# IV.A.5o Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

Robert C. Bowman, Jr. (Primary Contact),
Son-Jong Hwang (Caltech), Joseph W. Reiter,
Mauro Prina, and J. G. Kulleck

Jet Propulsion Laboratory (JPL)
4800 Oak Grove Dr., Mail Stop 79-24
Pasadena, CA  91109-8099
Phone: (818) 354-7941; Fax: (818) 393-4878
E-mail: robert.c.bowman-jr@jpl.nasa.gov

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

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## Introduction

JPL is participating in the Metal Hydride Center of Excellence (MHCoE) 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 has been working to: (1) validate initial storage properties (target: >6 wt% reversible hydrogen capacity) of light element metal hydrides including LiH destabilized with Si or Ge, borohydrides, $AlH_3$ phases, $LiBH_4$/$MgH_2$ mixtures, amides containing Li and Mg, and other hydrides as provided by MHCoE partners; (2) assess the reversibility and aging durability of the more promising hydrides during extended cycling (target: less than 10% capacity loss over >1,000 cycles); (3) support development of lighter weight, minimal volume, and thermally efficient hydride storage vessels and demonstrate their compatibility with complex and destabilized hydrides. In order to characterize critical hydrogen and metal diffusion and phase transformation processes, various solid state nuclear magnetic resonance (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.

## Approach

In active collaboration with several MHCoE partner organizations, JPL is investigating the reversible hydrogen storage parameters via volumetric measurements, the mechanisms involved in the phase transformations, and any degradation or decompositions that might occur in the more promising destabilized and complex hydrides.  The work focuses on testing hydride destabilization in Mg- and Li-based systems and mixed Li hydride/alanate/amide systems produced by Caltech, University of Hawaii (Hawaii), University of Utah (Utah), National Institute of Standards and Technology (NIST), and Sandia National Laboratories (SNL); borohydrides from GE, Caltech, and Hawaii; and various alane ($AlH_3$) phases from Hawaii, United Technolgies Research Center (UTRC), Savannah River National Laboratory (SRNL), Brookhaven National Laboratory (BNL), and the Institute for Energy Technology (IFE) in Norway.  Magic angle spinning (MAS)-NMR measurements are being performed at the Caltech Solid State NMR facility on numerous hydride systems to characterize the nature of the reactant and product phases that are complemented with X-ray diffreaction (XRD) measurements at JPL and Caltech along with nuclear vibration spectroscopy (NVS) and neutron powder diffraction (NPD) investigations at NIST.  An important component of the JPL effort is to determine experimental thermodynamic and kinetic performance parameters of these hydrides for reversible hydrogen storage applications and their durability during repeated cycling.  In particular, any severe degradation behavior will be identified as quickly as possible to ascertain whether they can be controlled or whether that candidate material should be discarded so that more robust materials can be evaluated and developed. Finally, multinuclear MAS-NMR studies underway with Washington University using samples provided by Hawaii and IFE are providing new insights into the mechanisms of Sc-doping on reaction kinetics in sodium alanate and some borohydrides.

Development of low-mass prototype hydride storage vessels that are chemically compatible with complex hydrides and also provide efficient thermal management during hydrogen filling and discharging operations is critical to meeting the DOE performance targets for storage.  Thorough evaluations of all pertinent materials properties including hydrogen storage equilibrium and dynamic characteristics, physical conditions (i.e., particle size range and distribution), heat and mass transfer parameters, minimal weights, mechanical strength, and strict attention to all aspects related to safety are necessary.

JPL has previously used this approach to develop and produce metal hydride compressor beds for its space flight hydrogen sorption cryocoolers.  This expertise and experience is being exploited for the DOE prototype hydride storage systems.  JPL is adapting its design modeling and analysis tools so that these predictive and simulation models can use appropriate thermophysical parameters on complex hydrides and vessel components as provided by SNL, SRNL, and other MHCoE partners. JPL will also test advanced materials in various demonstration-class storage beds to verify sorbent bed operating performance parameters and look for any evidence of intrinsic degradation or formation of contaminates (i.e., methane, ammonia, etc.) within the hydride bed or from interactions with its structural and thermal management components.

