Final Report for the DOE Metal Hydride Center of Excellence

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Abstract

This report summarizes the R&D activities within the U.S. Department of Energy Metal Hydride Center of Excellence (MHCoE) from March 2005 to June 2010. The purpose of the MHCoE has been to conduct highly collaborative and multi-disciplinary applied R&D to develop new reversible hydrogen storage materials that meet or exceed DOE 2010 and 2015 system goals for hydrogen storage materials. The MHCoE combines three broad areas: mechanisms and modeling (which provide a theoretically driven basis for pursuing new materials), materials development (in which new materials are synthesized and characterized) and system design and engineering (which allow these new materials to be realized as practical automotive hydrogen storage systems). This Final Report summarizes the organization and execution of the 5-year research program to develop practical hydrogen storage materials for light duty vehicles. Major results from the MHCoE are summarized, along with suggestions for future research areas.

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(cc) = co-chair at some point

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One of the most helpful and constructive aspects of the Centers of Excellence program were the yearly reviews by the Hydrogen Storage Tech Team. These were day-long reviews in which we could get direct feedback and discussion on the progress in the MHCoE, constructive criticism of the results and advice on changes of R&D direction. Particular thanks are extended to Scott

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Executive Summary

The purpose of the Metal Hydride Center of Excellence (MHCoE), funded by DOE's Fuel Cell Technology Program within the Office of Energy Efficiency and Renewable Energy (EERE), has been to conduct highly collaborative and multi-disciplinary applied R&D to develop new reversible hydrogen storage materials that meet or exceed DOE 2010 and 2015 system goals for hydrogen storage materials. Although the MHCoE was originally tasked with system design and engineering, this latter responsibility shifted to the Hydrogen Storage Engineering Center of Excellence (HSECoE), which was established in 2009. This Final Report summarizes the organization and execution of a 5-year research program to develop practical hydrogen storage materials for light duty vehicles.

During the 5-year life of the MHCoE, the following organizations and institutions have been partners, providing technical leadership and making important technical contributions to the MHCoE R&D program:

- Brookhaven National Laboratory (BNL)
- California Institute of Technology (Caltech)
- Carnegie Mellon University (CMU)
- General Electric (GE)
- Georgia Institute of Technology (GT)
- HRL Laboratories, LLC
- Intematix
- Jet Propulsion Laboratory (JPL)
- National Institute of Standards and Technology (NIST)
- Oak Ridge National Laboratory (ORNL)
- Ohio State University (OSU)
- Sandia National Laboratories (SNL)
- Savannah River National Laboratory (SRNL)
- Stanford University
- United Technologies Research Center (UTRC)
- University of Hawaii at Manoa (UH)
- University of Illinois at Urbana-Champaign (UIUC)
- University of Nevada, Reno (UNR)
- University of New Brunswick (UNB)
- University of Pittsburgh (PITT)
- University of Utah

Sandia National Laboratories has served as the "lead partner" for the MHCoE. The technical work was originally divided into five "project groups," A–E. The purpose of the project areas was to organize the MHCoE technical work along appropriate and flexible technical lines and to foster collaboration. These projects included the following:

Project A (Destabilized Hydrides), whose objective has been to develop strategies for reducing hydrogen storage thermal requirements and improve kinetics by destabilizing metal hydrides systems. Project A also aimed to enhance kinetics by evaluating nanoengineering. In this Final Report, research highlights are given on destabilization studies of the $LiBH_4/Mg_2NiH_4$ system, which has shown the potential for destabilization to alter reaction pathways. Work is also described on the dramatic increase (50 times) in kinetics observed when metal hydride materials are confined to nanoscaffolds such as carbon aerogel.

Project B (Complex Anionic Materials), whose objective has been to predict and synthesize highly promising new anionic hydride materials, with a particular focus on borohydride materials. This report highlights the extensive work on the synthesis and reaction characterization of $Mg(BH_4)_2$. This material was shown to be reversible in MHCoE work, making it the highest weight capacity (12 wt. % hydrogen) reversible material in existence. Work is also presented here on the $Ca(BH_4)_2$ system and the reactivity of $[B_{12}H_{12}]^{2-}$ salts, which were found to be very important intermediates in borohydride hydrogen release reactions.

Project C (Amide/Imide Storage Materials), whose objective has been to assess the viability of amides and imides (materials containing $-NH_2$ and $-NH$ moieties, respectively) for onboard hydrogen storage. This Final Report gives highlights for the synthesis and characterization of LiMgN, with an 8 wt. % capacity to store hydrogen. An account is also given of work on the related material $2LiNH_2/MgH_2$, which has proven to be a fully reversible 5 wt. % system with attractive thermodynamics.

Project D (Alane, AlH_3), whose objective has been to understand the sorption and regeneration properties of alane (AlH_3) for hydrogen storage. AlH_3 is a nearly ideal hydrogen releasing material, but to regenerate AlH_3 directly from the end-product Al with gaseous H_2 requires unreasonably high pressures. This report summarizes the MHCoE successes in rehydrogenating Al by organometallic approaches, as well as by a novel electrochemical approach. Both of these are "off-board" rehydrogenation processes. A particulary novel way of regenerating $LiAlH_4$ is also described, which makes this a potential off-board reversible material with nearly 7 wt. % hydrogen.

Project E (Engineering Analysis and Design), whose objective was to understand the materials engineering properties of metal hydrides as they were undergoing cycling. The responsibilities of Project E ended with the commissioning of the Hydrogen Storage Engineering Center of Excellence (HSECoE) at SRNL in 2009. Nonetheless, a review of selected Project E highlights is given here, including the characterization of the thermal conductivity of $2LiNH_2 + MgH_2$, and a description of a detailed numerical model that was constructed for a general metal hydride bed that couples reaction kinetics with heat and mass transfer, for both hydrogen release and hydrogen charging of the metal hydride.

In addition to these formal projects, the MHCoE established a Theory Group (TG). The MHCoE TG made use of first-principles methods to predict new materials and their thermodynamic properties, provide new directions for experimentalists, and assist in the interpretation of experimental results. In many ways, the MHCoE Theory Group set a new standard for how collaboration amongst theorists can be achieved, and how that theoretical activity can guide experimental work. Highlights from the TG are given here, starting with a description of a reaction screening protocol that allowed over 20 million possible reactions to be screened for theoretically favorable hydrogen release properties. Favorable reactions so identified were followed up by the MHCoE experimentalists.

A powerful new theoretical method was developed in the MHCoE. This new Prototype Electrostatic Ground State (PEGS) method allows the prediction of crystal structures of unknown compounds. Knowing the crystal structure of a material is required to examine its thermodynamics, and examples of this are described here. Finally, given the importance of thermodynamics, it is very important to understand in ever finer detail the physical processes that affect reaction thermodynamics. A remarkably accurate theoretical account of the thermodynamics for the $LiBH_4$ material and for the $LiBH_4 + MgH_2$ reaction are described herein.

The MHCoE has been engaged in applied research with the goal of finding a practical material that satisfies the DOE hydrogen storage targets. It has been very important to quickly assess a material's real potential for practically satisfying the targets. This Final Report summarizes the criteria that were used for downselecting materials, namely discontinuing work on materials due to lack of promise, and continuing work on downselected materials that do show promiseExamples are given for discontinued materials. A comprehensive table is given in Appendix I for those materials that were discontinued, including the reasons for abandoning their study.

New materials continued to be investigated in the final months of the MHCoE, and a number of them showed promise, but there was insufficient data to warrant a downselect decision. These "Materials Examined Near Program End" included $Mg(BH_4)_2(NH_3)_2$, $(NH_4)_2B_{10}H_{10}$ and AlB_4H_{11} amongst others, and are described along with the high-priority materials that are discussed in the various project highlights.

A detailed comparison is made of the most promising materials coming from the MHCoE and the DOE hydrogen storage targets. This comparison is accomplished with a series of "spider charts" that are built from a number of material properties such as gravimetric density and volumetric density. These spider charts are presented for both the "off-board regenerated" materials AlH_3 and $LiAlH_4$, as well as for the "on-board regenerated" materials $Mg(BH_4)_2$, $2LiNH_2/MgH_2$, $LiNH_2/MgH_2$, $LiBH_4/Mg_2NiH_4$ and $LiBH_4/MgH_2$.

Given the progress made in the MHCoE, it is important to come away with recommendations on future high-priority fundamental R&D directions. These different directions are discussed, including more work on destabilized systems, nanoconfinement of metal hydrides in nanoporous materials, and the need to gain a better understanding of solid-state reaction kinetics and catalysis. The borohydrides are identified as a particulary important class of materials from which a truly remarkable hydrogen storage material may emerge.

Also given is a listing of the DOE awards garnered by the MHCoE and its participants.

Three appendices close out the report. Appendix I gives a full accounting of the materials that were discontinued, removing them from further study. Appendix II lists all publications coming from the MHCoE activity, organized according to Project. Appendix II also lists the publications coming from the TG, as well as patents coming from the MHCoE work. Finally, Appendix III reproduces the contents of a "lessons learned" facilitated review of the MHCoE that was conducted at the last face-to-face meeting of the MHCoE held at the University of Utah on November 4, 2009.

Benefits of the Center Construct

The MHCoE R&D effort over the 5-year duration of the project can be numerically summarized as follows. Ninety-four new material systems were explored, leading to 279 publications describing the MHCoE R&D activity. These papers were published in the best chemistry and physics journals in existence (e.g., *Physical Review Letters*, *Physical Review B*, *Journal of the American Chemical Society*, etc.). Approximately one-third of the publications were collaborative in nature, involving at least two different institutional partners in the MHCoE. Thirteen patents were submitted in the course of the MHCoE work.

The MHCoE was formed to allow collaborations amongst the scientific community to work on hard problems in hydrogen storage that require interdisciplinary effort and collaboration. At the same time, that collaboration cannot be at the expense of individual inspiration and the creative research ideas that arise from independent work. The level of collaboration achieved in the MHCoE was near optimal. Strong collaborations, often involving as many as six institutional partners, were brought to bear on challenging problems of hydrogen storage. At the same time, this collaboration was not the only way for the center to operate, and we maintained strong independent programs that made progress in different areas, but whose work was, as needed, enabled by the strong collaborations that came to exist within the MHCoE. This Final Report also documents the domestic collaborations between MHCoE investigators and the U.S. hydrogen storage community, as well as international collaborations throughout the world.

It was the consensus of the MHCoE Principal Investigators that the Center construct was an excellent way to achieve rapid progress in this field. Towards the end of the MHCoE, we held a facilitated "Lessons Learned" session. The report from that activity is provided in Appendix III. Regarding the usefulness of the center concept, the Lessons Learned Report was quite clear:

> *"The response that received the most consensuses from the participants was that the center concept provided an efficient way for technical collaboration that otherwise would not have occurred. The statement that more technical progress was made in the Center than would have in independent projects was the overarching theme of the Center Successes Session."*

The purpose of a Center is to solve hard technical problems requiring collaborations that cannot be established otherwise. Collaboration between two individuals is easy without a Center. Although a collaboration amongst three individuals or institutions is harder, this can also be established without a Center. However, collaborations amongst four or more institutions is best created within a Center construct. Was collaboration unique to a Center achieved in the MHCoE? It will be clear from this MHCoE Final Report that the answer to this question is "yes." In the MHCoE, sometimes five or six partners worked together on these materials. This was true for the MHCoE studies of $Mg(BH_4)_2$, AlH_3, and 1:1 $LiNH_2/MgH_2$, just to name a few examples. The collaboration between five or six partners at different institutions is highly unlikely without the funding and structure of a Center. Overall, the center concept was very successful for making rapid progress in this field.

Were hard technical problems solved? The reader will see that hard technical problems were indeed solved, although it will be evident that the hydrogen storage materials still need to be improved. The program did not find one material that simultaneously supports all of the DOE targets. However, as described in the Project Summaries, critical understanding was gained on many topics and important "sub problems" in the areas of theory, synthesis, characterization, and regeneration that lay the foundation for developing a truly remarkable solid-state H_2 storage material.

Major Accomplishments of the MHCoE

1. Dramatically expanded the scientific knowledge base of metal hydride hydrogen storage materials. Examined 94 material systems, published 279 papers, with approximately one-third of the publications being collaborative in nature, involving at least two different institutional partners in the MHCoE.

2. Developed 13 patents related to metal hydride hydrogen storage materials.

3. Solidified technical collaboration in hydrogen storage materials science. The MHCoE established technical collaborations with 17 domestic U.S. research institutions and 9 international research organizations.

4. Investigated 94 hydrogen storage materials systems in the MHCoE, providing a wide-ranging survey of the materials space, and giving clear directions and guidance for future work.

5. Investigated over 50 borohydride material systems for hydrogen storage, developing high-yield syntheses and characterizing their structural and hydrogen release properties. The work provides clear indication that a truly remarkable hydrogen storage material may reside amongst the borohydrides. Prior to the MHCoE only a few borohydrides had been studied for their hydrogen storage potential (OSU, SNL, UH, PITT, GT, SRNL, ORNL, Caltech, NIST, Utah, UTRC).

6. Discovered an approach allowing $Mg(BH_4)_2$ to reversibly store approximately 12 wt. % hydrogen, a record gravimetric capacity for a reversible hydrogen storage material. $Mg(BH_4)_2$ remains one of the most interesting compounds for H_2 storage due to the high theoretical wt. % H (14.8 %) and good hydrogen desorption enthalpy ($\Delta H = 40$ kJ/mole H_2). If the kinetic limitations can be overcome, then the thermodynamics of the system would allow facile hydrogen release and reversibility (OSU, UH, SNL, Caltech, NIST).

7. Devloped and demonstrated a method to increase 50-fold the dehydrogenation rate from $LiBH_4$ by its incorporation in 13-nm carbon aerogel. Incorporation into the aerogel also improves the cycling stability three-fold. The MHCoE established nanoconfinement as a general method for enhancing kinetics and cycling stability in metal hydride materials (HRL).

