little change in B-H coordination from initial dodecaborane structures following the reaction attempts.

Project B

Within MHCoe Project B (Complex Anionic Materials), JPL performed a great deal of work relating

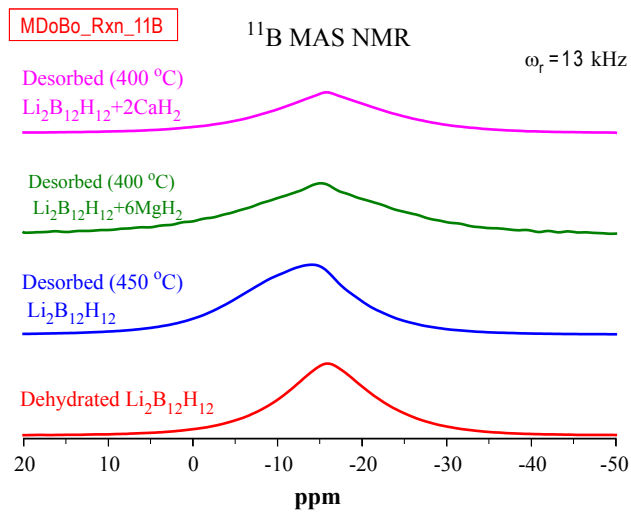


FIGURE 1. ¹¹B MAS NMR spectra showing the lack of predicted destabilization effects in the Li₂B₁₂H₁₂ + MH₂ (M = Mg, Ca) system.

to phase identification and reaction elucidation of the various borohydrides. In the $\text{Ca}(\text{BH}_4)_2$ system, partial reversibility of the compound at reasonable conditions (330°C, 80 bar) was seen via MAS-NMR. In Figure 2, MAS-NMR shows the confirmation of the system's reversibility. Following hydrogenation at 330°C, about 57% of boron is now present as $\alpha\text{-Ca}(\text{BH}_4)_2$; the intermediate $\sim 30\%$, $\text{CaB}_6 \sim 13\%$. In other samples provided by SNL, the use of catalyst showed change of crystalline polymorphs of the rehydrogenated powder ($\alpha \rightarrow \beta$ phase). This interesting result shows various additional transformations among different polymorphs around the reaction temperature. Figure 3 shows that although the Ca-B-H intermediate is not yet fully characterized, its chemical shift is very close to $\text{CaB}_{12}\text{H}_{12}$.

Various dodecaborane samples were characterized by NMR and other spectroscopic tools in collaboration with SNL, S. Jalisatgi (University of Missouri-Columbia), J.-C. Zhao (OSU), and T. Udovic (NIST). Figure 4 shows NMR spectra from the results of this study. In addition, ^{11}B MAS-NMR spectra show that the BH_4 icosahedrons become highly mobile as water molecules are introduced to the crystalline phases. The most significant finding in this regard is the suggestion that removal of crystalline water may become a challenging issue for certain metal cations (e.g. Mg) in the polyborane system; this special water affinity may present issues for the manufacture and maintenance of borohydride storage systems in the practical aspect.

In a related study, direct dehydrogenation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ material was attempted in order to elucidate reaction pathways in the M-B-H system (M = Li, Mg, Ca). While probably not a practical storage medium,

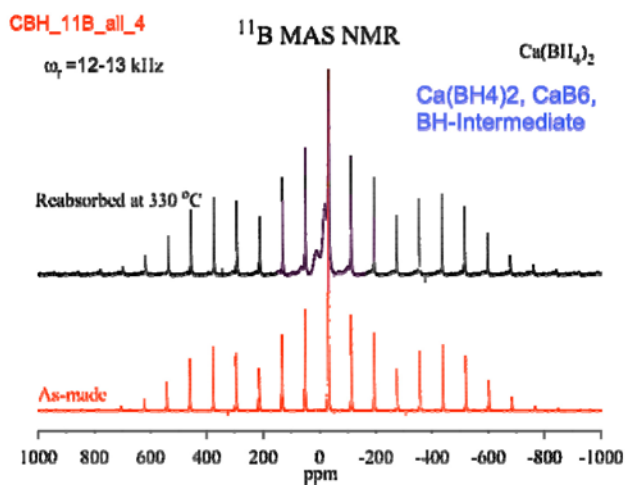


FIGURE 2. ^{11}B MAS NMR spectra following the rehydrogenation of $\text{Ca}(\text{BH}_4)_2$ at 330°C. The crystalline phase $\text{Ca}(\text{BH}_4)_2$ is seen after absorption via the powder pattern from the spinning sidebands and chemical shift position of the subject peaks.