## Results

During FY 2007, most of our efforts have been on characterizations of phase compositions and transformations in destabilized hydride systems and other light element hydrides provided by our MHCoE partners at Caltech, Utah, GE, Hawaii, NIST, and SRNL as well as IFE (Norway).  While some studies of hydride behavior were performed at JPL by volumetric measurements and other techniques, solid state NMR methods including MAS-NMR, often with cross polarization, double and multiple quantum excitations of the resonant nuclei, were primarily utilized to obtain unique perspectives on the formation and relative stabilities of these hydrides.  Our current emphasis is to improve understanding of the destabilization phenomenon and its reversibility in borohydrides and mixed amide/alanate phases.  In collaboration with NIST and HRL, we were able to complete our characterizations of the LiH-Si, LiH-Ge, and $CaH_2$-Si systems via their $^1H$, $^7Li$, and $^{29}Si$ MAS-NMR spectra. Identification and crystal structures for the novel ternary $Li_4Si_2H$ and $Li_4Ge_2H$ phases have been reported in our joint presentations and publications during FY 2007, where it was shown that formation of the ternary phases limit reversibility in these destabilized mixtures. Consequently, these specific LiH-based systems are no longer being evaluated as candidates for reversible hydrogen storage.

Recent theoretical studies [1] predicted that $LiBH_4$-$ScH_2$ mixtures could be viable destabilized hydrogen storage candidates with attractive thermodynamics; however, there were no experimental results available to substantiate this claim.  Consequently, a series of volumetric measurements were performed at JPL in collaboration with Caltech on ball milled (BM) mixtures of $ScH_2+2LiBH_4$ and $ScB_2+2LiH$ to look for these proposed hydrogen desorption and absorption reactions, respectively.  Representative $^{11}B$ and $^{45}Sc$ MAS-NMR spectra for the desorption reactions are given in Figure 1
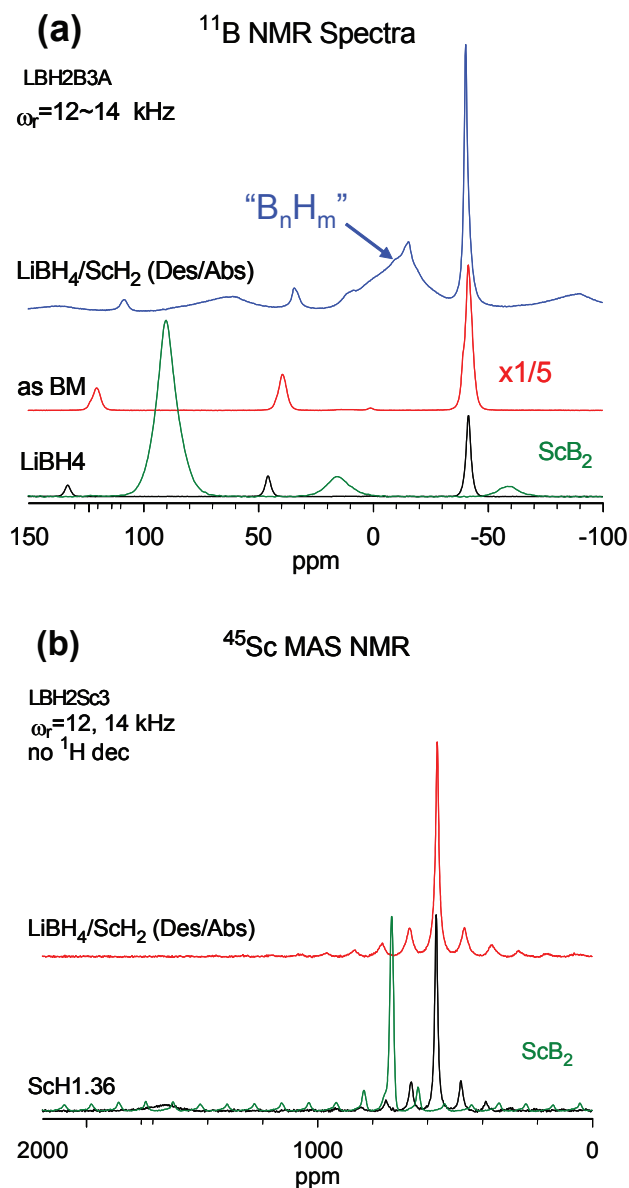