8. Developed a flexible low-temperature homogenous organometallic approach to incorporate Al- and Mg-based hydrides into carbon aerogels, leading to high loadings without degradation of the nano-porous scaffold (UH).

9. Developed two independent low-energy "off board regeneration" routes to rehydrogenate Al back to AlH_3 with energy efficiency approaching the DOE target. BNL developed an organometallic approach in which AlH_3 could be generated from H_2 in the presence of a stabilizing agent, with that stabilizing agent eventually removed to yield pure AlH_3. SRNL developed an electrochemical route in which spent aluminum could be converted to AlH_3 with high purity and good yield.

10. Created a remarkably facile method to regenerate $LiAlH_4$ with WTT efficiency approaching 60%. The method utilizes dimethyl ether, low (100 bar) hydrogen pressures

and room-temperature conditions to quantitatively convert spent Li-Al to LiAlH$_4$ (UNB and UH).

11. Developed theoretical methods to screen over 20 million different reaction conditions (composition, T, P) to search for promising hydrogen storage systems, and the influence of multistep reactions on the reactive pathways. These methods revolutionized the way materials can be searched for desired reaction properties using computational techniques (PITT, GT).

12. Conceived the Prototype Electrostatic Ground State (PEGS) method for predicting crystal structures beyond the use of the ICSD database, thereby increasing accuracy and enabling thermodynamic predictions for new structural phases of materials. This is a breakthrough theoretical development with a wide applicability to diverse hydrogen storage compositions (SNL).

13. Investigated 20 new "destabilized" hydrogen storage systems, expanding by a factor of 10 the number of known destabilized storage systems. Established "destabilization" as a general method for reducing the enthalpy barriers to hydrogen release (HRL, Caltech, PITT, GT, SNL).

14. Discovered a hydrogen storage system (LiBH$_4$/Mg$_2$NiH$_4$) that exhibited full reversibility, reaction through a direct low-temperature kinetic pathway, formation of a ternary boride phase, and low reaction enthalpy coupled with low entropy. This interesting system reveals in many ways the full power of the destabilization approach, and points the way to possible future hydrogen storage R&D involving ternary borides (HRL).

15. Elucidated the role of [B$_{12}$H$_{12}$]$^{2-}$ salts in the hydrogen storage reactions of borohydrides.. The MHCoE developed NMR methods of detecting the [B$_{12}$H$_{12}$]$^{2-}$ intermediates, and formulating straightforward synthesis methods to directly make MB$_{12}$H$_{12}$ materials to permit their further study (SNL, OSU, UH, Caltech, PITT, GT, NIST).

16. Discovered and developed the (2LiNH$_2$ + MgH$_2$) material system, which reversibly stores 5 wt. % hydrogen, has demonstrated 264 reversible cycles, and can be catalyzed with KH to readily release hydrogen at 180 ºC, providing a 20-bar equilibrium pressure. This material has been recommended to the HSECoE as an important "near-term" material for subsystem engineering development (SNL).

17. Discovered that LiMgN forms the basis for a reversible ~ 8 wt. % hydrogen storage material that releases H$_2$ at approximately 200 ºC, with a ΔH = 32 kJ/moleH$_2$. These experimental findings dramatically confirmed the earlier theoretical predictions made for this material by MHCoE theorists. This material has also been recommended to the HSECoE as an important "near-term" material for subsystem engineering development (Utah, GT, Caltech, SNL).

18. Developed quantitative first-principles theoretical methods for predicting enthalpies of selected reactions by taking into account contributions to the free energy arising from harmonic and non-harmonic vibrations. The techniques revealed the origin and importance of such vibrational effects in determining the structural transformations of LiBH$_4$ with temperature. For the first time, a quantitative explanation was given for the enthalpy of the reaction 2LiBH$_4$ + MgH$_2$ $\longleftrightarrow$ 2LiH + MgB$_2$ + 4H$_2$. This work

establishes a reliable means to include all vibrational effects, and yields quantitative predictions for the reaction enthalpies in all molecular-solid, H-storage materials (UIUC).

19. Conducted the first theoretical studies of the chemical interactions between nanoscaffolds and metal hydrides incorporated therein. Studies revealed the reactive stability of $Ca(BH_4)_2$ when incorporated into inorganic aerogels materials ZrO_2, Y_2O_3 and C (UTRC).

20. Conceived and developed the method of incorporating 20% N_2 into the hydrogen gas stream to increase the reversible storage capacity of the LiN_3-H system to 10.5 wt. % at the relatively low temperature of approximately 250 ºC. The increased capacity is explained by CALPHAD modeling that shows that small amounts of pure liquid lithium metal form during cycling, which the added N_2 converts to Li_3N and then eventually to Li_2NH. In this way, elemental Li, which is formed in the absence of N_2 and represents a loss in H_2 storage capacity, is recovered by the added N_2, preserving the full hydrogen storage capacity (UNR, NIST).

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Introduction

The purpose of the Metal Hydride Center of Excellence (MHCoE) has been to conduct highly collaborative and multi-disciplinary applied R&D to develop new reversible hydrogen storage materials that meet or exceed the DOE 2010 and 2015 system goals for hydrogen storage materials. The MHCoE combines three broad areas: mechanisms and modeling (which provide a theoretically driven basis for pursuing new materials), materials development (in which new materials are synthesized and characterized) and system design and engineering (which allow these new materials to be realized as practical automotive hydrogen storage systems). Driving all of this work are the hydrogen storage system specifications contained in the DOE targets for 2010 and 2015. Although the MHCoE was originally tasked with system design and engineering, as described above, this latter responsibility shifted to the Hydrogen Storage Engineering Center of Excellence (HSECoE) which was established in 2009.

The MHCoE has tackled well-defined technical barriers associated with reversible solid-state hydrogen storage systems in which hydrogen is desorbed and re-absorbed on-board the vehicle. This latter specification of "on-board" reversibility has been an important requirement for our materials search. These technical barriers are reproduced below from the onboard hydrogen storage section of the multi-year research development and demonstration plan (MYRDDP):

A. **Cost.** Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods.

B. **Weight and Volume.** Materials and components are needed that allow compact, lightweight, hydrogen storage systems while enabling greater than 300 mile range in all light duty vehicle platforms. Reducing weight and volume of thermal management components is required.

C. **Efficiency.** The energy required to get hydrogen in and out of the material is an issue for reversible solid-state materials. Thermal management for charging and releasing hydrogen from the storage system needs to be optimized to increase overall efficiency.

D. **Durability**. Materials and components are needed that allow hydrogen storage systems a lifetime of 1500 cycles with tolerance to fuel contaminants.

E. **Refueling Time.** There is a need to develop hydrogen storage systems with refueling times of less than three minutes for 5 kg of hydrogen, over the lifetime of the system. Thermal management during refueling is a critical issue that must be addressed.

F. **System Life Cycle Assessments.** Assessments of the full Life Cycle costs, efficiency, and environmental impact for hydrogen storage systems are lacking.

The goals for the MHCoE R&D program were made quantitative by the "system storage targets" outlined by the original FreedomCAR and Fuel Partnership Program for 2010 and 2015. A table showing the original DOE targets is reproduced below in Table 1. The targets have since been revised, but the MHCoE worked toward the original targets.

Table 1. Original DOE targets for on-board hydrogen storage systems, recently revised.

Storage Parameter	Units	2007	2010	2015
System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass)[a]	kWh/kg (kg H_2/kg system)	1.5 (0.045)	2 (0.06)	3 (0.09)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	1.2 (0.036)	1.5 (0.045)	2.7 (0.81)
Storage system cost[b] (& fuel cost)[c]	$/kWh net ($/kg H_2) $/gge at pump	6 (200) ---	4 (133) 2-3	2 (67) 2-3
Durability/Operability Operating ambient temperature[d] Min/max delivery temperature Cycle life (1/4 tank to full)[e] Cycle life variation[f] Min delivery pressure from tank; FC=fuel cell, I=ICE Max delivery pressure from tank[g]	°C °C Cycles % of mean (min) at % confidence Atm (abs) Atm (abs)	-20/50 (sun) -30/85 500 N/A 8FC/10ICE 100	-30/50 (sun) -40/85 1000 90/90 4FC/35ICE 100	-40/60 (sun) -40/85 1500 99/90 3FC/35ICE 100
Charging/discharging Rates System fill time (for 5 kg) Minimum full flow rate Start time to full flow (20°C)[h] Start time to full flow (-20°C)[h] Transient response 10%-90% and 90% -0%[i]	Min (g/s)/kW S S S	10 0.02 15 30 1.75	3 0.02 5 15 0.75	2.5 0.02 5 15 0.75
Fuel Purity (H_2 from storage)[j]	% H_2	99.99 (dry basis)		
Environmental Health & Safety Permeation & leakage[k] Toxicity Safety Loss of useable H_2[l]	Scc/h -- -- (g/h)/kg H_2 stored	Meets or exceeds applicable standards 1	0.1	0.05

MHCoE Management

Sandia National Laboratories has served as the "lead laboratory" for the MHCoE. Given the technical challenges, and geographical and organizational distribution of the Center partners, significant Center management and coordination activities were required. Sandia provided these management responsibilities for the Center with a strong emphasis on open and timely communications between the Center project teams, Sandia, and the DOE. The responsibilities for managing the Center resided with the DOE. A Coordinating Council was formed in Program Year 1 (2005), composed of the Sandia Management Team and technical leads from the Center Project Teams. The Sandia Management team originally consisted of Director James Wang, with

support from Deputy Director Jay Keller and MHCoE administrator Marcina Moreno. In Program Year 2 (2006), Dr. Lennie Klebanoff replaced Dr. Wang, with Keller and Moreno continuing on in their respective roles. The Sandia Management Team from 2006–2010 is shown in Figure 1 below.

Figure 1. Sandia MHCoE Management Team (L-R): Director Lennie Klebanoff, Business Manager Marcina Moreno, and Deputy Director Jay Keller.

The Sandia management team made full use of communications capabilities (e.g., email, Webex, teleconferencing, etc.) as well as other collaborative tools (such as SharePoint) to track progress and facilitate collaboration and communication between participating institutions. The program's technical progress was tracked at the following intervals:

1. Quarterly program progress reports scheduled among Center team members and DOE.

2. Biannual face-to-face program meetings of the entire program team for the purpose of sharing information and discussing program needs and opportunities, both technical and programmatic.

3. Attendance at the DOE Hydrogen Program Annual Merit Review, with review by external reviewers invited by DOE, and an annual progress report submitted to DOE.

4. Presentations to the Hydrogen Storage Technical Team on an annual basis.

5. Monthly phone calls held between Sandia Management and the DOE and more frequently as needed.

MHCoE Partners

During the 5-year life of the MHCoE, the following organizations and institutions have been partners, providing technical leadership and making important technical contributions to the MHCoE R&D program.

Brookhaven National Laboratory (BNL): The BNL point of contact (POC) has been Dr. Jim Wegrzyn. The research direction being pursued by Brookhaven has been focused on use of alane

(AlH$_3$) as a storage material, and developing methods to regenerate alane from Al metal. Their overall strategy has been to first fully understand the structure and hydrogen release properties of AlH$_3$, and then to pursue "off-board" methods of regenerating AlH$_3$ with stabilizing additives.

California Institute of Technology: The Caltech POC has been Dr. Channing Ahn. Caltech has been engaged with experimentally evaluating the most promising hydride destabilization systems using Sieverts volumetric techniques to determine actual gravimetric hydrogen release and the associated kinetics aided by standard catalysts. The Caltech group, in collaboration with the neighboring Jet Propulsion Laboratory (JPL), has brought to the MHCoE state-of-the-art NMR facilities in order to gain insights into these metal hydride systems, as they oftentimes show no long-range crystallographic order that could otherwise be studied with standard X-ray diffraction (XRD) techniques. Advanced transmission electron microscopy (TEM) work was also conducted at Caltech in collaboration with MHCoE partners.

Carnegie Mellon University (CMU): The CMU point of contact was Dr. David Sholl. CMU was a partner from the origin of the MHCoE until 2008 when Prof. Sholl moved to the Georgia Institute of Technology (GT). Dr. Sholl and coworkers have focused on developing and using state-of-the-art theory to predict promising hydrogen storage materials based on the predicted thermodynamics of hydrogen release reactions. Specific goals include prediction of the heats of formation and other thermodynamic properties of alloys from first principles methods, identification of new alloys that can be tested experimentally, and calculation of surface and energetic properties of nanoparticles. This work was conducted in close collaboration with Dr. Karl Johnson at nearby University of Pittsburgh.

General Electric: The GE point of contact was Dr. J.-C. Zhao. GE was a MHCoE partner from 2005 until 2008. GE brought to the MHCoE a powerful array of synthesis and analytical techniques, including combinatorial / high-throughput materials screening, and a synchrotron-based in-situ X-ray diffraction apparatus equipped with gas sampling that allowed hydriding and de-hydriding reactions to be followed in real time. This combination allowed the rapid experimental synthesis of promising materials, followed by detailed reactive and structural study of the most promising candidates.

Georgia Institute of Technology (GT): GT became a participant in the MHCoE in 2008, with the arrival of Dr. Sholl on the GT faculty. The course of the theory work remained the same as with CMU, and the original collaboration with U. Pitt continued as well.

HRL Laboratories, LLC: The point of contact for HRL was originally Dr. Greg Olson from 2005 to 2007. With Dr. Olson's retirement in 2008, Dr. Ping Liu served as the HRL POC. The contributions of HRL to the MHCoE centered on the development and implementation of hydride "destabilization" strategies for light-metal hydrides containing Li and Mg. Furthermore, HRL created approaches for the efficient and controlled synthesis of thermodynamically tuned nanophase metal hydrides, and worked to improve kinetic properties by introducing metal hydrides into nanoconfined environments (e.g. aerogels).

