

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

Joseph W. Reiter (Primary Contact),
Robert C. Bowman, Jr., Son-Jong Hwang
(Caltech), Jason A. Zan, Brenda J. Hernandez,
and James G. Kulleck

Jet Propulsion Laboratory (JPL)
4800 Oak Grove Drive, Mail Stop 79-24
Pasadena, CA 91109-8099
Phone: (818) 354-4224; Fax: (818) 393-4878
E-mail: Joseph.W.Reiter@jpl.nasa.gov

DOE Technology Development Manager:
Ned Stetson

Phone: (202) 586-9995; Fax: (202) 586-9811
E-mail: Ned.Stetson@ee.doe.gov

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pressure hydride storage tank can be accomplished with simple off-the-shelf code and reduce cooling demands during refueling.



Introduction

JPL is participating in DOE's 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 performs in several roles in the Center.

Much effort has been applied to the validation of initial storage properties (target: >6 wt% reversible gravimetric, 45 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. In addition, JPL has a charter to assess the reversibility and aging durability of the more promising hydrides during extended cycling. Finally, JPL has performed analytical work to support the development of lighter weight, low volume, and thermally efficient hydride storage vessels as well as demonstrate their compatibility with candidate hydrides. In the course of these tasks, 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. 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 has historically been widespread, and continues as such, touching all the individual projects within the Center scope. JPL has actively participated in the discovery and characterization of destabilized Mg/Li/N systems in collaboration with Center partners University of Hawaii (UH), University of Utah (UU), the National Institute of Standards and Technology (NIST) and Sandia National Laboratories (SNL). In the area of complex anionic materials, JPL has worked closely with SNL towards an understanding of the characteristics of the Ca(BH₄)₂ system; borohydrides from Caltech, General Electric

Objectives

- Validate the storage properties and assess reversibility of novel light-element hydrides.
- Support the development of light-weight, thermally efficient hydride storage vessels.

Technical Barriers

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

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

Accomplishments

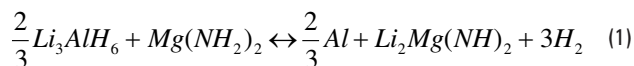
- Modeling of a low-enthalpy transition-metal hydride in a "hybrid" high-pressure hydride storage tank.
- Determined that effective modeling of a low-enthalpy transition-metal hydride in a "hybrid" high-

(GE), UH, Ohio State University, and Savannah River National Laboratory (SRNL) have also been part of JPL's collaborative role.

A comprehensive materials development and characterization project continues to be the central focus of JPL's many roles in the MHCoe. Since no exceptionally strong candidate material has yet been identified by the Center partners, the need to continue development of reversible, high-hydrogen content hydride materials with good kinetics drives the nature of JPL's approach to materials discovery and development. 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 X-ray diffraction (XRD) may be used at JPL to determine material compositions where applicable. In collaboration with the Solid-State NMR Facility at Caltech, magic angle spinning – nuclear magnetic resonance (MAS-NMR) measurement techniques can be applied in short order; 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. In addition to these techniques, a close partnership with NIST allows the use of nuclear vibrational spectroscopy and inelastic neutron scattering to further explore kinetic parameters.

Results

Investigations involving the Mg/Li alanate–amide system continue to produce interesting data. In collaboration with partners at UU, reversibility at high pressure (>2,000 psia) has been confirmed by MAS-NMR, in particular the ^{27}Al and ^6Li resonances. During this year, much focus in this area was on investigations of the reversibility of $\text{Li}_2\text{Mg}(\text{NH})_2$:



Reversibility is well illustrated in Figure 1, which shows a MAS-NMR plot following rehydrogenation at several conditions. A particular sensitivity of the conversion to the hexa-alanate “ Li_3AlH_6 ” is seen to depend closely on heating rate.