**FIGURE 1.**  MAS-NMR spectra of BM and dehydrogenated $ScH_2 + 2LiBH_4$ mixture.  (a) $^{11}B$ spectra: pure $ScB_2$ and $LiBH_4$ are given by green and black curves, respectively.  Only $LiBH_4$ is seen in red curve for BM sample while no $ScB_2$ phase is found in the blue curve after dehydrogenation, which has broad asymmetric peak from amorphous boron and an unknown "$B_nH_m$" phase.  (b) $^{45}Sc$ spectra: Black and green curves are for pure $ScH_x$ and $ScB_2$, respectively.  The spectrum shown in red for the dehydrogenated sample indicates only $ScH_x$ is present (i.e., no formation of the $ScB_2$ phase).

but do not reveal the expected $ScB_2$ product phase but rather the formation of amorphous elemental boron and previously unknown "$B_nH_m$" phases as established from separate $^1H$-$^{11}B$ cross-polarization MAS-NMR (CPMAS) measurements.  More intensive CPMAS and MQ-NMR studies are presently underway to determine the compositions of these amorphous "$B_nH_m$" phases.  There was also no evidence for $H_2$ absorption by the $ScB_2$-LiH

mixtures even with $TiCl_3$ added as a possible catalyst [2].  Apparently the high stabilities of the $ScH_x$ and $ScB_2$ phases as well as probable very slow reaction kinetics have precluded our observations of the predicted destabilization behavior predicted by Alapati, et al., [1].

Detailed MAS-NMR studies are providing characterizations for several other borohydrides [i.e., $LiBH_4$, $Ca(BH_4)_2$, $Sc(BH_4)_3$, and $Mg(BH_4)_2$] on samples produced at Hawaii, SNL, GE,  HRL, and Caltech. Analyses of MAS-NMR spectra are on-going and are providing new insights on the phase compositions and local chemical bonding parameters from crystalline and highly disordered (i.e., amorphous) phases formed at various stages of reactions for all these light element hydrides, including the destabilized and partially reversible $LiBH_4$-$MgH_2$ samples [2] as well as ternary Li-Sc-B-H phases.  Unique $^{11}B$ and $^{45}Sc$ peaks are seen in these latter MAS-NMR spectra for the borohydride phases that allow monitoring of their formation and stability under various reaction conditions.  Figure 2 compares the $^{11}B$ spectra for the high temperature (HT)-phase $Mg(BH_4)_2$ as prepared and after desorption at two elevated temperatures.  While formation of some $MgB_2$ is observed following dehydrogenation at ~720 K, most of the boron is still in some other amorphous (i.e., no detectable XRD peaks) phase that also contain large amounts of hydrogen as was definitely established via $^1H$-$^{11}B$ CPMAS measurements.  Similar NMR $^{11}B$ spectra were also obtained from desorbed Li-Sc-B-H samples.  Since it is likely that decompositions of all these borohydrides probably involve various "$B_nH_m$"
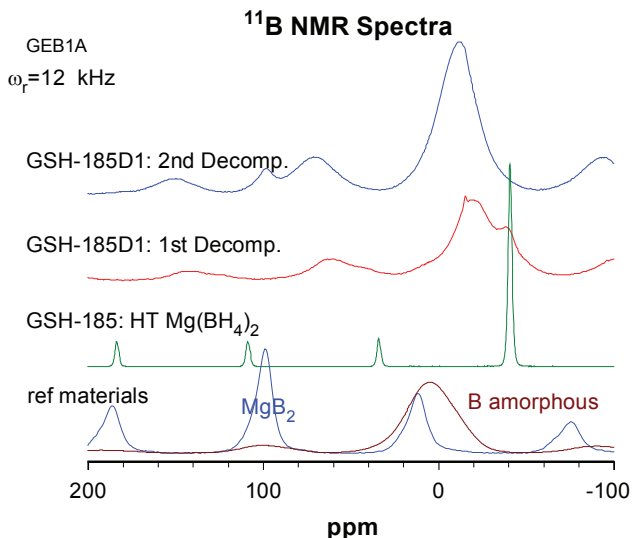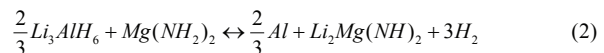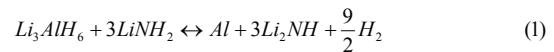