Intematix: Intematix was an original partner in the MHCoE, and participated until 2008. At that time, Dr. Jonathan Melman served as the Intematix POC. Intematix brought a powerful

combinatorial chemistry methodology to the MHCoE. Combinatorial synthesis enables preparation of arrays of materials with multiple elements and various ratios in one batch. To screen these materials, Intematix developed high-throughput screening apparatus which allow these materials to be studied in parallel for targeted properties via their optical and reflective properties. Intematix contributed to the MHCoE program by synthesizing and identifying new metal hydride systems, as well as catalysts, using these combinatorial techniques.

Jet Propulsion Laboratory (JPL): The JPL point of contact was originally Dr. Bob Bowman. With Dr. Bowman's retirement in 2009, Dr. Joe Reiter assumed the POC responsibilities. JPL has contributed to the MHCoE by understanding the storage properties of light element metal hydrides including borohydrides and amides, and assessing the reversibility and aging durability of the more promising hydrides during extended cycling. JPL also brought considerable engineering expertise to the project, and in the early years of the MHCoE supported the development of lighter weight, minimal volume, and thermally efficient hydride storage vessels. JPL collaborated with Caltech in providing state-of-the-art NMR analysis for all of the MHCoE partner research.

National Institute of Standards and Technology (NIST): The NIST point of contact was Dr. Terry Udovic. NIST brought powerful neutron-based structural and spectroscopic analytical techniques to the MHCoE. Using neutron-based probes, NIST has provided diffraction and spectroscopic characterization to many of the materials systems examined in the MHCoE in order to understand the geometric structure, hydrogen bonding, and effect of doping in metal hydride systems. In a separate activity, led by Dr. Ursula Kattner, NIST provided Calphad thermodynamic modeling in order to make critical theoretical assessments of hydrogen content, character and heats of reaction, and phase-reaction sequences during hydrogen charge-discharge cycling of MHCoE-developed metal-hydride systems.

Oak Ridge National Laboratory (ORNL): The ORNL point of contact was Dr. Gilbert Brown. The focus of the ORNL work has been the development of synthetic methods based on solution chemistry. Wet-chemistry synthesis methods were developed and reactions studied for a number of borohydrides and amides. In addition ORNL collaborated with BNL on the use of solution organometallic chemistry to improve the reversibility of reactions.

Ohio State University (OSU): The point of contact has been Prof. J.-C. Zhao, who moved to OSU from GE in 2008. The OSU approach has been to take advantage of the excellent solution synthesis facilities (including five vacuum lines) and boron chemistry expertise at OSU to synthesize new boron-containing lightweight compounds and then use various analytical facilities at both OSU and MHCoE partner sites to study the structures and dehydrogenation and re-hydrogenation properties of these compounds. On-site facilities at OSU include solution NMR, IR, XRD, DSC, and PCT (pressure-composition-temperature) tests.

Sandia National Laboratories (SNL): The technical point of contact for both the MHCoE as a whole, and the Sandia technical effort within the MHCoE, has been Dr. Lennie Klebanoff (Director of the MHCoE). In addition to the MHCoE management responsibilities, SNL was a technical leader, predicting, synthesizing and characterizing new high-hydrogen content complex metal hydrides. Sandia experimental capabilities brought to the table included a high-pressure

(15,000 psi) sintering vessel for synthesizing new materials. New Monte-Carlo-based theoretical methods were developed for rapidly assessing compound stability and structure, and the theory was developed to assess the role of non-hydrogen gas-phase species in determining the thermodynamic course of reactions.

Savannah River National Laboratory (SRNL): The SRNL point of contact was Dr. Don Anton. The SNRL effort was divided into three main areas. The first area considered the early MHCoE engineering materials R&D activity. Secondly, SRNL also worked on the problem of AlH_3 regeneration by adopting an electrochemical approach (lead by Dr. Ragaiy Zidan). Finally, SRNL developed a strong experimental program devoted to making and characterizing amide materials and their compounds with borohydrides.

Stanford University: The Stanford point of contact has been Prof. Bruce Clemens. The Stanford group employed a combination of thermodynamic modeling efforts with thin-film material synthesis and various characterization techniques to gain a better understanding of the underlying kinetic mechanisms present in the metal hydride phase transformations. Epitaxial thin-film growth techniques were used to produce model systems with atomic-level control over structure and composition. X-ray diffraction (XRD) techniques, using both in-house facilities and facilities at the Stanford Synchrotron Radiation Laboratory (SSRL), were used to characterize the structural changes of material systems as they undergo phase changes during hydrogen absorption and desorption. This structural information could then be correlated with kinetic data to relate the structure of materials to their kinetic behavior.

United Technologies Research Center (UTRC): The UTRC point of contact was Dr. Dan Mosher. UTRC has been a MHCoE partner since 2008. UTRC worked to incorporate solvated and other forms of complex metal hydrides (with a focus on borohydrides) into nano-scale frameworks of low density, high surface area skeleton materials. The purpose of the nanoconfinement was to stabilize, modify thermodynamics, catalyze and control desorption product formation associated with complex metal hydrides. In addition to an experimental program, UTRC used atomistic / thermodynamic modeling to investigate carbon and inorganic nano-framework structured (NFS) materials.

University of Hawaii at Manoa (UH): The UH point of contact has been Prof. Craig Jensen. The UH group focused on the properties of Group I and II salts of anionic transition metal borohydrides with high hydrogen content, and also developed new organometallic-based approaches to incorporating metal hydrides into carbon aerogels. In collaboration with the University of New Brunswick (UNB), the UH group worked to develop facile "off-board" efforts to regenerate AlH_3 and $LiAlH_4$. These studies were supported by extensive IR, solid state MAS ^{11}B NMR, and/or powder X-ray diffraction and thermal desorption analyses.

University of Illinois at Urbana-Champaign (UIUC): The UIUC point of contact was Prof. Ian Robertson. The work at UIUC focused on resolving issues within current hydrogen storage materials using a combination of theoretical and electron microscopy methodologies. The Illinois group tied together theoretical understanding of electronic, enthalpic, thermodynamic, and surface effects affecting performance of storage materials with microchemical and microstructural experimental analysis. State-of-the-art microscopy tools were used to investigate

the microstructural and microchemical changes that occur in candidate material systems of interest to the MHCoE partners during the uptake and release of hydrogen.

University of Nevada, Reno (UNR): The UNR point of contact was Prof. Dhanesh Chandra. UNR conducted extensive (hundreds of cycles) pressure cycling and aging tests of materials developed by the MHCoE partners. The effects of common impurities in commercial hydrogen (such as O_2, CO, H_2O and CH_4) on materials cycling behavior were also examined. In addition in-situ X-ray diffraction studies of crystal structures were performed as well, which revealed new phase formation due to impurities in gases, before and after cycling tests. This X-ray capability was also brought to bear on structural questions stemming from materials developed by MHCoE Partners.

University of New Brunswick (UNB): The UNB point of contact was Prof. Sean McGrady. UNB became a partner in the MHCoE in 2008, and participated for the remainder of the Center. In collaboration with UH and other MHCoE partners, UNB studied the rehydrogenation of Al metal under supercritical fluid conditions. In addition, UNB developed facile methods for rehydrogenation of LiH (to form $LiAlH_4$). Isothermal desorption studies and gas chromatographic analyses, as well as X-ray and NMR work was brought to bear on these "off-board regeneration" approaches for Al and LiH.

University of Pittsburgh (PITT): The PITT point of contact was Prof. Karl Johnson. In collaboration with Prof. Sholl of CMU and later GT, the PITT effort focused on state-of-the-art theory and modeling to study the structure, thermodynamics, and kinetics of hydrogen storage materials. Specific goals include prediction of the heats of formation and other thermodynamic properties of alloys from first principles methods, identification of new alloys that can be tested experimentally, calculation of surface and energetic properties of nanoparticles, and calculation of kinetics involved with H_2 desorption/adsorption processes.

University of Utah: The point of contact for Utah was Prof. Zak Fang. The Utah group focused on the use of an innovative chemical vapor synthesis method directed to synthesizing nanosized powders as precursors for making metal hydrides. Furthermore, there was a strong effort on nitrogen containing materials, in particular, light metal amide materials and their interactions with other hydrides. Variable energy ball milling techniques were applied in the synthesis of new hydrogen storage materials.

The MHCoE work was performed under a standard non-disclosure agreement (NDA) bearing the signature of all the institutions above. Summarizing, eleven universities, six national laboratories, and four industrial partners contributed resources, leadership and technical prowess to the MHCoE. A photo of the MHCoE participants from a December 2007 face-to-face meeting at Sandia National Labs in Livermore CA is shown below in Figure 2.

Figure 2. MHCoE face-to-face partners meeting at Sandia National Laboratories, Livermore, CA, in December 2007.

MHCoE Project Structure

The MHCoE organizational structure from 2005–2010 is shown in Figure 3 below. The chart indicates that the DOE is the overall technical manager. A "Coordinating Council" was formed, populated by the management team, the project leads, and the senior technical members of the MHCoE. The purpose of the Coordinating Council was to have a representative group to give broad technical feedback on questions that arose (for example downselect decisions) as needed. The Coordinating Council also addressed problems of Center-wide resource allocation, and also conducted Phase I to Phase II review of our partners. These partner reviews were particularly constructive, as it gave the partner being reviewed an opportunity to hear constructive feedback on the course of their work.
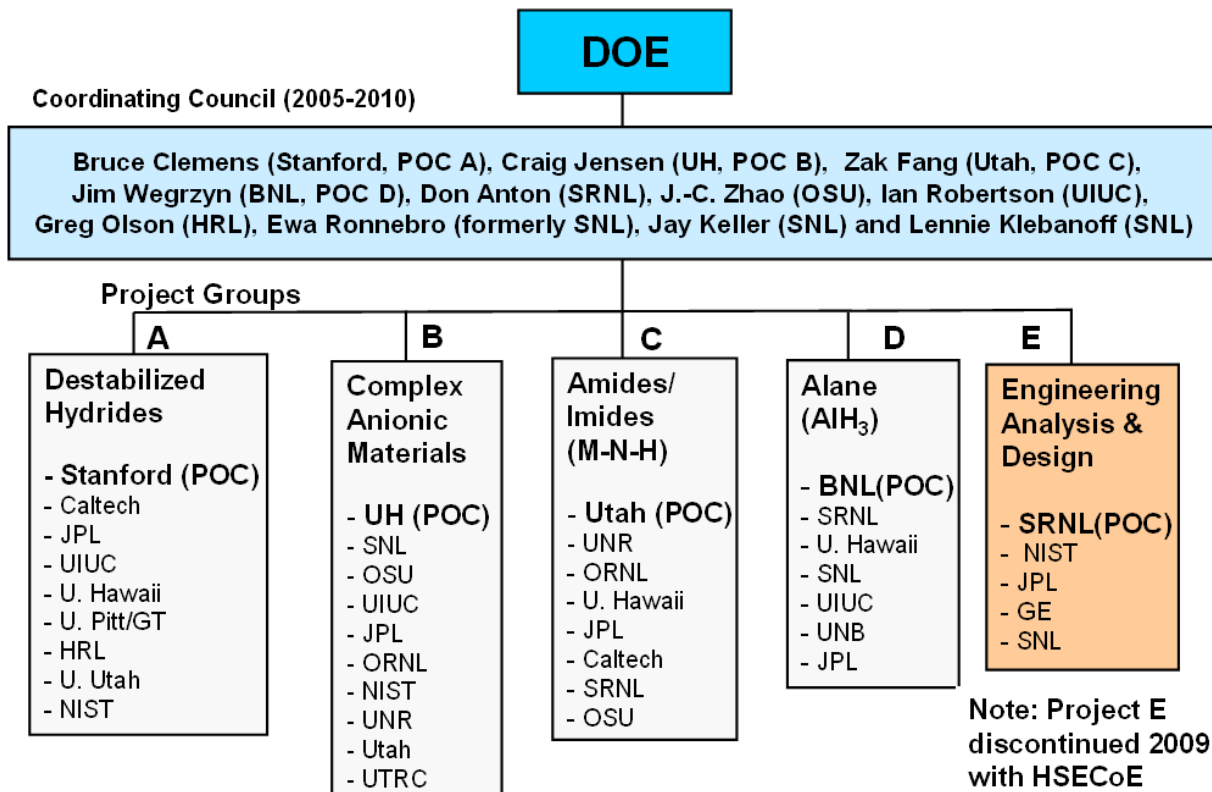
Figure 3. Organization of the MHCoE, with project areas given.

The technical work was originally divided into five "Project Groups" A–E. The purpose of the project areas has been to organize the MHCoE technical work along appropriate and flexible technical lines and to foster collaboration. Early on, the decision was made to organize the work in "materials space." There were other possible choices for the organization, for example organizing groups in alignment with materials challenges, for example a Kinetics Group, or a Thermodynamics Group. A drawback of the "challenge space" alignment is that it is not possible to consider thermodynamic issues separate from kinetic issues, as all the problems need to be resolved simultaneously for a given material. The chosen "material space" organization of the MHCoE allowed all technical challenges to be addressed in a concerted way, and also allowed for strong collaborations to be formed because the different researchers within a material group can focus on that class of materials (for example amides) and share experience and assistance for that material.

Project A (Destabilized Hydrides) was led by Dr. Greg Olson (HRL) from 2005–2008. Thereafter, Prof. Bruce Clemens, Stanford University led Project A until the completion of the MHCoE. The objective of Project A was to develop strategies for reducing hydrogen storage thermal requirements and improve kinetics by destabilizing metal hydrides systems. The technical approach to alter the thermodynamics of the storage system is based on "destabilizing" the metal hydride hydrogen release through alloying, thereby reducing the energy needed to liberate hydrogen from the material, and reducing the desorption temperature. Project A also

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aimed to enhance kinetics by evaluating nanoengineering approaches to minimizing the required hydrogen diffusion distance by decreasing particle size and creating nano-engineered scaffolds.