In this case, NMR was central to the identification of a reversible phase. Further investigations of the reaction pathways present in this and related systems will utilize particular sensitivity of the NMR technique to ^{15}N labeling of amide/imides, a capability that JPL will be leveraging in the coming year.

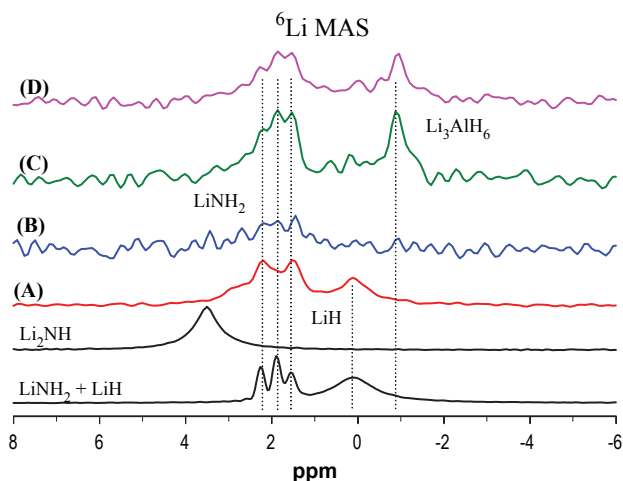


FIGURE 1. ^6Li MAS NMR spectra of catalyzed $3\text{Li}_2\text{NH}/\text{Al}$ after hydrogenation at 300°C under 2,500 psia hydrogen pressure at different heating rates. A) $1^\circ\text{C}/\text{min}$; B) $2^\circ\text{C}/\text{min}$; C) $5^\circ\text{C}/\text{min}$ and D) $10^\circ\text{C}/\text{min}$. The ^6Li MAS NMR spectra of pure Li_2NH , mixture of LiNH_2 and LiH are provided for reference.

During Fiscal Year 2008, JPL's activities in the system engineering area have been focused on a parametric approach to performance prediction and thermal/mass transport modeling of so-called “hybrid” hydride vessels. The interest in this area is related to the potential of these systems, when used with hydrides of appropriate characteristics, to significantly reduce cooling requirements for onboard refueling of hydrogen-fueled vehicles. Such an approach, when combined with an effective heat-exchange design, may be able to realize good system response, fast filling and simple thermal management. The JPL effort was designed to leverage existing in-house expertise as well as finite element system models originally designed for performance prediction of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ hydride beds. The initial effort utilized a “lumped-parameter” approach which was able to feed-forward to the actual modeling effort; preliminary results from this model are shown in Figure 2.

For a preliminary assessment, the charging pressure was increased until the fueling time was 5 minutes. The cooling loop thermal resistance from the fluid to the alloy was minimized to account for the maximum cooling power required. The conductivity of each alloy was kept constant while assuming aluminum foam embedded in each.

Conclusions and Future Directions

Conclusions

- No current destabilized hydride system shows a good candidate for cycling studies, as they suffer from deficiencies in storage capacity, kinetic performance, and/or simple reversibility.