**$^{11}B$ NMR Spectra**

GEB1A
$\omega_r$=12  kHz

GSH-185D1: 2nd Decomp.

GSH-185D1: 1st Decomp.

GSH-185: HT $Mg(BH_4)_2$

ref materials    $MgB_2$      B amorphous

200       100       0       -100

**ppm**

**FIGURE 2**.  $^{11}B$ MAS-NMR spectra obtained from an as-prepared $Mg(BH_4)_2$ sample (GSH-185) with the HT structure, after a first desorption at ~620 K (GSH-185D1), and after a second desorption at ~720 K (GSH185-D2) compared to spectra for $MgB_2$ and amorphous element boron (B).  Dehydrogenation of $Mg(BH_4)_2$ mainly produces at least one new "$B_nH_m$" species with only a small quantity of $MgB_2$ at the highest temperature.

species as recently suggested by Orimo, et al. [3,4] for $LiBH_4$, additional NMR studies are in progress to clarify these dehydrogenation pathways in the quest for truly reversible storage systems that have so far remained elusive.  JPL is exploring options for mass-spectrographic instrumentation techniques to detect boron-hydride gaseous species during future *in situ* desorption and cycling experiments.

Characterizations of amides and imides have been extended to include mixtures of the lithium alanates processed at Utah.  MAS-NMR spectra of the $^{27}Al$ and $^6Li$ nuclei have provided independent and conclusive validation of reversibility for the reactions:

$$Li_3AlH_6 + 3LiNH_2 \leftrightarrow Al + 3Li_2NH + \frac{9}{2}H_2 \qquad (1)$$

$$\frac{2}{3}Li_3AlH_6 + Mg(NH_2)_2 \leftrightarrow \frac{2}{3}Al + Li_2Mg(NH)_2 + 3H_2 \qquad (2)$$

The conversions between Al metal and $Li_3AlH_6$ phases for reaction (2) are clearly evident from the $^{27}Al$ spectra in Figure 3, where the unexpected formation of $LiAlH_4$ at lower concentration is also observed under these hydrogenation conditions.  Prior XRD and infrared spectroscopy measurements had been unable to confirm these reactions.  The reversibility of $Mg(NH_2)_2$ and $Li_2Mg(NH)_2$ phases will be investigated soon via $^{15}N$ MAS-NMR measurements on isotope enriched samples now being prepared at JPL.

Static and MAS-NMR techniques continued to be applied during FY 2007 for characterizing various $AlH_3$ and sodium alanate samples that were synthesized by IFE, BNL, and Hawaii.  From the analyses of $^{27}Al$ MAS-NMR spectra, NMR characterizations of four different crystalline alane phases (i.e., α, α′, β, and γ–$AlH_3$) were completed.  Unlike α, α′, and β phases, the γ phase was found to consist of two distinct sites with the occupation ratio 2:1 and with more distorted coordination geometries compared to the other three phases.  Decomposition of the γ phase at room temperature and upon heating, which was monitored by both $^1H$ and $^{27}Al$ MAS-NMR is illustrated by the $^{27}Al$ spectra in Figure 4(a).  The corresponding rate constant k at ~23ºC obtained from α, which is the fractional decomposition of γ-$AlH_3$, by plotting [-ln(1- α)] vs. time in Figure 4(b) is 5.8 (±0.2) x$10^{-7}$ s$^{-1}$, which is an order of magnitude smaller than observed at 60ºC [5].  The stability of the α-phase $AlH_3$ at ambient temperature was also confirmed by NMR for both various BNL, Hawaii, and UTRC materials.