Project B (Complex Anionic Materials) was led by Dr. Ewa Ronnebro (formerly of SNL) from 2005–2009. Thereafter, Project B was led by Prof. Craig Jensen (U. Hawaii) until the end of the Center. The objective of Project B was to predict and synthesize highly promising new anionic hydride materials. The technical approach utilized formal theory and chemical intuition to select promising target complex hydrides. Candidate materials were then synthesized by a variety of techniques, followed by extensive structural and hydrogen sorption characterization. The syntheses and characterization often involved multiple partner collaboration. A particular focus of Project B in the latter stages of the MHCoE was on borohydride materials.

Project C (Amide/Imide Storage Materials) was led initially by Dr. Weifang Luo (SNL) until 2006. Thereafter, Project C was led by Prof. Zak Fang of the University of Utah. The objective of Project C was to assess the viability of amides and imides (organic materials containing $-NH_2$ and $-NH$ moieties, respectively) for onboard hydrogen storage. The technical approach was to reduce thermal requirements of these materials by alloying, understanding and elucidating the chemical pathways by which these materials release and absorb hydrogen, and determining the initial engineering issues (thermal cycling) of these materials.

Project D (Alane, AlH$_3$) was led by Dr. Jim Wegrzyn (BNL) throughout the 5-year term of the MHCoE. The objective of Project D was to understand the sorption and regeneration properties of alane (AlH_3) for hydrogen storage. The technical approach was to synthesize the various structural forms of AlH_3, and characterize the structure and hydrogen sorption properties of these forms. In the latter stages of the MHCoE, the focus turned to regenerating AlH_3 using organometallic, electrochemical and supercritical fluid methods. Off-board regeneration of $LiAlH_4$ was also considered in Project D.

Project E (Engineering Analysis and Design) was led by Dr. Don Anton (SRNL). The purpose of Project E was to understand the materials engineering properties (thermal expansion, heat capacity, volumetric stress associated with phase changes) of metal hydrides as they were undergoing cycling. In addition, Project E provided a practical "real world" knowledge base that allowed only materials with some practical chance of succeeding to be pursued. The responsibilities of Project E ended with the commissioning of the Hydrogen Storage Engineering Center of Excellence (HSECoE) at SRNL in 2009.

In addition to these formal "Projects," the MHCoE formed a Theory Group. The MHCoE Theory Group (TG) was coordinated by Dr. Mark Allendorf (SNL), and made use of first-principles methods to predict new materials and their thermodynamic properties, provide new directions for experimentalists and assist in the interpretation of experimental results. The TG consisted of researchers at five institutions: SNL, Pitt/GT, UIUC, NIST and UTRC. To make maximum use of the different areas of expertise, joint TG efforts were guided by SNL not only in terms of technical direction, but also to ensure that TG efforts were internally complementary and had effective synergy with experimentalists.

General Approach of the MHCoE

The general method of work in the MHCoE is indicated in Figure 4 below.
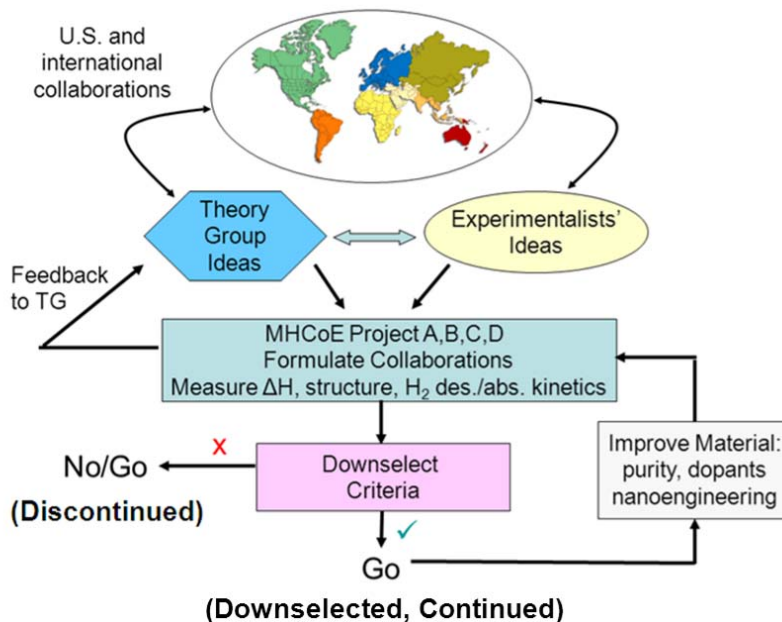
Figure 4. Overall scientific work process for the MHCoE.

Ideas for materials and experiments arose from either our TG, or the MHCoE experimentalists. Ideas for research also arose from the extensive US and International collaborations of the MHCoE (see Tables II and III below). The ideas for work were then passed down to the Projects, the scientific questions (thermodynamics, structure, kinetics, hydrogen capacity, etc.) were established and the needed collaborations formulated. Work then proceeded on the material.

After an initial investigation phase, the material's properties and performance were compared to our MHCoE Downselect Criteria (to be discussed). If the initial properties of the materials precluded a reasonable path to meeting the DOE storage targets (for example the material was completely irreversible), then a "No" decision was made, and the material entered our list of "discontinued materials," where "discontinue" means remove from further study. However, in many cases, the material had some promise, and the material, after initial review, was fed back into the appropriate Project, usually with a strategy to improve the material's properties through the use of additives, or through nanoengineering (nanoconfinement in a nanoporous material). After additional work, the material was compared again against the Downselect criteria, and so on. Many materials eventually were discontinued, while others survived this cycle of research and evaluation, and "downselected" for further study. In a number of cases, the material being investigated was suggested by our TG as a good candidate for investigation. As indicated in Figure 4, the experimental realities of a given material were shared with the TG to compare against the original prediction. For example, the temperatures observed for hydrogen release, or the measured geometric structure of the original metal hydride was fed back to our TG. This

allowed the TG to assess cases where there was good agreement, and investigate further those cases where there was disagreement between theory and experiment. Valuable feedback to the TG also came from the DOE Hydrogen Program Annual Merit Review process, and the annual Hydrogen Storage Tech Team meetings.

Collaborations Outside the MHCoE

For the work of the MHCoE to be maximally useful to the Nation as well as informed and relevant, it was very important that the applied R&D work not be performed in isolation. The MHCoE was very proactive in ensuring that our technical program incorporated significant input and collaboration not only from domestic US scientists engaged in this field, but also international collaborators as well. Tables II and III below indicate the extensive domestic and international collaboration of the MHCoE. In all, MHCoE scientists collaborated with seventeen domestic US institutions in the technical work, and nine foreign institutions.

Table 2. Domestic collaborations of the MHCoE.

MHCoE Partner	US Institution (not MHCoE)	US Collaborator and Topic
BNL	UC Davis	P. Power (solution chemistry of alane complexes)
UH	UOP, LLC	L. Knight, G. Lewis, J. Low, A. Sachtler (XRD and MS)
UH	U. Nevada LV	R. Kumar (neutron diffraction)
UH	U. South Florida	S. Srinivasan (DSC)
UH, HRL	PNNL	T. Autrey (Synthesis, mesoporous carbon)
HRL	LLNL	T. Baumann (porous carbon materials)
HRL	U. Conn	L. Shaw (optimizing kinetics using milling)
NIST	U. Maryland	M. Yousufuddin, J.-H. Her, J. Rush, H. Wu and W. Zhou neutron and x-ray measurements, DFT calculations)
NIST	GM	F. Pinkerton, M. Meyer (Li-B-N-H phases)
NIST	Penn	T. Yildirim (DFT calculations)
NIST	Michigan	M. Hartman (isotopically labelled H_2 storage compounds)
SNL	UCLA	V. Ozolins (theory)
SNL	LLNL	J. Herberg (NMR)
SNL	Northwestern	C. Wolverton (theory)
SNL	U. Maryland	J-H Her (Neutron)
SRNL	U. South Carolina	H. zur Loye (XRD analysis)
UTRC	Albemarle Corp.	F.-J. Wu, J. Strickler (nanoconfinement)

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Table 3. International collaborations in the MHCoE.

MHCoE Partner	International Institution	International Collaborator and Topic
BNL	IFE (Norway)	V. Yartys, B. Hauback (AlH_3 chem., structure)
BNL	U. Geneva (Switzerland)	K. Yvon, (oxidation of AlH_3, synchrotron)
UH	KEK	R. Kuboto (muon spin resonance)
UH	AIST (*Japan*)	E. Akiba, K. Sakaki (positron annihilation studies)
UH	Tohoku University (*Japan*)	S. Orimo, Y. Nakamori (synthesis, DSC and XRD)
UH/UNR	U. Rome (*Italy*)	R. Cantelli (analastic spectroscopy)
UH	IFE (*Norway*)	B. Hauback, M. Sorby; (Sync. X-ray, Neutron Diff.)
UH	U. Geneva (*Switzerland*)	H. Hagmann, R. Černý; (XRD, IR, Raman Spec.)
UNR	U. Geneva (*Switzerland*)	K. Yvon (sabbatical host, XRD studies)
GA Tech/Pitt	U. Geneva (*Switzerland*)	R. Černý (High res. XRD, neutron scattering)
SNL/UNR	ESRF (*France*)	Y. Filinchuk (Synchrotron X-ray Diffraction)
U. Utah	Dalian Institute (*China*)	P. Chen (amide synthesis)
SNL	Mahidol U. (Thailand)	N. Poonyayant, P. Pakawatpanurut (synthesis)

MHCoE Funding

The funding for the MHCoE by the DOE Office of Energy Efficiency and Renewable Energy (EERE) was as follows on a Center-wide basis:

FY 2005: **$5.0M (1/2 year)**

FY 2006: $6.3M

FY 2007: $8.6M

FY 2008: $9.3M

FY 2009: $10.7M

FY 2010: $5.0M (1/2 year)

TOTAL = $44.9M

Appendix II lists all publications performed under the auspices of the MHCoE during the period March 2005 thru June 2010. We now summarize some of the highlights from each of the Projects A–E below. The purpose of these highlights is to discuss in some detail the highest impact research within the MHCoE, while also giving a sense of how the Center operated and what technical challenges arose, and in many cases, overcome.

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Summary and Highlights from Project A: Destabilized Hydrides

Destabilized
Hydrides

- Stanford (POC)
- Caltech
- JPL
- UIUC
- U. Hawaii
- U. Pitt/GT
- HRL
- U. Utah
- NIST

**Bruce Clemens, Stanford U.
Project A Lead**

Many light element compounds are known that have high hydrogen capacities, as reviewed by Orimo and co-workers [*Chemical Reviews C*, **107,** 4111 (2007)]. However, most of these materials are thermodynamically too stable, and they release and store hydrogen much too slowly for practical use. In Project A we developed new light element chemical systems that have high hydrogen capacities while also having more suitable thermodynamic properties. In addition, we developed methods for increasing the rates of hydrogen exchange in these new materials.

Project A has made significant advancements in four major areas: (1) the application of combined hydride systems for tuning thermodynamic properties, (2) the use of nanoengineering for improving hydrogen reaction kinetics, (3) the development of a deeper understanding of hydrogen absorption kinetics in Mg-based systems and (4) the use of advanced NMR to unravel the reaction pathways of metal hydride hydrogen storage systems. We have found that our strategy for thermodynamic tuning allows both entropy and enthalpy to be favorably adjusted. In addition, we demonstrated that using porous supports as scaffolds to confine hydride materials to nanoscale dimensions can improve the rates of hydrogen exchange by more than 50 times.

Here we review some selected highlights from Project A. Space does not permit a full discussion of the R&D output from Project A. Appendix II lists 73 publications from Project A, with the publication titles indicated to aid the reader in identifying content. We refer the interested reader to those publications for a deeper account of the work. Here, we focus on the overall destabilization results, and how nanoconfinement has improved materials properties.

Metal Hydride Destabilization

During the five-year tenure of the MHCoE, approximately 20 new "destabilized" hydrogen storage systems were developed and tested including $LiBH_4/MgF_2$, $LiBH_4/MgCl_2$, $LiBH_4/MgI_2$,

LiBH$_4$/MgS, LiBH$_4$/MgSe, LiBH$_4$/Mg$_2$Si, LiBH$_4$/Mg$_2$Cu, LiBH$_4$/Mg$_2$NiH$_4$, LiH/B$_4$C, LiBH$_4$/Si, CaSiN$_2$, MgSiN$_2$, LiBC, Mg(BC)$_2$, LiH/TiO$_2$, LiH/SiO$_2$, and LiBH$_4$/SiO$_2$. Although light element hydrides have high hydrogen contents, thus far, no single compound has been identified that has the thermodynamic properties required to meet all of the DOE targets.

The LiBH$_4$/Mg$_2$NiH$_4$ system was studied by Dr. John Vajo of HRL in detail because of its remarkable features that include: full reversibility, reaction through a direct low-temperature kinetic pathway, formation of a unique ternary boride phase, and low reaction enthalpy coupled with low entropy [Vajo et al., *Chem. Comm.* **46**, 6687 (2010)]. We give a more complete description of this interesting system below, as it reveals in many ways the full power of the destabilization approach, and points the way to possible future courses of study.