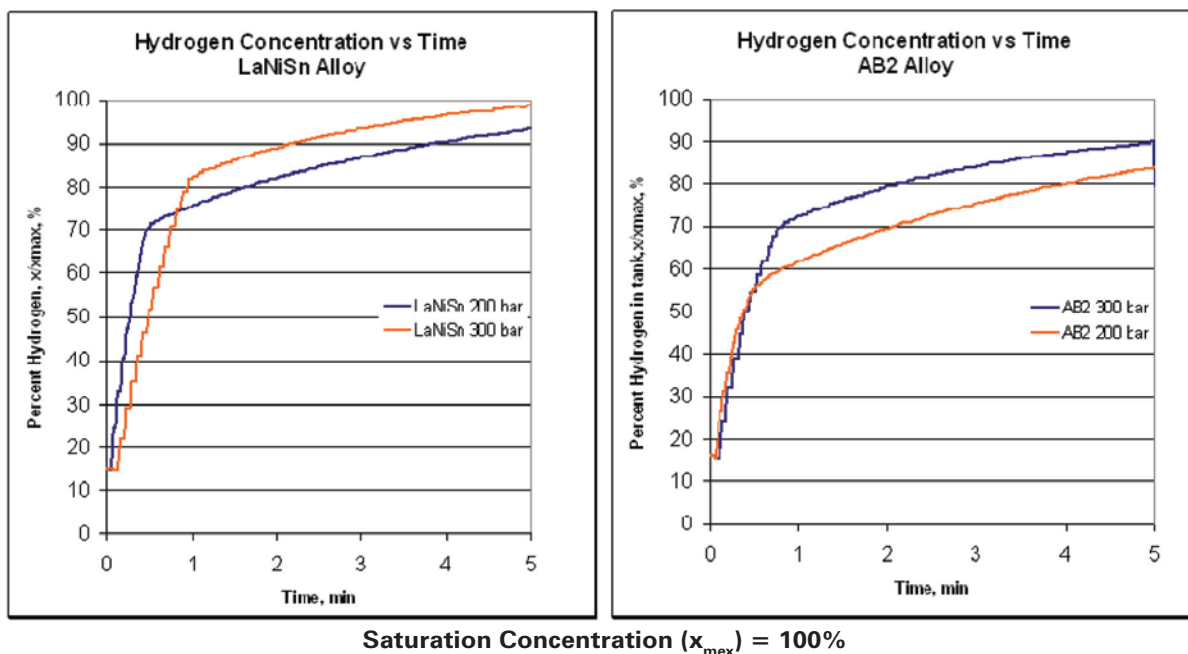


FIGURE 2. Preliminary Modeling Results

Future Directions

- Continue phase transformation and reversibility studies of the $\text{Ca}(\text{BH}_4)_2$ system in collaboration with SNL and Caltech, lending support with volumetric characterizations as well as MAS-NMR and XRD analytical techniques.
- 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.
- Perform long-term accelerated cycling studies to assess material stability and degradation should a hydride system with acceptable performance within the DOE goals be identified.
- Collaborate with NIST to perform real-time neutron imaging of $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ hydride beds during hydriding/dehydriding in order to improve the fidelity of JPL's current approach of modeling AB_5 and AB_2 hydrides in a "hybrid" storage tank.
- Utilizing JPL's novel modeling approach, perform model analyses of "hybrid" storage tank scenarios with candidate light-element hydride material systems such as a destabilized alanate or a mixed-cation borohydride.
- Continue collaboration with SRNL, United Technologies Research Center (UTRC), and others to complete literature review of "state-of-art" hydride bed design techniques and produce survey article.
- 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).
- In collaboration with Caltech, investigate the potential for structured carbon-based materials (aerogels, graphitic carbons, high-surface area materials) as dopants in a destabilized hydride system utilizing volumetric, NMR, and XRD techniques.

FY 2008 Publications/Presentations

1. S.-J. Hwang, "Characterization of Complex Metal Hydrides by High Resolution Solid State NMR Methods" Invited presentation at the 2007 Gordon Research Conference on Hydrogen-Metal Systems, Waterville, ME, July 8-13, 2007. [Caltech & JPL]
2. R.C. Bowman, J.W. Reiter, D.A. Mosher, G. Thomas, D.L. Anton, "Survey of Solid State Hydride Tanks for Hydrogen Storage and Energy Conversion Applications", Invited presentation at MS&T'07 Meeting, Detroit, MI, September 19, 2007. [JPL, SRNL, & UTRC]
3. R.C. Bowman, Jr. J.W. Reiter, S-J. Hwang C. Kim, and H. Kabbour, "Characterization of Complex Metal Hydrides by High-Resolution Solid State NMR Spectroscopy" Invited presentation at Int. Symp. Materials Issues Hydrogen Economy, Richmond, VA, November 12-15, 2007. (Paper submitted to Proceedings) [JPL & Caltech]