Since no currently assessed destabilized hydride system or complex (i.e., alanate, borohydride, or amide) hydrides sufficiently meet the DOE performance targets, extended cycling studies were deferred in FY 2007.  Instead, attention was focused on assessing the reversibility and short term durability of more promising combinations of destabilized alanates/borohydride (i.e.,
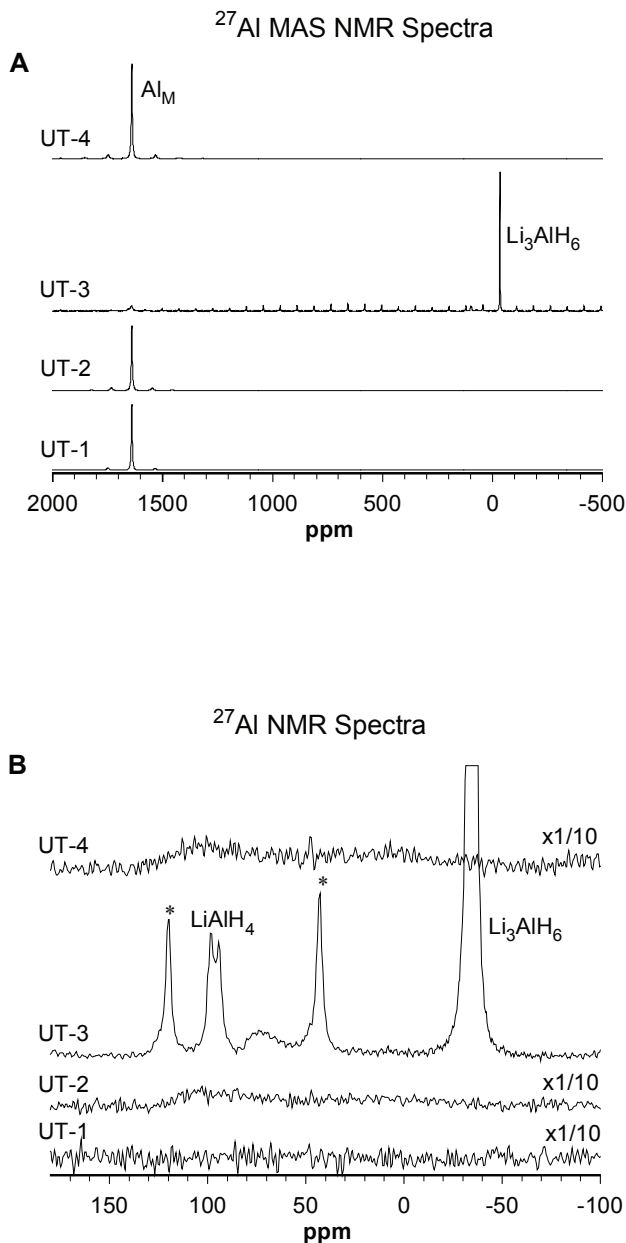
## $^{27}$Al MAS NMR Spectra

**A**



## $^{27}$Al NMR Spectra

**B**



**FIGURE 3.** $^{27}$Al MAS-NMR spectra of a BM mixture of TiCl$_3$ catalyzed Al-LiNH$_2$-MgH$_2$ [Sample UT-1];  Same mixture after dehydrogenation at 240°C for 3 hours [Sample UT-2]; After hydrogenation at 300°C and 2,500 psi H$_2$ for 10 hours of the desorbed mixture [Sample UT-3]; and the mixture after a second dehydrogenation [Sample UT-4]. Note that in spectra B, the vertical scale of sample UT-3 is 10 times less than the rest.

LiBH$_4$/Ca(AlH$_4$)$_2$ with Caltech) and  alanates/amides (i.e., Li-Mg-Al-N-H mixtures with Utah) to evaluate their potential and also look at additives as possible catalysts to enhance reaction rates.