Dehydrogenation of a mixture of 4LiBH$_4$ + 5Mg$_2$NiH$_4$ is shown in Figure 5.
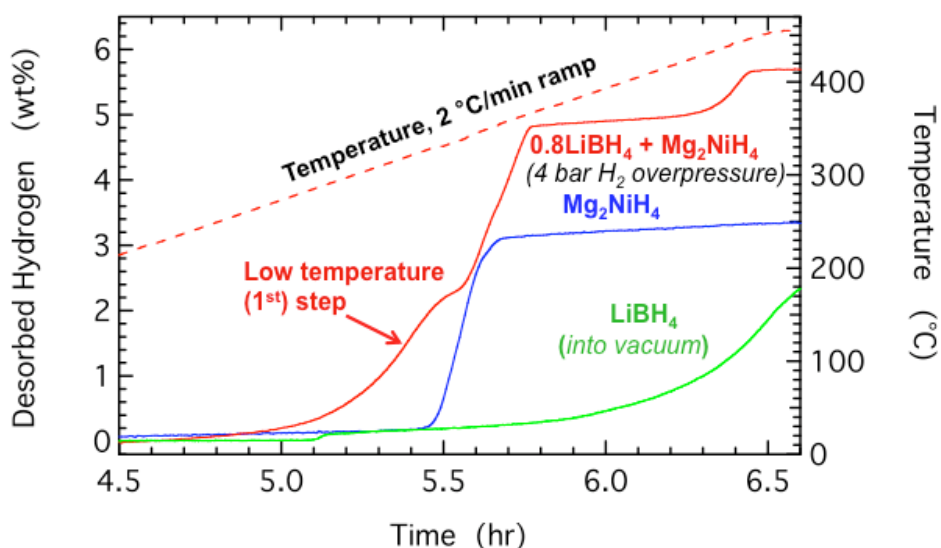
Figure 5. Dehydrogenation of 4LiBH$_4$ + 5Mg$_2$NiH$_4$, Mg$_2$NiH$_4$, and LiBH$_4$. Dehydrogenation was conducted using a 2 °C/min temperature ramp in 4 bar of H$_2$ for 4LiBH$_4$ + 5Mg$_2$NiH$_4$ and Mg$_2$NiH$_4$, and (initial) vacuum for LiBH$_4$. The small desorption step for LiBH$_4$ (at 5.1 hr) occurs at the melting point (~285 °C). Thus, the 1st step for the 4LiBH$_4$ + 5Mg$_2$NiH$_4$ mixture begins below the melting point for LiBH$_4$.

The reaction occurs in 3 steps. The first step is consistent with the reaction given by:

$$4LiBH_4 + 5Mg_2NiH_4 \leftrightarrow 2MgNi_{2.5}B_2 + 4LiH + 8MgH_2 + 8H_2$$

This reaction step releases 2.6 wt. % hydrogen. As shown in Figure 5, dehydrogenation occurs at temperatures lower than the dehydrogenation temperature for either pure LiBH$_4$ or pure Mg$_2$NiH$_4$. This is a critically important feature, as it indicates that a new hydrogen release pathway has been opened up by mixing the LiBH$_4$ and Mg$_2$NiH$_4$ materials. This pathway likely involves direct reaction between LiBH$_4$ and Mg$_2$NiH$_4$, rather than H$_2$ release from either of the

individual components. The reaction begins at temperatures as low as 250 °C, which is very low for borohydride-based systems. The low reaction temperature is possibly due to the catalytic nature of Ni in the $[NiH_4]^{2-}$ anion. Thus far, this system appears to be the only reversible destabilized system that reacts through a (new) direct reaction pathway. In contrast, the well-studied $LiBH_4/MgH_2$ system reacts sequentially with initial dehydrogenation of MgH_2 followed by reaction of Mg with $LiBH_4$. We believe that to achieve the full benefit of the mixed hydride system destabilization strategy, reaction through new pathways is essential. Thus, this system represents an important demonstration that such new pathways are possible.

As indicated above, reaction of $LiBH_4$ with Mg_2NiH_4 leads to the formation of the ternary boride $MgNi_{2.5}B_2$. Formation of the ternary boride $MgNi_{2.5}B_2$ is significant because very few boride phases reversibly hydrogenate under mild conditions ($\sim$ 100 bar H_2). In addition, ternary transition metal-based boride phases have not previously been considered as hydrogen storage materials. Identification of this phase suggests that other ternary (or higher order) transition metal-based boride phases should be experimentally or computationally tested for reversible hydrogenation activity.

The good kinetics of the $LiBH_4/Mg_2NiH_4$ reaction allow its equilibrium to be characterized over the temperature range 270 °C to 360 °C, as shown by the van't Hoff plot in Figure 6. This range extends below the lowest temperatures measured for the $LiBH_4/MgH_2$ system (315 °C) because of the improved kinetics, with the lowest temperature data point below the melting temperature for bulk $LiBH_4$ (T_m = 280 °C). The pressure varies logarithmically with the inverse temperature characterized by a change in enthalpy (ΔH) of 15 kJ/mol-H_2 and a change in entropy (ΔS) of 62 J/K-mol-H_2.
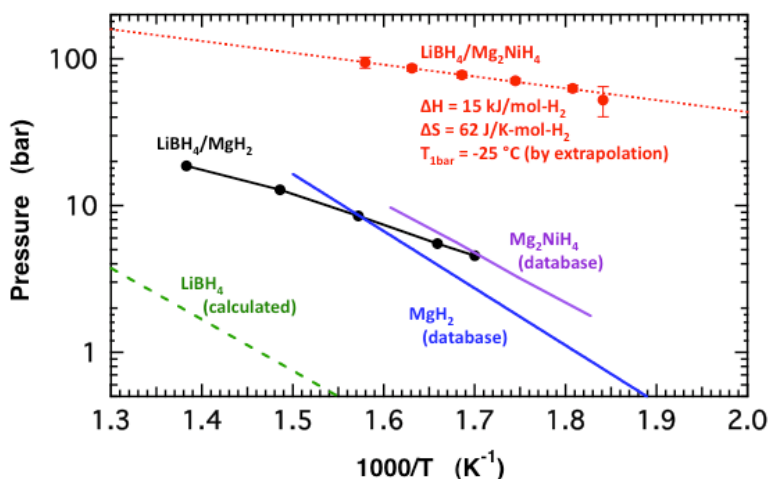
Figure 6. Van't Hoff plots for the $LiBH_4/Mg_2NiH_4$ destabilized system, pure $LiBH_4$, pure Mg_2NiH_4, the $LiBH_4/MgH_2$ system, and pure MgH_2. The red curve ($LiBH_4/Mg_2NiH_4$) shows equilibrium pressures at 0.67 wt. % for the 1st reaction step shown in Fig. 5. This hydrogen content is at the midpoint of the reversible capacity for this step. The green curve ($LiBH_4$) was calculated from tabulated thermodynamic data using HSC. The blue and purple curves (MgH_2 and Mg_2NiH_4, respectively) were obtained from the Sandia database. The black curve ($LiBH_4/MgH_2$) was obtained from measured isotherm data.

This change in enthalpy is very low for a reversible system. A low enthalpy is very advantageous for practical systems in which heat must be supplied to release hydrogen and dissipated during rehydrogenation. However, systems with low enthalpies ($<\sim$ 30 kJ/mol-H_2) typically cannot be rehydrogenated because the equilibrium temperatures, given by $T_{eq} = \Delta H/\Delta S$, are too low. Remarkably, for this system ΔS is also very low, which raises the equilibrium temperature and enables reversibility. We speculate that the low ΔS originates from the relatively high entropy of two complex hydride anion species, $[BH_4]^-$ and $[NiH_4]^{2-}$, in the hydrogenated phase.

Overall, the capacity for the direct low temperature step shown above is too low for practical use. However, Mg_2NiH_4 is a transition metal-based complex hydride of which there are numerous (>100) known examples. Therefore, the remarkable behavior of this system holds promise that other $LiBH_4$/transition metal-based complex hydride systems could be found with higher hydrogen capacities.

Another example of destabilization from the MHCoE concerns salts of the interesting intermediate $[B_{12}H_{12}]^{2-}$ anion. Work in the MHCoE has shown that ionic salts of these $[B_{12}H_{12}]^{2-}$ anions are typically undesired and thermodynamically stable intermediates in hydrogen release reactions involving borohydrides. The possibility of destabilizing these intermediates, allowing hydrogen release at lower temperatures, was predicted by Ozolins, Majzoub and Wolverton [*JACS*, **131**, 230-237 (2009)] for a number of $[B_{12}H_{12}]^{2-}$ systems. For $CaB_{12}H_{12}$, it was predicted that destabilization with CaH_2 would lower ΔH considerably, thereby lowering the expected temperature for which 1 bar of hydrogen pressure would be attained (T_{1bar}):

$$CaB_{12}H_{12} \longrightarrow CaB_6 + 6B + 6H_2 \quad \Delta H\ (0K) = 65\ kJ/moleH_2\ ;\ T(1bar) = 306\ °C$$

$$CaB_{12}H_{12} + CaH_2 \longrightarrow 2CaB_6 + 7H_2\ \Delta H = 38.6\ kJ/moleH_2\ ;\ T(1bar) = 86\ °C$$
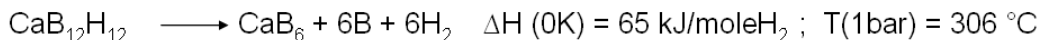
Investigations of the destabilization of $Ca(BH_4)_2$ with CaH_2 was conducted by Dr. Vitalie Stavila of Sandia within MHCoE Project A. It was found that introducing CaH_2 does indeed lower the thermodynamic requirements, although the material is severely kinetically limited. $CaB_{12}H_{12}$ by itself does not release any hydrogen for temperatures below 700 °C. However, when mixed with CaH_2, there is a dramatic reduction in the temperature required for H_2 release. As indicated in Figure 7 below, hydrogen release is observed at ~450 °C for the destabilized system. These temperatures are of course too high for a practical hydrogen storage system, and suggest a severe kinetic limitation to the material. Nevertheless, the results are a dramatic confirmation of destabilization theory, and indicate a strategy for liberating hydrogen from these stable $[B_{12}H_{12}]^{2-}$ intermediates.
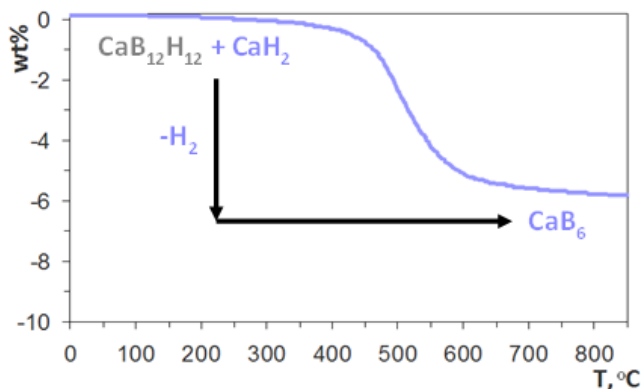
Figure 7. Destabilization of $CaB_{12}H_{12}$ with CaH_2.

Nanoconfinement of Metal Hydrides in Nanoporous Scaffolds

One of the guiding hypotheses for this work in Project A was that the slow hydrogen exchange rates for light metal hydrides are due to slow rates of diffusion which, in turn, originate from the covalent and ionic bonding characteristic of light elements. Based on this hypothesis, Project A sought to improve the hydrogen exchange rates by restricting the hydride particle size to the nanometer scale. Diffusion times vary as the square of the diffusion length; thus, decreasing particle size by a factor of 10 decreases diffusion times by a factor of 100. Restricting the particle size of hydride materials is difficult considering that particle size growth occurs as hydrogen is cyclically released and stored. To address this issue, our approach was to use nanoporous scaffolds to confine hydride materials incorporated into the pores to nanoscale dimensions and to maintain these dimensions during cycling.

Dr. John Vajo of HRL led the MHCoE efforts on nanoconfinment. To characterize the effect of incorporating hydride materials into nanoporous scaffolds, HRL measured isothermal dehydrogenation rates for $LiBH_4$ incorporated into carbon aerogels with 4 nm and 25 nm pore sizes and compared with measurements on samples with 13 nm pores. The comparison is shown in Figure 8. The 4-nm sample was prepared at Lawrence Livermore National Laboratory (LLNL) (courtesy Dr. Ted Baumann) while the 13 nm and 25 nm samples were prepared at HRL. For all the nanoconfined samples, the rate of hydrogen desorption was 50 times higher than for a control sample in which the $LiBH_4$ was physically mixed with a graphite sample that did not contain nanopores.
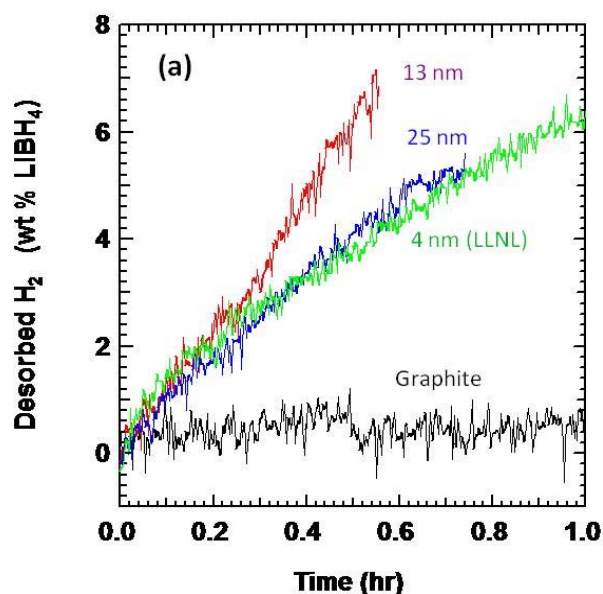
Figure 8. Effect of aerogel pore size on the dehydrogenation rate of $LiBH_4$. The figure shows the hydrogen desorbed in wt. % $LiBH_4$ vs. time at 300 °C for $LiBH_4$ in 4 nm, 13 nm, and 25 nm aerogels and for $LiBH_4$ mixed with graphite.

The effect of nanoconfinement on the capacity retention during cycling was also studied. In bulk $LiBH_4$, the capacity retention is poor as the material is cycled, as less than 30% of the capacity remains after three cycles. In contrast, when confined within a nanoporous scaffold the retained capacity can be as high as 70% after three cycles.