4. R.C. Bowman, Jr., J.W. Reiter, D.A. Mosher, G. Thomas, D.L. Anton, "Survey of Metal Hydride Storage Vessels for Fuel Cell Systems", Presented at DOE SSAWG Meeting, Washington, D.C., December 04, 2007. [JPL, SRNL, & UTRC]
5. R.C. Bowman, Jr., S.-J. Hwang, J. W. Reiter, C. Kim, H. Kabbour, J. Purewal, C.C. Ahn, "Evaluations of Formation and Reversibility of Metal Borohydrides via Volumetric and Nuclear Magnetic Resonance Methods" Invited presentation at Materials Innovations in an Emerging Hydrogen Economy, Cocoa Beach, FL, February 24-27, 2008. [JPL & Caltech]
6. R.C. Bowman, Jr., S.-J. Hwang, and C. Kim, "NMR Characterization of Complex Metal Hydrides", Poster at DOE/BES Contractors Meeting on Physical Behavior of Materials, Warrenton, VA, March 16-19, 2008. [JPL & Caltech]
7. S.-J. Hwang, C. Kim, R. C. Bowman, Jr., J.W. Reiter, H. Kabbour, "Characterization of metal tetrahydroborate systems by high resolution multinuclear solid state NMR", Oral presentation at Spring 2008 MRS Meeting, San Francisco, CA, March 24-28, 2008. [JPL & Caltech]
8. C. Kim, S.-J. Hwang, R.C. Bowman, Jr., J.W. Reiter, H. Kabbour, "High resolution multinuclear solid state NMR studies of Sc-Li-B-H systems", Poster presentation at Spring 2008 MRS Meeting, San Francisco, CA, March 24-28, 2008. [JPL & Caltech]
9. J. Lu, Z.Z. Fang, H.Y. Sohn., R. Bowman Jr, and S.-J. Hwang, "Potential and Reaction Mechanism of Li-Mg-Al-N-H System for Reversible Hydrogen Storage", Oral presentation at Spring 2008 MRS Meeting, San Francisco, CA, March 24-28, 2008. [UU, JPL & Caltech]
10. J. Graetz, J.J. Reilly, J.G. Kulleck, and R.C. Bowman, Jr., "Kinetics and Thermodynamics of the Aluminum Hydride Polymorphs", *J. Alloys Compounds* 446-447 (2007) 271-275. [JPL & BNL]
11. 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* 446-447 (2007) 290-295. [Caltech, JPL, BNL, & UH]
12. 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* 446-447 (2007) 264-266. [Caltech, JPL, and BNL]
13. 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" *J. Phys. Chem. C* 111 (2007) 16686-16692. [Caltech, JPL, and UU]
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15. S.-J. Hwang, R.C. Bowman, Jr., J.W. Reiter, J. Rijssenbeek, G. L. Soloveichik, J.-C. Zhao, H. Kabbour, and C. C. Ahn, "NMR Confirmation for Formation of $[\text{B}_{12}\text{H}_{12}]^{2-}$ Complexes during Hydrogen Desorption from Metal Borohydrides", *J. Phys. Chem. C* 112 (2008) 3164-3169. [JPL, Caltech, & GE Global]
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19. J. Lu, Z. Zak Fang, Y.J. Choi, H.Y. Sohn, R.C. Bowman, Jr., S.-J. Hwang, and C. Kim, "Study of the Reaction Mechanism of Li-Al-N-H System during the Hydrogenation Process", *J. Phys. Chem. C* (In preparation). [Caltech, JPL, and UU]

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4. E.Hahne, J. Kallweit, "Thermal Conductivity of Metal Hydride Materials for Storage of Hydrogen: Experimental Investigation", *Int. J. Hydrogen Energy*, Vol. 23, No. 2, pp. 107-114.