JPL has been actively participating in several Hydride Storage Vessel system engineering team workshops to help formulate design development and
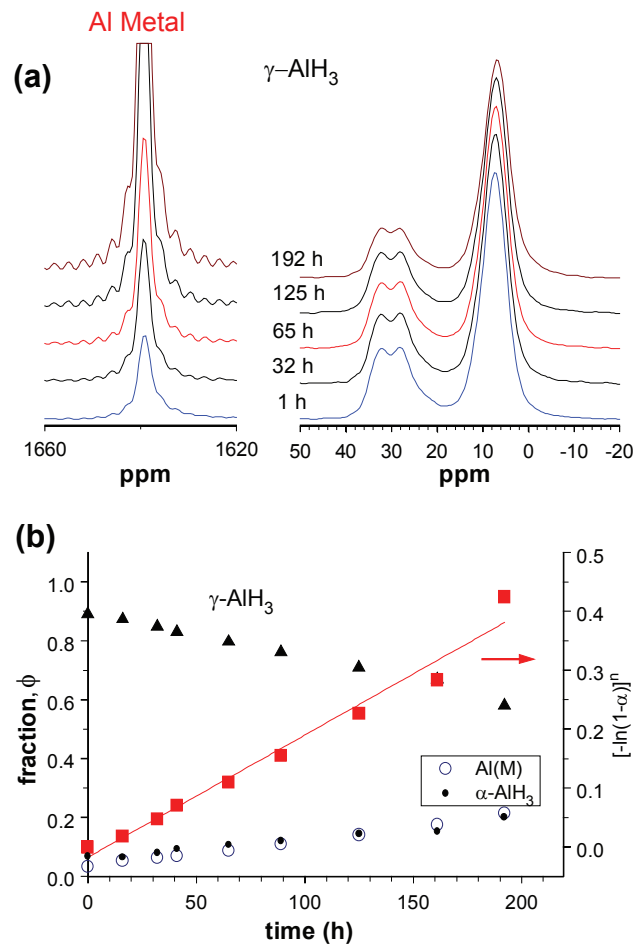
**(a)**



**(b)**



**FIGURE 4.**  (a) $^{27}$Al MAS-NMR spectra of $\gamma$-AlH$_3$ phase undergoing self-decomposition at room temperature where peaks for Al metal [Al(M)] has a shift of $\sim$1,640 ppm; (b) Plot of fraction ($\phi$) of  $\gamma$-AlH$_3$, Al(M), and $\alpha$-AlH$_3$ phases during the decomposition of the $\gamma$-AlH$_3$ sample, and plot of [-ln(1-$\alpha$)] vs. t, where $\phi$ is the fractional decomposition of $\gamma$-AlH$_3$.

analysis schemes.  We are currently leading a MHCoE systems engineering sub-team (i.e., members are from JPL, SRNL, UTRC, SNL, and DOE/EERE) to assess state-of-art for previous and current metal hydride storage bed designs and performance models from a detailed survey of published literature.  The intent is to submit our findings in a draft report to DOE at the end of 2007.  JPL is also performing thermal analyses and simulations on prototype designs for metal hydride beds that are being adapted from methods and models used on sorption cryocoolers.  Initial work utilizes a hydride with fast reaction kinetics and relatively high thermal conductivities (i.e., LaNi$_{4.8}$Sn$_{0.2}$H$_x$).  After obtaining baseline results, these models will be modified to handle various complex hydrides where the kinetics are much slower and heat transfers are less efficient.  The objective is to clarify the design requirements to optimize thermal performance levels with overall system weight and

volume targets for hydrogen storage with fuel cell powered vehicles.

## Conclusions and Future Directions

### Conclusions

- Solid state NMR continued to demonstrate great usefulness for characterizing new hydrogen-storage materials being prepared the MHCoE team. Examples include:
  - Demonstrating reversibility of the Li-Mg-Al-N-H reactions using $^{27}$Al MAS-NMR spectra.
  - Discovering formation of amorphous "$B_nH_m$" species during dehydrogenation of several borohydrides (e.g., Li-Sc-B-H, $Mg(BH_4)_2$, $Sc(BH_4)_3$).
  - Evaluating decomposition reactions of metastable $\gamma$-$AlH_3$ and other alane phases.