A significant breakthrough in our nanoconfinement studies came from the organometallic synthesis methods developed by Prof. Craig Jensen of the University of Hawaii (UH). The original syntheses of nanoconfined $LiBH_4$ required infusing the carbon aerogel with liquid (i.e. melted) $LiBH_4$. However, this method is not very versatile and also can damage some nanoframeworks since elevated temperatures are used. The UH group developed a low-temperature homogenous organometallic approach to incorporation of Mg based hydrides into carbon aerogels that has resulted in high loadings without degradation of nano-porous scaffold. The strategy is shown in Figure 9 below:
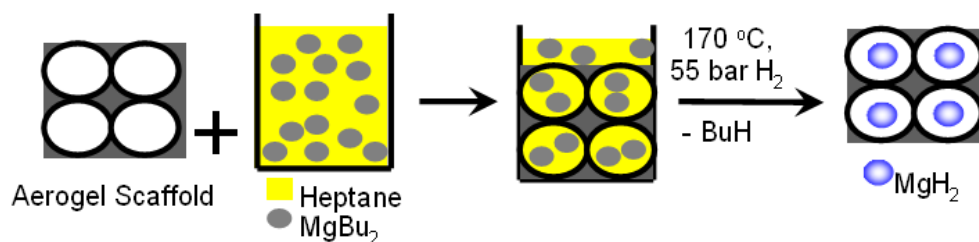
Figure 9. Organometallic approach to incorporation of metal hydrides into C aerogels.

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Figure 9 shows how precursor MgBu$_2$ can be infused in the aerogel scaffold using heptane as a solvent. Then, the MgBu$_2$ can be thermally decomposed, yielding nanoconfined Mg which can then be hydrogenated to give scaffold-incorporated MgH$_2$.

Studies of this approach have shown that high, (9-16 wt. %) MgH$_2$ loadings can be achieved in the carbon aerogel without host degradation. Figure 10 shows that the rate of dehydrogenation from MgH$_2$ incorporated in 13 nm pores in C-aerogel is, at 252 ˚C, ~17 times faster than the initial rate found for bulk ball-milled MgH$_2$. The rate remains the same over 4 cycles of dehyrogenation-rehydrogenation, indicating the Mg is well confined in the pores even when thermally cycled.
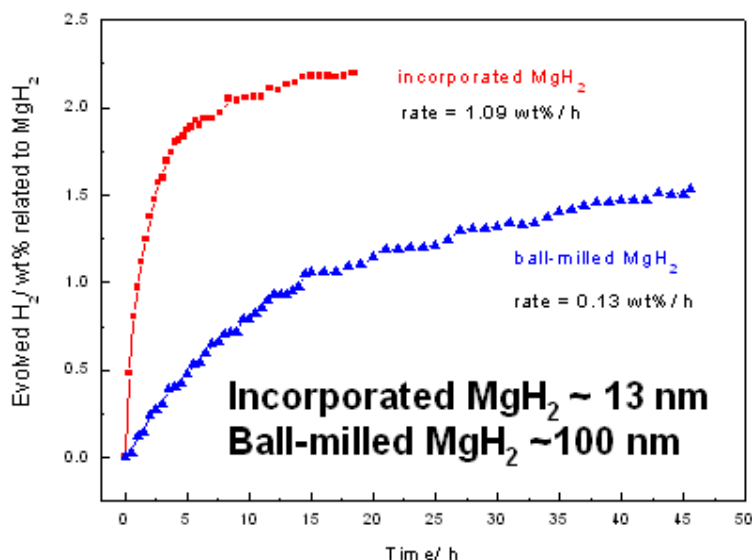
Figure 10. Comparison of H$_2$ evolution from bulk-like ball milled MgH$_2$
with MgH$_2$ confined in 13 nm pores in carbon aerogel.

One might wonder if the incorporation of MgH$_2$ into 13 nm pores alters the thermodynamics of the hydrogen release from MgH$_2$. It turns out that equilibrium studies of the plateau pressure of hydrogen at 250 ˚C from MgH$_2$ confined to 13 nm pores agree well with database plateau pressure for bulk MgH$_2$ to within 10% accuracy. If there were a change in the thermodynamics, there would be a corresponding change in the equilibrium hydrogen pressure at a given temperature, which was not observed experimentally to within 10%. Presumably, one needs to make the MgH$_2$ particle significantly smaller than 13-nm diameter to see a significant change in the thermodynamics of H$_2$ release.

Practical Consideration of Using Scaffolds for Nanoconfinement

In addition to favorably altering the kinetics (and perhaps eventually the thermodynamics) of a confined hydride, use of a scaffold must be practical when considering the overall gravimetric and volumetric hydrogen capacities and the chemical and mechanical stabilities during cycling.

The scaffold pore size, topology, and surface chemistry must be optimized for the hydride thermodynamics and kinetics; the specific pore volume must be optimized for the overall capacities; and the scaffold composition must be optimized for stability.

Ideally, the scaffold itself would also store hydrogen and contribute to the storage capacity. However, this is extremely challenging, and thus far, the scaffolds studied simply contribute extra weight to the system, thereby penalizing the system both gravimetrically and volumetrically. To be practical, these penalties must be reduced.

As analyzed by Dr. Vajo of HRL, the gravimetric capacity of a nanoconfined metal hydride including the mass of the scaffold relative to the bulk capacity [$C_{G,scaffold}/C_{G,bulk}$] depends on the hydride density [$\rho_{hydride}$ (g/cm^3)] and the specific Pore Volume of the scaffold [PV (cm^3/g)]. This dependence, expressed as a percentage and denoted as the Retained Gravimetric Capacity, is given by:

$$C_{G,scaffold}/ C_{G,bulk} = 100\% \bullet \rho_{hydride} \bullet PV / (\rho_{hydride}\bullet PV + 1)$$

A plot of the Retained Gravimetric Capacity as a function of scaffold pore volume for different hydride materials is shown in Figure 11.
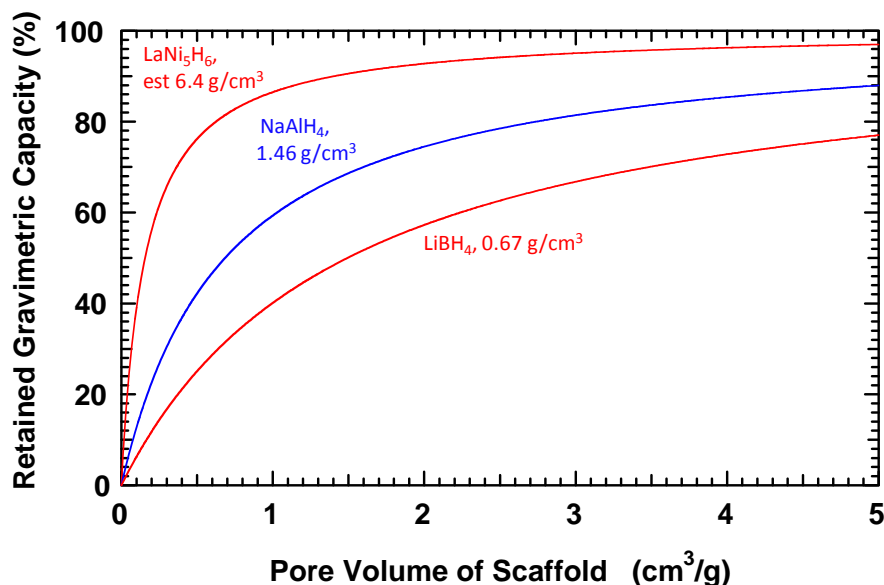
Figure 11. Retained gravimetric capacity for hydrides nano-confined within scaffold hosts. Capacities are shown versus scaffold pore volume for selected hydride densities.

Overall, the retained capacity is increased for larger pore volume scaffolds and denser hydride materials. For example, if a scaffold were used to confine LaNi$_5$H$_6$, which has a relatively high density of 6.4 g/cm^3, the retained capacity could be >80% for a scaffold with a pore volume of ~1 cm^3/g. In contrast, for LiBH$_4$, which has one of the lowest densities of any hydride, a pore volume of ~4 cm^3/g is required for a retained capacity of 70%. The scaffolds used in the studies

described above have specific pore volumes of 0.5–1.5 cm^3/g. However, much larger specific pore volumes are possible (T. Bauman, private communication). For example, aerogels can be synthesized with pore volumes >4 cm^3/g. The challenge will be combining a sufficient pore volume with the desired pore size in a structurally stable scaffold capable of withstanding multiple sorption cycles, and infusing this material with a high-density metal hydride with high gravimetric hydrogen capacity.

Similarly, the Retained Volumetric Capacity [$C_{V,scaffold}$ /$C_{V,bulk}$] depends on the scaffold density [$\rho_{scaffold}$ (g/cm^3)] and the pore volume as given by

$$C_{V,scaffold} /C_{V,bulk} = 100\% \bullet \rho_{scaffold} \bullet PV / (\rho_{scaffold} \bullet PV + 1).$$

A plot of the Retained Volumetric Capacity for carbon-based scaffolds is given in Figure 12.
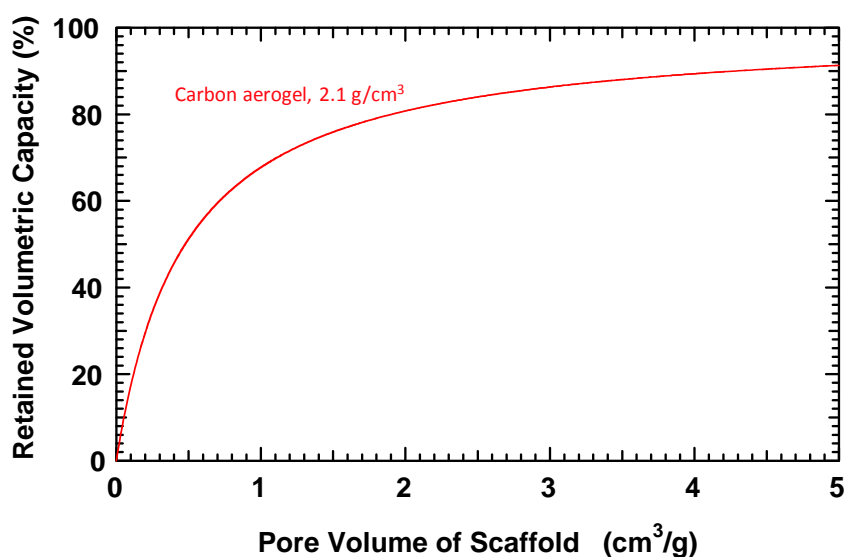
Figure 12. Retained volumetric capacity for hydrides nano-confined within scaffold hosts. Capacities are shown versus scaffold pore volume for a scaffold density of 2.1 g/cm^3, which is typical for porous carbon materials including carbon aerogel.

From this plot, ~80% retained volumetric capacity can be achieved using carbon scaffolds with pore volumes of 1.5–2 cm^3/g. Thus, for low-density hydride materials, retaining the volumetric capacity places a lower requirement on the scaffold pore volume than the gravimetric capacity. Overall, it appears that nano-confined hydride materials with ~80% retained capacities are feasible.

Because studies of nano-confinement using porous hosts is still in the beginning stages, R&D addressing the interactions with the confined metal hydride with the nanoporous host are only just beginning. The MHCoE partner UTRC has investigated the reactive stability of Ca(BH$_4$)$_2$ when mixed with inorganic aerogels materials ZrO$_2$, Y$_2$O$_3$ and C. UTRC has also used VASP DFT calculations to model the metal hydride/nanopore thermodynamics to understand better the

effect of nanoconfinement on stability. While the inorganic aerogels may be more chemically stable, the carbon aerogels are more widely available. For $LiBH_4$ confined in carbon aerogel, preliminary measurements of CH_4 formation during dehydrogenation showed that CH_4 was detectable, but small ($<\sim 0.2$ wt. %). Further work is needed to understand the chemical stability of the scaffolds during repeated cycling.

Summarizing, Project A has significantly advanced our understanding and characterization of destabilized systems. Destabilization offers a proven method of reducing the thermodynamics of hydrogen storage reactions, opening up new reaction pathways, and mitigating undesired intermediates. We also found that nanoengineering improves metal hydride kinetics, and reversibility, but the nanoscaffolds need to be made with larger pore volume if they are to form the basis of practical hydrogen storage materials.

Summary and Highlights from Project B: Complex Anionic Materials

Complex Anionic Materials

- UH (POC)
- SNL
- OSU
- UIUC
- JPL
- ORNL
- NIST
- UNR
- Utah
- UTRC

**Prof. Craig Jensen,
U. Hawaii**

Project B, Complex Anionic Materials, has focused on the synthesis and characterization of high-weight-capacity metal hydrides that contain well-defined chemical moieties. Particular attention has been paid to 1) the alanate materials that contain AlH_6^{3-} and AlH_4^- moieties; 2) boroyhdride materials that contain the BH_4^- moiety; 3) the use of advanced analytical instrumentation such as in-situ XRD and state-of-the-art NMR techniques to understand reaction pathways and intermediates and 4) understanding the role of $[B_{12}H_{12}]^{2-}$ salts in borohydride hydrogen storage chemistry. Project B was originally led by Dr. Ewa Ronnebro (formerly of Sandia). In the last two years of the MHCoE, Project B has been led by Prof. Craig Jensen of the University of Hawaii.

In the early stages of the MHCoE, much work was performed on alanates, for example $NaAlH_4$, K_2LiAlH_6, and other compounds. However, it soon became apparent that the alanates are fairly limited in their weight capacity. Realizing that with expected "system" penalties for weight and volume approaching 50%, emphasis shifted in the MHCoE away from the alanates, and towards materials with very high weight percent, namely the borohydrides. In fact, MHCoE partners investigated over 50 borohydride material systems. The studies involved developing high-yield syntheses of borohydrides, characterizing their structural and hydrogen release properties, and understanding the intermediates that were observed during hydrogenation. From a theoretical point of view, much new ground was struck on understanding the theoretical reaction pathways of boron containing materials.

Here we review some selected highlights from Project B. Space does not permit a full discussion of the R&D output from Project B. Appendix II lists 101 publications from Project B, with the publication title. We refer the reader with a deeper interest in these subjects to those publications.

In this report, we focus on some of the results from borohydrides, as this class of material may hold the most potential for a truly remarkable solid-state hydrogen storage system.

