IV.A.4f Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

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Introduction

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, AlH_3 phases, $LiBH_4/MgH_2$ mixtures, amides containing Li and Mg, and other hydrides as provided by the Metal Hydride Center of Excellence (MHCoE) partners; (2) initiated assessments of the aging durability of the more promising hydrides during extended cycling (target: less than 10% capacity loss over >1,000 cycles); and (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 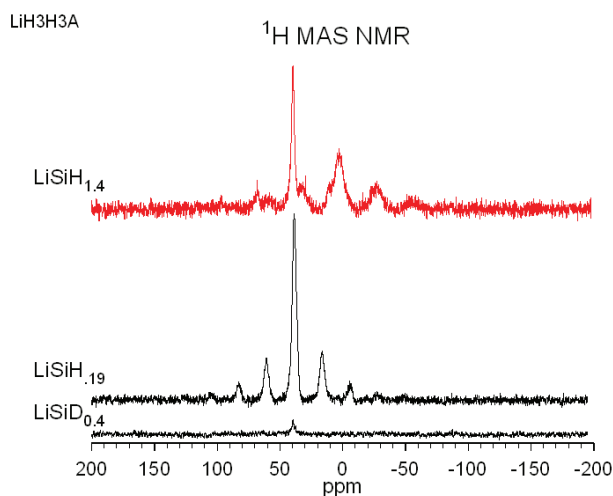work focuses on testing hydride destabilization in Mg- and Li-based systems and mixed Li hydride/amide systems produced by HRL, Caltech, NIST, and Sandia National Laboratory (SNL) as well as various alane (AlH_3) phases from Brookhaven National Laboratory (BNL) and U. Hawaii. Magic angle spinning nuclear magnetic resonance (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 diffraction (XRD) measurements and neutron vibrational 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.

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, Savannah River National Laboratory (SRNL), and other MHCoE partners. JPL will also test advanced materials in prototype 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.
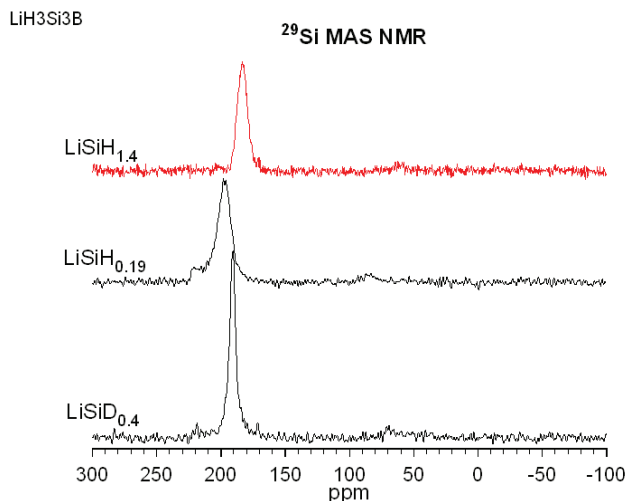
Results

During FY 2006 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 HRL, BNL, NIST, and U. Hawaii as well as IFE (Norway). While some studies of hydride behavior were performed by volumetric measurements and other techniques, solid state NMR methods including MAS-NMR, often with double and multiple quantum excitations of the resonant nuclei, were 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 collaboration with NIST and HRL, we were able to obtain ^{1}H, ^{7}Li, and ^{29}Si MAS-NMR spectra (see Figures 1 and 2) from a ternary $Li_xSi_yH_z$ hydride previously detected only as an impurity phase in cycled LiH+Si destabilized mixtures. The combination of all these spectra from this NIST sample clearly indicated formation of just the ternary Li-Si-H phase and crystalline silicon without LiH or Li_ySi_z intermetallics found in LiH+Si mixtures with 2.5:1 and 4.4:1 ratios. These findings are in full agreement with the NVS and NPD results obtained at NIST on all these Li-Si-H materials.