- None of the current destabilized systems are viable candidates for long term cycling studies, as their kinetics are either much too slow or they suffer from other issues with their capacity, reversibility, or desorption pressures.

### Future Directions

- Complete phase formation and reversibility studies on the model Li-Mg-B-H and Li-Sc-B-H systems during the coming year.
- Extend systematic MAS-NMR studies of $^{15}$N nuclei in enriched samples of Li-Mg-$^{15}$N-H, Li-Al-$^{15}$N-H, and Li-B-$^{15}$N-H to assess trends in the N-H chemical bonds, phase conversion, and dynamics that can be correlated with the NMR parameters of the other nuclei (i.e., $^6$Li, $^{11}$B, $^{27}$Al,) to gain more insight into their destabilization mechanisms and reaction kinetics.
- Complete MAS-NMR studies of phase transitions and decompositions for $Mg(BH_4)_2$ and $Ca(BH_4)_2$ systems in collaboration with GE, SNL, and LLNL.
- Measure isotherms at JPL on Mg-based and doped alanate samples provided by HRL and Caltech to assess the potential of using encapsulation with nanoparticles of destabilized and other hydrides in carbon scaffolding.
- Use NMR and volumetric methods to improve understanding of catalysts, dopants, and processing on alanates, borohydrides, and other light element hydrides such as $NaMgH_3$ in a cooperative study with the Washington University/Caltech team that is funded by DOE/Basic Energy Sciences.
- Initiate long term accelerated cycling studies of the degradation behavior if a hydride with sufficient potential to meet the DOE performance requirements can be identified.

- Complete literature survey review on state-of-art for metal hydride storage vessel design and performance.
- Complete modeling analyses and initiate laboratory testing that compare thermal performance of a traditional hydride (i.e., $LaNi_{4.8}Sn_{0.2}$) with destabilized or catalyzed complex hydrides.
- Support development of more efficient storage vessel conceptual designs, etc. with SRNL, SNL, UTRC, and other MHCoE partners.

## Special Recognitions & Awards/Patents Issued

**1.** R. C. Bowman: Co-Chair - 2006 International Symposium on Metal-Hydrogen Systems (Metal Hydrides 2006), October 2006.

## FY 2007 Publications/Presentations

**1.** H. Wu, M. R. Hartman, T. J. Udovic, J. J. Rush, W. Zhou, R. C. Bowman, Jr. and J. J. Vajo, "Crystal Structure of the Novel Ternary Hydrides $Li_4Tt_2D$ (Tt=Si and Ge)," *Acta Cryst*. B 63 (2007) 63-68.

**2.** M. R. Hartman, J. J. Rush, T. J. Udovic, R. C. Bowman, Jr., and S.-J. Hwang, "Structure and Vibrational Dynamics of Isotopically Labeled Lithium Borohydride Using Neutron Diffraction and Spectroscopy," *J. Solid State Chem.* 180 (2007) 1298-1305.

**3.** J. Graetz, J.J. Reilly, J. G. Kulleck, and R. C. Bowman, Jr., "Kinetics and Thermodynamics of the Aluminum Hydride Polymorphs," *J. Alloys Compounds* (in press – 2007).

**4.** S.-J. Hwang, R. C. Bowman, Jr., J. Graetz, J. J. Reilly, W. Langley, and C.M. Jensen, "NMR Studies of the Aluminum Hydride Phases and their Stabilities," *J. Alloys Compounds* (in press – 2007).

**5.** H. Kabbour, C. C. Ahn, S.-J. Hwang, R. C. Bowman, Jr., and J. Graetz, "Direct Synthesis and NMR Characterization of Calcium Alanate,"*J. Alloys Compounds* (in press – 2007).

**6.** R. C. Bowman, Jr., S-J. Hwang, C. C. Ahn, M. R. Hartman, T. J. Udovic, J. J. Rush, and J. J. Vajo, "Destabilization Behavior and Phase Compositions for LiH-Ge," poster presentation at MH2006, Maui, HI, October 1–5, 2006.