Magnesium Borohydride, Mg(BH$_4$)$_2$

We discuss now in some detail MHCoE results on Mg(BH$_4$)$_2$. As with many borohydrides, Mg(BH$_4$)$_2$ is attractive because of the exceptionally high theoretical hydrogen weight percent, 14.9% for this material. Mg(BH$_4$)$_2$ was first synthesized by V.N. Konoplev [Zhurnal Neorganicheskoi Khimii, **25,** 1739 (1980)]. Konopolev reported on the synthetic procedures, and also reported on the first-order hydrogen desorption properties. He observed H desorption from Mg(BH$_4$)$_2$ above 320 ^{o}C, ΔH ~ 53 kJ/mole H$_2$. However, almost nothing was known about the reaction pathway, and nothing was known about the possible reversibility of the system.

MHCoE partner GE, under the direction of Dr. J.-C. Zhao, spearheaded the first MHCoE work on Mg(BH$_4$)$_2$. A great deal of effort was devoted to understanding the crystal structures of the material as it was heated and eventually releasing hydrogen. Using a unique in-situ XRD method that also allowed full characterization of emitted volatiles, GE was able to directly correlate crystal structure with temperature, and hydrogen release. Some of this data is shown below in Figure 13. As can be seen from the left hand side of Figure 13, at 185 °C, the material undergoes a phase transition from a low-temperature (LT) form to a high-temperature (HT) form. The RGA data on the right indicates that this structural phase transition occurs before H$_2$ is released.
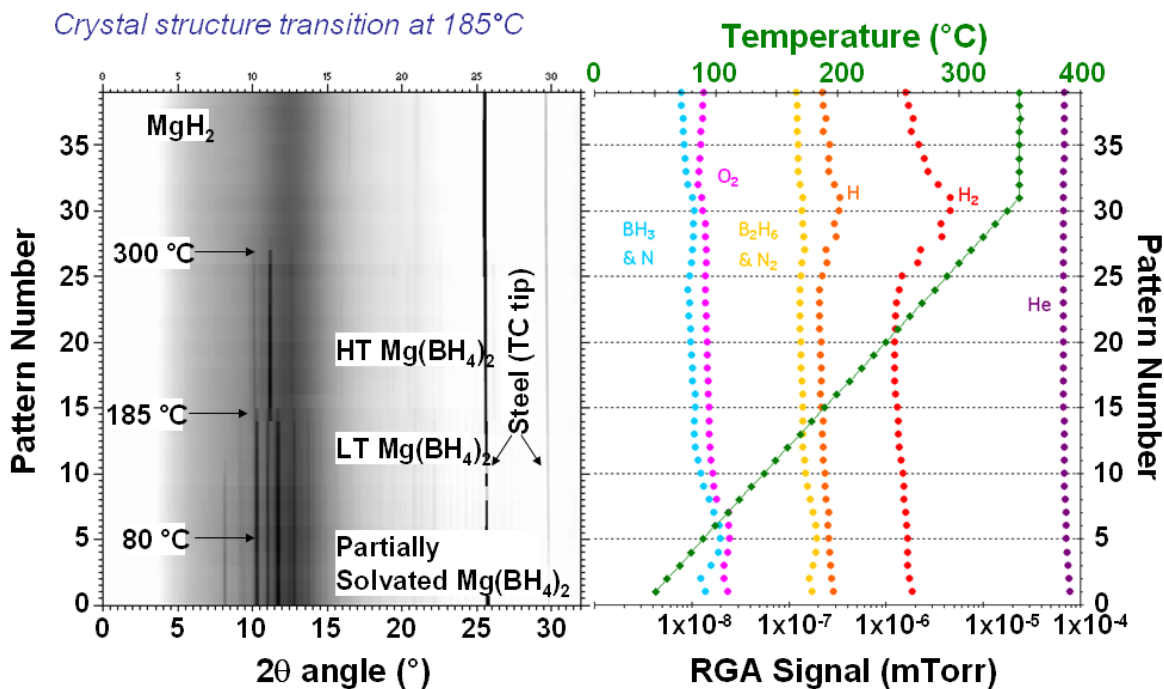
Figure 13. In-situ XRD and RGA studies of hydrogen release from Mg(BH$_4$)$_2$. The left-hand figure plots the behavior or certain characteristic XRD peaks (appearing at various 2Θ angle positions) as the temperature is increased. The right-hand figure shows the partial pressure (as recorded by the RGA) of various gas phase species (H$_2$, O$_2$, B$_2$H$_6$, N$_2$, BH$_3$, H and N) as the temperature is ramped in the same experiment as recorded in the left hand figure.

No toxic gaseous species (such as diborane, B$_2$H$_6$) or other impurities were found in the desorbed gas in this study. An intermediate MgB$_{12}$H$_{12}$ was observed which turned out to have widespread implications for hydrogen storage from borohydride materials. From these initial studies, an attractive ΔH for hydrogen desorption of ~ 40 kJ/mole H$_2$ was observed, indicating a decent chance for reversibility under reasonable conditions if no kinetic limitations existed.

The overall reaction sequence for hydrogen release from Mg(BH$_4$)$_2$ is shown in Figure 14 below:
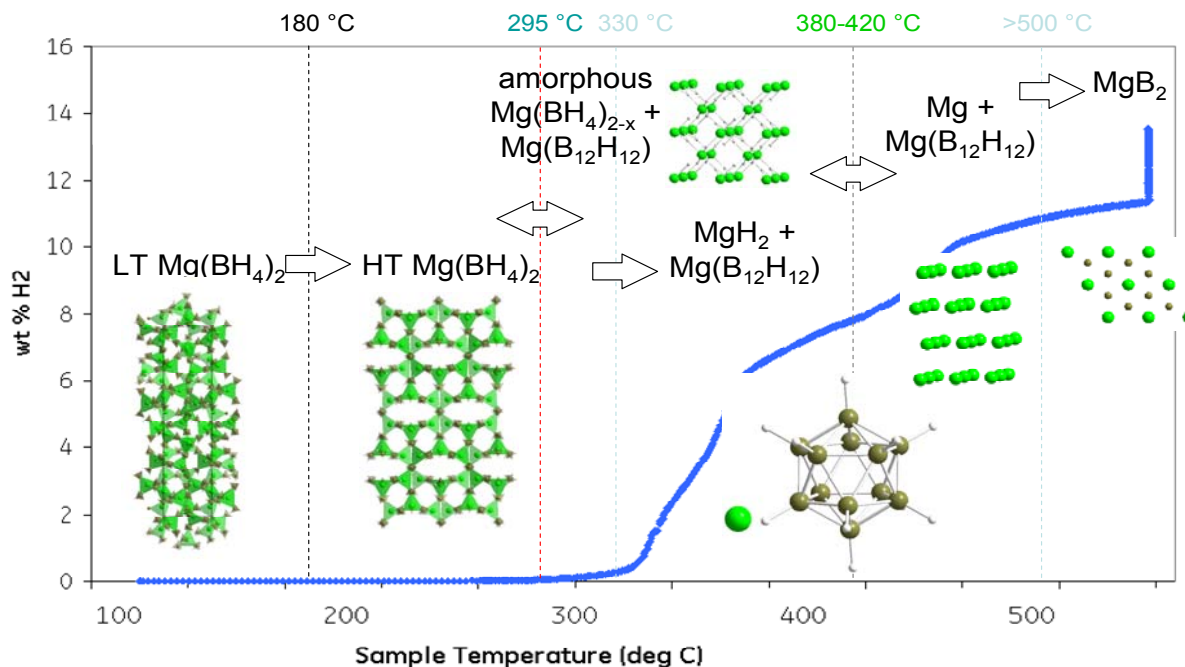
Figure 14. Overall reaction sequence for the release of hydrogen from $Mg(BH_4)_2$.

The overall reaction sequence can be written:

$$6Mg(BH_4)_2 \longrightarrow 5MgH_2 + Mg(B_{12}H_{12}) + 13H_2\uparrow \tag{1}$$

$$5MgH_2 + Mg(B_{12}H_{12}) \longrightarrow 5Mg + 5H_2\uparrow + Mg(B_{12}H_{12}) \tag{2}$$

$$5Mg + Mg(B_{12}H_{12}) \longrightarrow 6MgB_2 + 6H_2\uparrow \tag{3}$$
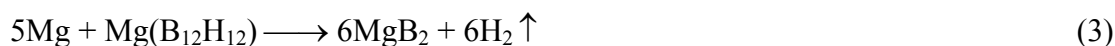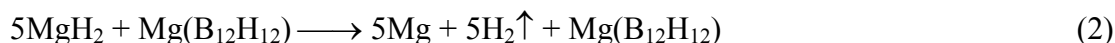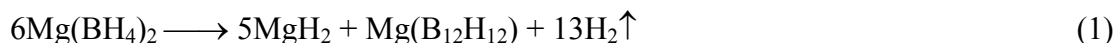
Thus, hydrogen is first released from $Mg(BH_4)_2$ to form MgH_2 and $Mg(B_{12}H_{12})$. MgH_2 then releases H_2, followed by eventual release at high temperature from the highly stable $MgB_{12}H_{12}$ material. A full 12 wt. % of hydrogen is released from the material, and the low ΔH of desorption indicates facile hydrogenation of MgB_2 should be possible. Unfortunately, due presumed kinetic limitations, the reaction was not reversible under the conditions used for these initial GE studies.

The question of $Mg(BH_4)_2$ reversibility was taken up by the Sandia (Ronnebro, Majzoub) and U. Hawaii (Jensen) collaborations in Project B. The end product of dehydrogenation from $Mg(BH_4)_2$, namely MgB_2, was subjected to hydrogenation at high pressures (15,000 psi) and high temperatures (500 °C) using the high pressure hydrogenation cell at Sandia. The results of the experiments showed that $Mg(BH_4)_2$ could in fact be produced by the hydrogen exposure, and that the $Mg(BH_4)_2$ thus produced released 12 wt. % of hydrogen when heated. Figure 15 displays Magic Angle Spinning (MAS) ^{11}B NMR spectroscopy of the product generated by hydrogenation of MgB_2. The use of ^{11}B NMR is critical, as possible $MgB_{12}H_{12}$ may be amorphous and thus cannot be detected by the traditional XRD studies. By contrast, ^{11}B NMR is

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able to detect all boron containing materials in the product mixture. As seen in Figure 15, only one major boron containing product is observed. The chemical shift of -41 ppm allows its clear identification as $Mg(BH_4)_2$ as the shift exactly matches that which has been observed for an authentic sample of $Mg(BH_4)_2$. Only a very minor signal is observed for $MgB_{12}H_{12}$, at -24 ppm indicating that it represents <5 % of the product mixture.

$Mg(BH_4)_2$

$Mg(B_{12}H_{12})$

0 -10 -20 -30 -40 -50 -60
ppm
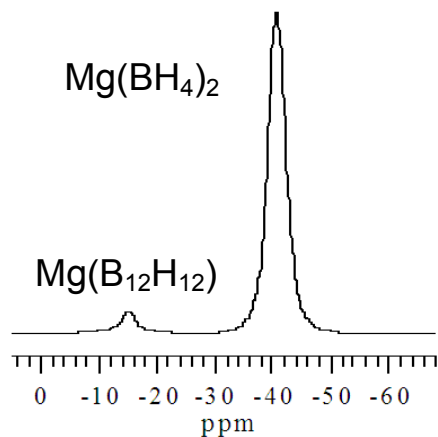
Figure 15. ^{11}B NMR data indicating that over 90% of the hydrogenated product is $Mg(BH_4)_2$ after hydrogenation of MgB_2 at high pressure and temperature.

Figure 16 shows that the $Mg(BH_4)_2$ product produced by the high pressure hydrogenation can in fact release large amounts (~12 wt. %) of hydrogen, albeit at a higher than desired temperature of 500 °C.

H$_2$ Desorption at 530 °C

Wt % H$_2$

Time/hours
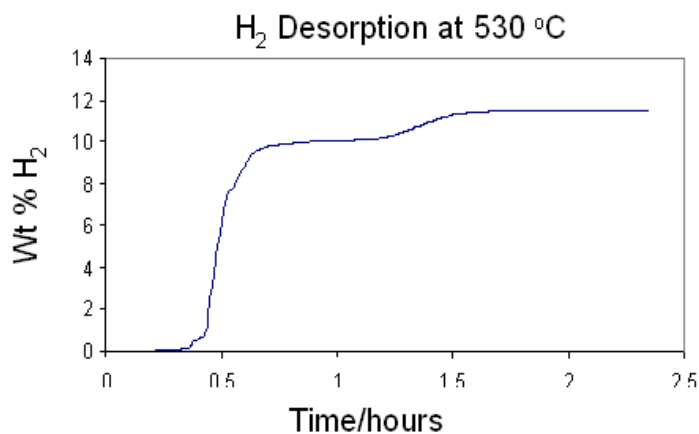
Figure 16. Isothermal desorption of hydrogen from $Mg(BH_4)_2$ (formed by high pressure hydrogenation of MgB_2) at 530 °C.

Summarizing, it has been shown that in the case of $Mg(BH_4)_2$, 12 wt. % of hydrogen could be released, and that the end product (MgB_2) could then be rehydrogenated all the way back to $Mg(BH_4)_2$. This is shown in the equation below:

$$MgB_2 \xrightarrow[\text{700 - 950 atm } H_2; \text{ 350 - 400 °C}]{} Mg(BH_4)_2$$

$$Mg(BH_4)_2 \xrightarrow[\text{400 °C}]{} MgB_2$$
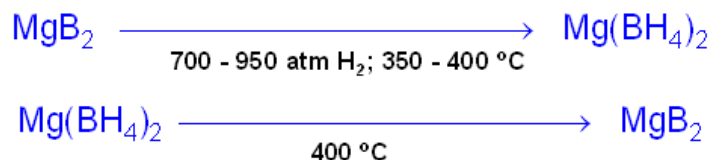
This ~ 12 wt. % reversibility for $Mg(BH_4)_2$ makes it a record-breaking material for reversible hydrogen storage. Although the process conditions of pressure and temperature for both dehydrogenation and hydrogenation are higher than desired, $Mg(BH_4)_2$ has the highest reversible capacity for any metal hydride material discovered thus far. $Mg(BH_4)_2$ remains one of the most interesting compounds for H_2 storage due to the high theoretical wt.% H (14.8 %), good ΔH (40 kJ/mole H_2) for hydrogen desorption, and demonstrated reversibility at high temperature and pressure. We believe that if the kinetic limitations can be overcome, then the thermodynamics of the system would allow facile hydrogen release and reversibility. As a result of this promise, $Mg(BH_4)_2$ has been recommended to the HSECoE has a high-priority "medium-term" material for investigation. By "medium term" we mean a material with high promise, but needing more material R&D before an engineered system could be fabricated and tested.