Further MAS-NMR studies have supported phase characterizations (i.e., structure & bonding properties) for borohydrides [i.e., $LiBH_4$, $Ca(BH_4)_2$ and $Mg(BH_4)_2$] and silicide hydrides [i.e., Na-Si-H and Ca-Si-H] with NMR in collaboration with SNL, NIST, Caltech, and Lawrence Livermore National Laboratory. For example, the ^{29}Si and ^{1}H MAS-NMR spectra in Figures 3 and 4, respectively, were obtained from Ca-Si-H samples made
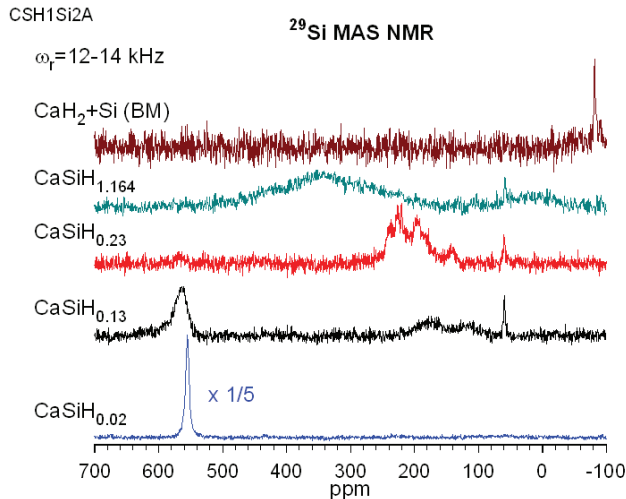

FIGURE 2. ^{29}Si MAS-NMR spectra for mixed phase Li-Si-H sample ($LiSiH_{1.4}$) and the ternary and NIST samples [$LiSiH_{0.19}$ and $LiSiD_{0.4}$] of just the $Li_xSi_yH_z$ phase.
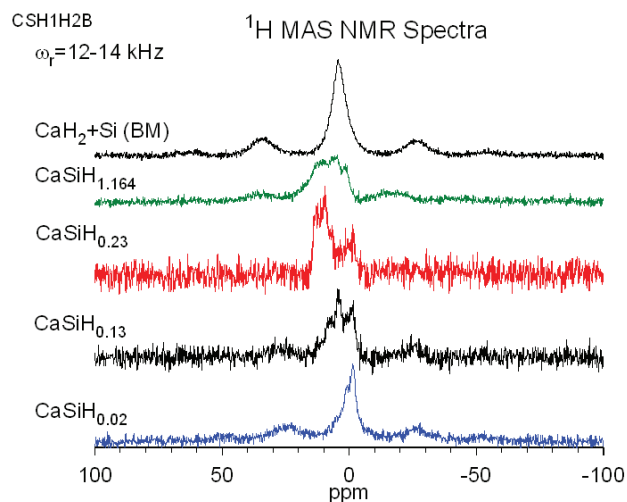

FIGURE 3. Proton MAS-NMR spectra for Ca-Si-H samples from NIST show only modest difference with spectrum of initial CaH_2.

at NIST and are showing changes from the original ball-milled (BM) mixture of CaH_2+Si with different hydrogen contents that are similar to distinctive differences in the NVS results from NIST due to different site occupancy and local structure. Analyses of MAS-NMR spectra are on-going to provide insights on the phase compositions and local chemical bonding parameters for crystalline and highly disordered (i.e., amorphous) phases at various stages of reactions for all these light element hydrides including destabilized $LiBH_4$-MgH_2 samples from HRL and Li-Mg-N-H samples from SNL. For more detailed assessments of the destabilized amides using ^{15}N NMR spectroscopy, samples isotope enriched $Li^{15}NH_2$ and $Mg(^{15}NH_2)_2$ have been prepared at JPL and initial NMR data collected at Caltech.

FIGURE 1. Proton MAS-NMR spectra for mixed phase Li-Si-H sample ($LiSiH_{1.4}$) with has LiH and the ternary NIST samples [$LiSiH_{0.19}$ and $LiSiD_{0.4}$] of just the $Li_xSi_yH_z$ phase.