**7.** R. C. Bowman, Jr., "Applications of Nuclear Magnetic Resonance to Hydrogen Storage Materials," invited tutorial at the 2006 Fall Meeting of the Materials Research Society, Nov. 27, 2006.

**8.** S-J. Hwang, R.C. Bowman, Jr., M. S. Conradi, T. M. Ivancic, M. Mendenhall, P. H. L. Notten, W. P. Kalisvaart, and P.C.M.M. Magusin, "NMR Studies of the Mg-Sc-H System," presented at the 2006 Fall Meeting of the Materials Research Society, Boston, MA, Nov. 27–30, 2006.

**9.** R.C. Bowman, Jr., S-J. Hwang, M. S. Conradi, T. M. Ivancic, and H. W. Brinks, "Studies of Sc and Ti Doped NaAlH$_4$," presented at the 2006 Fall Meeting of the Materials Research Society, Boston, MA, Nov. 27–30, 2006.

**10.** R. C. Bowman, Jr., S.-J. Hwang, and M. S. Conradi, "Advanced Nuclear Magnetic Resonance Methods for Novel Metal Hydrides," presented at the IEA HIA-Task 22 Experts Workshop, Monterey, CA, January 30, 2007.

**11.** R. C. Bowman, Jr., S.-J. Hwang, J. W. Reiter, J. G. Kulleck, and W. Luo, "NMR Studies of the Li-Mg-N-H Phases," presented at 2007 March meeting of the American Physical Society, Denver, CO, March 6, 2007.

**12.** X. Tang, B. Laube, D. Anton, S.-J. Hwang, R. Bowman, "Stability Studies of Aluminum Hydride," presented at 2007 March meeting of the American Physical Society, Denver, CO, March 6, 2007.

**13.** M. Conradi, L. Sendheera, E. Carl, T. M. Ivancic, R. C. Bowman, Jr., S.-J. Hwang, and T. J. Udovic, "Trapped H$_2$ in AlH$_3$," presented at March 2007 meeting of the American Physical Society, Denver, CO, 6 March 2007.

**14.** M. S. Conradi, E. Carl, T. M. Ivancic, and R. C. Bowman, Jr., "Slow H Hopping Motions in MgH$_2$ and Alanates," presented at 2007 March meeting of the American Physical Society, Denver, CO, 7 March 2007.

**15.** R. C. Bowman, Jr. and S-J. Hwang, "Nuclear Magnetic Resonance Studies of Hydrogen Storage Materials," *Materials Matters* 2 (No. 2) (2007) 29-31.

**16.** H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, T. Yildirim, M. R. Hartman, R.C. Bowman, Jr., J. J. Vajo, "Neutron Vibrational Spectroscopy and First-principles Study of Novel Ternary Hydrides: Li$_4$Si$_2$H(D) and Li$_4$Ge$_2$H(D)," submitted to *Phys. Rev. B.* (May, 2007).

**17.** J. Lu, Z. Z. Fang, H. Y. Sohn, R. C. Bowman Jr., and S-J. Hwang, "Potential and Reaction Mechanism of Li-Mg-Al-N-H System for Reversible Hydrogen Storage," submitted to *J. Phys. Chem.* C (June, 2007).

## References

**1.** S.V. Alapati, J. K. Johnson, and D. S. Sholl, *J. Alloys Compd.* (2006), doi:10.1016/j.jallcom.2006.10.166 [in press].

**2.** J. J. Vajo, S. L. Skeith, and F. Mertens, *J. Phys. Chem.,* B **109**, 3719 (2005).

**3.** S.-I. Orimo, Y. Nakamori, N. Ohka, K. Miwa, M. Aoki, S.-I. Towata, and A. Zuttel, *Appl. Phys. Lett*., **89**, 021920 (2006).

**4.** N. Ohba, K. Miwa, M. Aoki, T. Noritake, S.-I. Towata, Y. Nakamori, and S.-I. Orimo, and A. Zuttel, Phys. Rev., B 74, 075110 (2006).

**5.** J. Graetz and J. J. Reilly, *J. Phys. Chem.,* B **109**, 22181 (2005).