the lithium dodecaborane salt presents a reasonable experimental system in which to study the mobility and reactivity of the BH_4/BH_3 anion. Dehydrogenation to 500°C of 525 mg of this material yields an initial 3.7% loss, with most activity occurring between 300-400°C. Based on several experiments, it appears that in the $\text{MB}_{12}\text{H}_{12}$ system (M = Li, Mg, Ca), high affinity with H_2O results in B-OH formation during heating, even as water

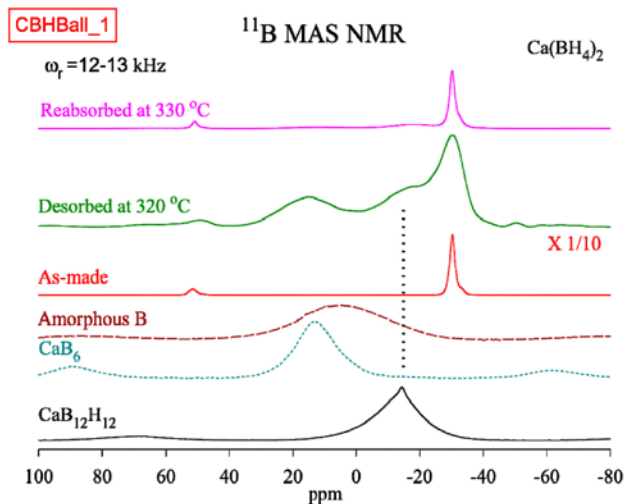


FIGURE 3. ^{11}B MAS NMR spectra of several samples of $\text{Ca}(\text{BH}_4)_2$ in different stages of hydrogenation/dehydrogenation. The dotted line indicates the presence of an intermediate compound in the dehydrogenation product that despite its shift alignment with the reference $\text{CaB}_{12}\text{H}_{12}$ may be unique and unidentified. Dissolution of the desorbed material in water did not show the presence of the $[\text{B}_{12}\text{H}_{12}]^{2-}$ phase, unlike LiBH_4 or MgBH_4 cases.

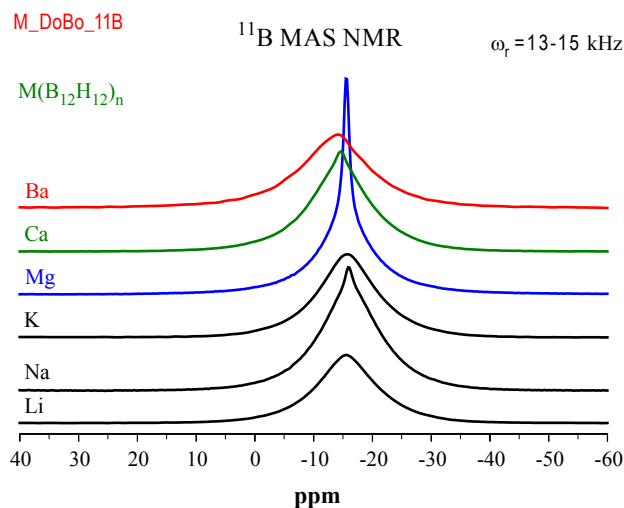


FIGURE 4. ^{11}B MAS NMR spectra showing the results of a study of metal-dodecaborane materials. One can see characteristic down field shifts for polyborane compounds with alkali metal vs. alkali earth metal cations.

is being removed. The conclusion reached at this stage is that the presence of water in these material systems proves a universal difficulty in practice as there are several hydration states in each system.

In addition, JPL and Caltech collaborated with OSU and ORNL in the discovery of a new type of aluminoborane material that looks promising for storage. The $\text{AlB}_4\text{H}_{11}$ compound was developed jointly by OSU/ORNL, with JPL/Caltech providing volumetric/kinetic measurements and NMR spectroscopy. Extensive characterization of this new material, produced by ORNL, gave a capacity of 11.4% H_2 by weight via 400°C desorption (see Figure 5); most significantly, however, a large portion of the H_2 release occurred in the range 140-200°C. Initial NMR spectra revealed a complex boron environment in the products, including both B-H complexes and possibly elemental boron with other features, partially avoiding the $\text{B}_{12}\text{H}_{12}$ route.

Project C

In MHCoe Project C (Amides/Imides), JPL played a role in the investigation of the $\text{Li}_3\text{AlH}_6 + \text{Li}_2\text{NH}$ system via NMR, in collaboration with Z. Fang at UU, who provided samples for NMR spectroscopy.

It was determined that preferential formation of AlN or Li_3AlH_6 depends on heating rate; Li_3AlH_6 formation needs heating rate of 5°C/min, and $T_{\text{react}} > 250^\circ\text{C}$. Characterization of this system has shown the collaborators that MAS-NMR can be a good probe of pathways via ^{27}Al spectra.

Conclusions and Future Directions

As currently planned, the MHCoe project will be coming to an end in December 2009. Nevertheless, there are several broad areas in which JPL plans specific accomplishments, mostly based upon progress made over the course of the project. These areas, then, are the means by which JPL hopes to “sum up” its materials development and characterization efforts.