Static and MAS NMR techniques have been efficiently applied to characterize various AlH_3 samples produced at BNL and U. Hawaii. From the analyses of ^{27}Al MAS NMR spectra, NMR characterizations of three different crystalline alane phases (i.e., α, β, and $\gamma-$ AlH_3)

FIGURE 4. ^{29}Si MAS-NMR spectra for Ca-Si-H samples from NIST reveal significant changes with hydrogen content reflecting to be determined variations in bonding and structures.
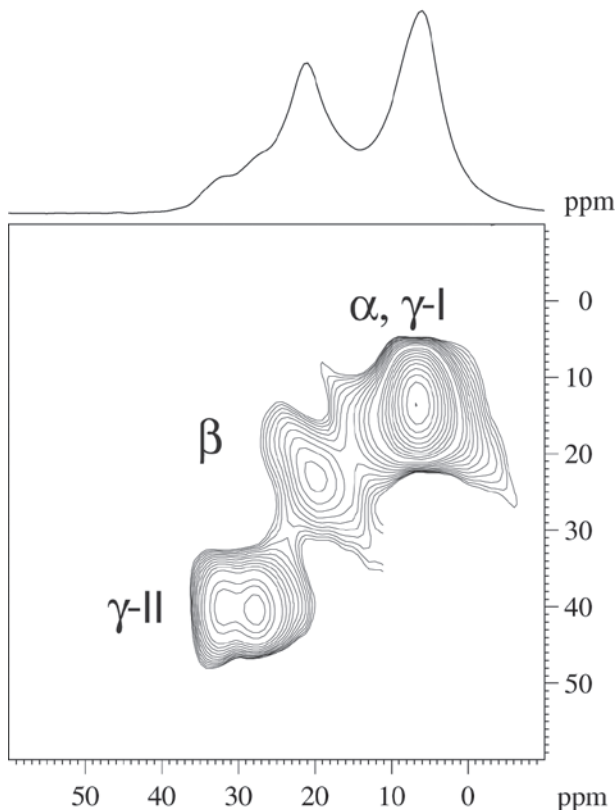
FIGURE 5. A 2D [27]Al MQMAS spectrum for a combined $\alpha+\beta+\gamma$ phase AlH_3 made at BNL showing contour plots of the Al sites in different phases.

were made for the first time. The [27]Al peaks from 2D MQMAS measurements on a mixed phase BNL sample are evident in Figure 5. Unlike 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 two phases. Faster decomposition of the γ phase at room temperature, which was monitored by both ^{1}H and ^{27}Al MAS NMR, represents a greater instability than for α-AlH_3 that was also found in recent decomposition rate studies at elevated temperature [1,2] where this result may be correlated with distorted geometry in γ-AlH_3. The stability of the α phase at ambient temperature was also confirmed by NMR for both old and new BNL materials.

JPL has been participating in several Hydride Storage Vessel system engineering team workshops and teleconferences to help formulate a design development and analysis scheme. We have begun to evaluate metal hydride system models from ANL "MH-tool" simulation code as written and to adapt it for storage vessels using either known hydrides (i.e., $LaNi_{4.8}Sn_{0.2}$) or other complex hydrides.

Conclusions and Future Directions

1. Solid state NMR has demonstrated its usefulness for characterizing new hydrogen-storage materials investigated by the MHCoE:
   – Distinct Al sites have been identified from the ^{27}Al MAS-NMR spectra.
   – Discovered unexpected new phases (e.g., $Li_xSi_yH_z$) and incomplete reversibility of phase conversion (e.g., $LiBH_4$-MgH_2).
   – Identified trapped H_2 gas in passivated α-AlH_3 and cycled Sc-doped $NaAlH_4$.

2. During the coming year we will complete phase formation and reversibility studies on the model LiH-Si, LiH-Ge, and MgH_2-Si systems.

3. None of the current destabilized systems (i.e., LiH-Si, $LiBH_4$-MgH_2, MgH_2-Si, or Li-Mg-N-H) 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.

4. We plan to perform 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 the NMR parameters of the other nuclei (i.e., ^{1}H, ^{2}H, [7]Li, [11]B, [27]Al, etc.) to gain understanding into their destabilization mechanisms and reaction kinetics.

5. Finish MAS-NMR studies on Ca-Si-H system this year and explore any other promising Si-based systems provided by SNL and NIST.

6. Use NMR and volumetric methods to improve understanding of catalysts, dopants, and processing on alanates, borohydrides, amides, and other light element hydrides.

7. Initiate long-term accelerated cycling studies of the degradation behavior of one or more candidate with sufficient potential to meet the DOE performance requirements (i.e., destabilized amide or borohydride with appropriate catalysts).

8. Coordinate a systems engineering team to review alternative analysis methodologies for hydride storage beds to facilitate an integrated MHCoE effort to model and predict performance of advanced hydrides and bed designs.

9. Support development of more efficient storage vessel conceptual designs, etc. with SRNL, SNL and other MHCoE partners.

Special Recognitions & Awards/Patents Issued

1. MRS Trophy Award as Best Paper entitled "NMR and X-ray Diffraction Studies of Phases in the Destabilized LiH-Si System" published proceedings for Symposium N "Materials for Hydrogen Storage" held during the 2004 Fall MRS Meeting, Boston, MA.

FY 2006 Publications/Presentations

1. R. C. Bowman, Jr., S.-J. Hwang, C. C. Ahn, and J. J. Vajo, "NMR and X-ray Diffraction Studies of Phases in the Destabilized LiH-Si System", Mater. Res. Soc. Symp. Proc. **837** (2005) paper N3.6.1.

2. R. C. Bowman, Jr., "Behavior and Properties of Metal Hydrides for Reversible Hydrogen Storage" WE-Heraeus-Seminar on Hydrogen Storage with Novel Nanomaterials, Bad Honnef, Germany (October, 2005).

3. M. R. Hartman, T. J. Udovic, J. J. Rush, R. C. Bowman, Jr., J. J. Vajo, and C. C. Ahn, "Neutron Scattering Investigations of a Destabilized LiH:Si System for Hydrogen Storage Applications" 2005 Fall MRS Meeting, Boston, MA (December, 2005).

4. R. C. Bowman, Jr., S-J. Hwang, C. C. Ahn, A. Dailly, M. R. Hartman, T. J. Udovic, J. J. Rush, and J. J. Vajo, "Reversibility and Phase Compositions of Destabilized Hydrides Formed from LiH", Spring 2006 MRS Meeting (April, 2006).

5. Son-Jong Hwang, R. C. Bowman, Jr., Jason Graetz and J. J. Reilly, "NMR Studies of the Aluminum Hydride Phases and their Stabilities", Spring 2006 MRS Meeting (April, 2006) Mater, Res. Soc. Symp., Vol. 927 (2006), paper 0927-EE03-03.

6. M. R. Hartman, T. J. Udovic, J. J. Rush, R. C. Bowman, Jr., J. J. Vajo, and C. C. Ahn, "Neutron Scattering Investigations of a Destabilized LiH:Si System for Hydrogen Storage Applications" Spring 2006 MRS Meeting (April, 2006).

7. R. C. Bowman, Jr., "Current Status in Developing Advanced Metal Hydrides for Reversible Hydrogen Storage", 209th Meeting of Electrochemical Society, Denver, CO (May 10, 2006).

8. R. C. Bowman, Jr., J. G. Kulleck, S.-J. Hwang, M. R. Hartman, T. J. Udovic, and J. J. Rush, "Characterization of Phase Compositions and Structures for Metal Hydrides Used in Hydrogen Storage" Amer. Crystallographic Soc. Meeting, Honolulu, HI (July, 2006).

9. 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. (Submitted 2006).

References

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

2. S. Orimo, Y. Nakamori, T. Kato, C. Brown, and C. M. Jensen, *Appl. Phys. A* **83**, 5 (2006).