- **Project A - Destabilized Hydride Systems**
 - Fiscal Year 2009: Investigate the potential for structured carbon-based materials (aerogels, graphitic carbons, high-surface area materials) as dopants in destabilized hydride systems utilizing volumetric, NMR, and XRD techniques.
 - Investigate pore size effects.

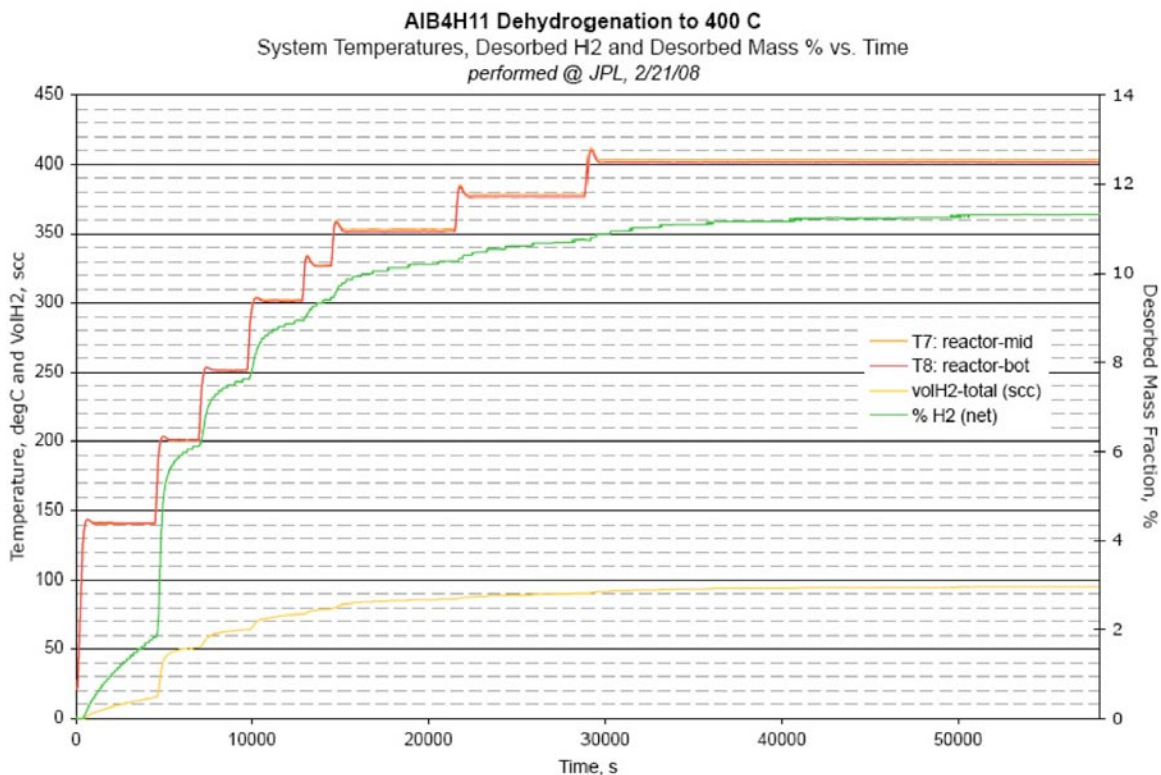


FIGURE 5. Experimental volumetric results from the desorption of $\text{AlB}_4\text{H}_{11}$, showing a mobile H_2 content in excess of 11% by weight. ^1H NMR suggests partial reversibility of an H_2 bearing phase, and ^{27}Al NMR following reabsorption suggests the possibility of reduced Al metal, but this is a topic for further study.

- **Project B - Complex Anionic Materials**
 - FY 2009: Continue phase transformation and reversibility studies of the $\text{Ca}(\text{BH}_4)_2$ system in collaboration with MHCoe partners, lending support with volumetric characterizations as well as MAS-NMR, XRD, and Raman analytical techniques.
 - FY 2009-2010: Assess initial cycling data for $n \sim 10$ -100 cycles (SNL, Caltech, UH). Continue studies of possible destabilization routes in material systems containing the $[\text{B}^{12}\text{H}^{12}]^{2-}$ anion, especially as it pertains to avoiding the production of this stable intermediate in the Mg-B-H, Li-B-H, Ca-B-H and mixed cation borohydride systems.
- **Project C - Amides/Imides**
 - FY 2009-2010: Perform systematic investigations of ^{15}N -enriched amine-borohydride materials, leveraging MAS-NMR techniques for the purpose of assessing reaction kinetics, bonding dynamics, and phase transformation effects in the M-B-N-H system (M = Li, Al, Mg), especially for mixed cation and/or ternary systems.

FY 2009 Publications/Presentations

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