A significant effort was devoted in the MHCoE towards developing methods of detecting amorphous species appearing in reactions, primarily by the NMR techniques available to the MHCoE at Caltech and the UH. In addition, given the importance of borohydrides as high-weight-percent materials, the MHCoE devoted particular effort to understanding the structure and chemistry of $B_{12}H_{12}$ salts.

The difficulty posed by these intermediates is clearly revealed in the Sandia work on calcium borohydride, $Ca(BH_4)_2$.

Calcium Borohydride, $Ca(BH_4)_2$

$Ca(BH_4)_2$ received considerable attention from Dr. Ewa Ronnebro and Dr. Eric Majzoub (both formerly Sandia) as well as other MHCoE partners. It possesses a high theoretical (9.5%) hydrogen capacity, and early indications were that is was reversible, albeit at high temperature and pressure:

Dehydrogenation:

$$3Ca(BH_4)_2 \xrightarrow[\text{360 °C}]{} CaB_6 \ + \ 2CaH_2 \ + 10H_2$$
$$\textbf{(9.6 wt. \%released)}$$

Hydrogenation:

$$CaB_6 \ + \ 2CaH_2 \xrightarrow[\text{400 °C}]{\text{700 bar } H_2} \text{Rehydrided}$$
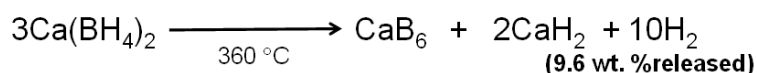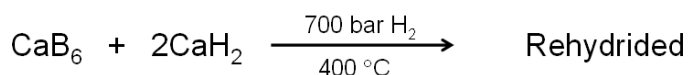
Early indications suggested that the system was at least partially reversible. However, it soon became apparent that with cycling, the reversibility decreased. When investigations were made of the cycling behavior of $Ca(BH_4)_2$, it was found that there was a steadily decreasing ability to recover the material by these recharging processes, as shown by Figure 17.
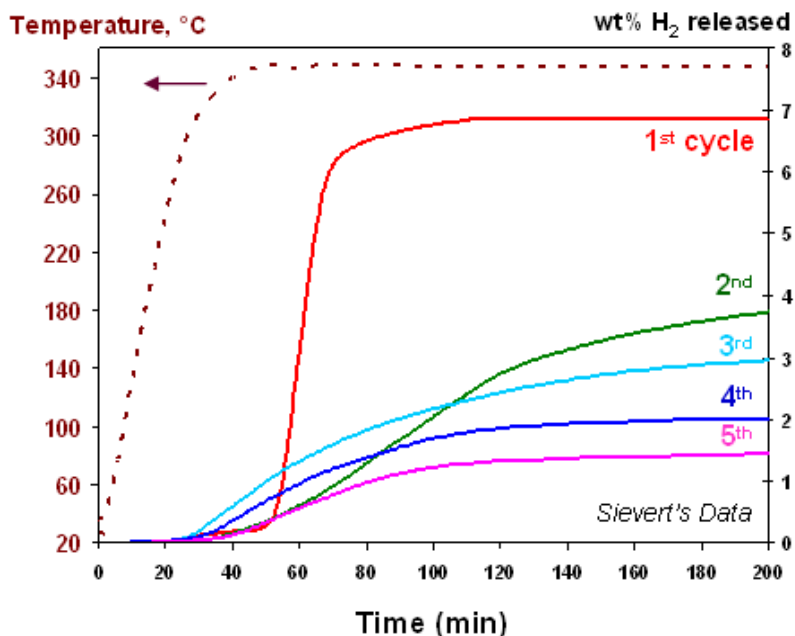
Figure 17. Repeated hydrogen desorption/adsorption cycles for $Ca(BH_4)_2$. This sample contained 4 wt. % $PdCl_2$, but the behavior is representative of pure $Ca(BH_4)_2$.

^{11}B NMR studies were conducted by Dr. Sonjong Wang of Caltech to try to understand the cause of this decrease. The results are shown in Figure 18. The NMR spectrum for the dehydrogenated state after the first cycle (red) clearly shows a much reduced $Ca(BH_4)_2$ at -33.0 ppm. An increased CaB_6 peak also occurs at 14.7 ppm. Both of these observations are consistent with the expectations for hydrogen release from $Ca(BH_4)_2$. However, a new peak is growing in at approximately -16 ppm, increasing in intensity as the sample is cycled. In fact, it appears in both the hydrogenated and dehydrogenated state. This peak was identified as $CaB_{12}H_{12}$ by comparison of known sample of $MB_{12}H_{12}$.

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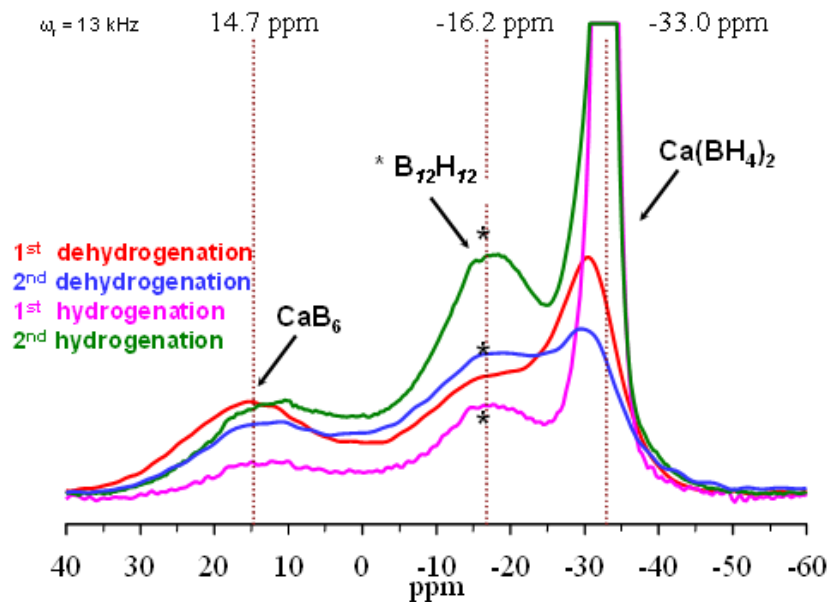
Figure 18. ^{11}B NMR studies of various states of $Ca(BH_4)_2$. The peak at ~18 ppm is assigned to a $B_{12}H_{12}$ species.

Figure 19 shows NMR data for a series of known boron compounds that could be candidates for the intermediate observed in Figure 18, namely B, $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$. Interestingly there is a strong variation of the NMR spectra which should allow these species to be easily distinguished from each other. The peak at -16.2 in Figure 18 corresponds well to the peak at -18ppm in the reference compound $K_2B_{12}H_{12}$. The correspondence is not perfect, but strongly suggests the species growing in and accumulating as $Ca(BH_4)_2$ is cycled is $CaB_{12}H_{12}$. Since studies by Sandia show that $CaB_{12}H_{12}$ is not readily hydrogenated to $Ca(BH_4)_2$, nor can it readily release hydrogen, it acts as a chemical sink which steadily accumulates as the material is cycled. Figure 19 also shows for comparison NMR data for the dehydrogenated states of $LiBH_4$, $Mg(BH_4)_2$, $(Ca(AlH_4)_2 + 6LiBH_4)$ and $(ScCl_3 + 3LiBH_4)$. It seems that a peak near that for $K_2B_{12}H_{12}$ is present in all these dehydrogenated materials, suggesting that the formation of a $[B_{12}H_{12}]^{2-}$ intermediate species is a general issue for borohydrides.
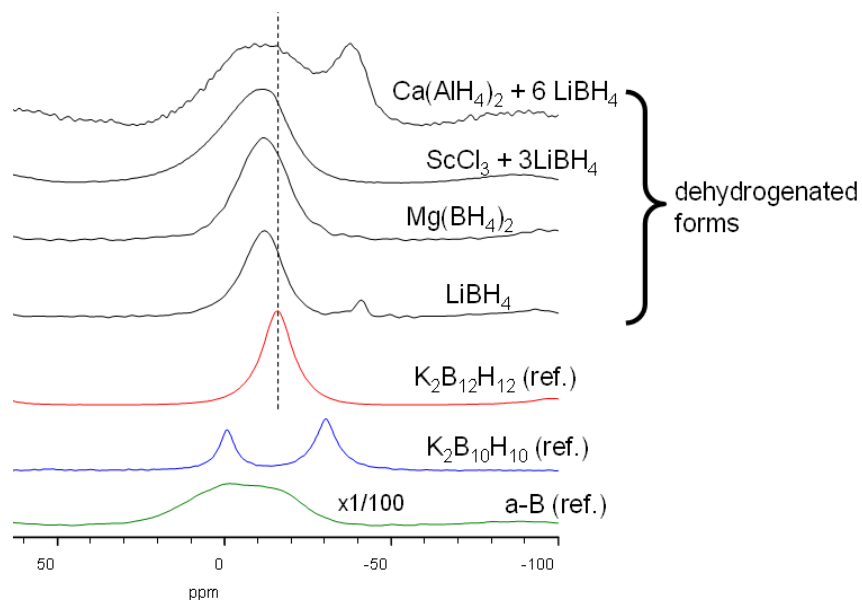
Figure 19. ^{11}B NMR data for the calibration compounds B, $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$. Also shown are NMR data for the dehydrogenated states of $LiBH_4$, $Mg(BH_4)_2$, $(Ca(AlH_4)_2 + 6LiBH_4)$ and $(ScCl_3 + 3LiBH_4)$.

The appearance of these relatively unknown $MB_{12}H_{12}$ salts led to a great deal of work. Dr. Vitalie Stavila at Sandia developed a straightforward synthesis method to directly make $MB_{12}H_{12}$ materials in an unsolvated state, allowing the properties of pure $CaB_{12}H_{12}$, $Li_2B_{12}H_{12}$, and $NaB_{12}H_{12}$ to be examined for the first time. Both NMR and neutron diffraction studies indicate that the structure of a $[B_{12}H_{12}]^{2-}$ anion is dodecahedral, as indicated in Figure 20 below:
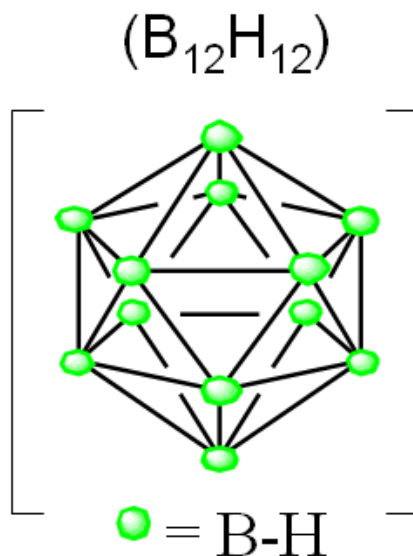
Figure 20. Geometric structure of $[B_{12}H_{12}]^{2-}$ anion.

Interestingly, it proved difficult to synthesize $MgB_{12}H_{12}$. These $B_{12}H_{12}$ salts were investigated extensively theoretically, as will be described in the Theory Group Summary later in this Final Report.

In order to understand the reactivity of these intermediates, their reaction with binary hydrides was examined. The destabilization of $CaB_{12}H_{12}$ with CaH_2 was discussed in the Summary of Project A results. Both experiment and theory show that significant lowering of the energy required to release H_2 from $CaB_{12}H_{12}$ can be achieved with a stoichiometric quantity of CaH.

Summarizing the work of Project B, a great deal of progress was made in understanding the chemistry of complex anionic materials, and how they released hydrogen. The borohydrides were emphasized heavily due to their exceptional gravimetric storage density. The reaction pathways of borohydrides were elucidated, and in the case of $Mg(BH_4)_2$, a fully reversible material was found. Extensive work was devoted to understanding the role of $B_{12}H_{12}$ intermediates in borohydride reactions.

Summary and Highlights from Project C: Amide/Imide Materials

Amides/
Imides
(M-N-H)

- Utah (POC)
- UNR
- ORNL
- U. Hawaii
- JPL
- Caltech
- SRNL
- OSU

**Prof. Zak Fang, U. Utah,
Project C Lead**

This project investigating N containing materials for hydrogen storage was inspired by the 2002 paper by Dr. Ping Chen [P. Chen et. al, *Nature,* **420,** 302 (2002)], then of the National University of Singapore. Dr. Chen observed that LiMgN uptook a significant amount of hydrogen, and the resulting material (proposed to be $LiNH_2 + 2LiH$) could also desorb H_2, giving a reversible hydrogen storage system operating below ~ 250 ºC. During the course of the MHCoE program, 15 different amide related systems were investigated, including mixtures of amides and borohydrides, amides and alanates, and LiMgN itself. Please consult the "downselect" chart for a full list of systems investigated in Project C, and also the Publication List for those papers derived from Project C work. We present here a description of the more prominent systems, $(2LiNH_2 + MgH_2)$ and LiMgN that have been recommended to the HSECoE as important "near-term" materials for further testing and possible subsystem engineering development. We also present results for the practical effects of low level (~100ppm) impurites in the hydrogen stream on the cycling of an amide material.

Investigations of ($2LiNH_2$ + MgH_2) for Hydrogen Storage

In order to produce lower temperatures in the desorption process, Dr. Weifang Luo of Sandia followed an approach to destabilizing the ($LiNH_2$-LiH) system by replacing LiH with MgH_2. A PCT measurement from the material is shown in Figure 21:
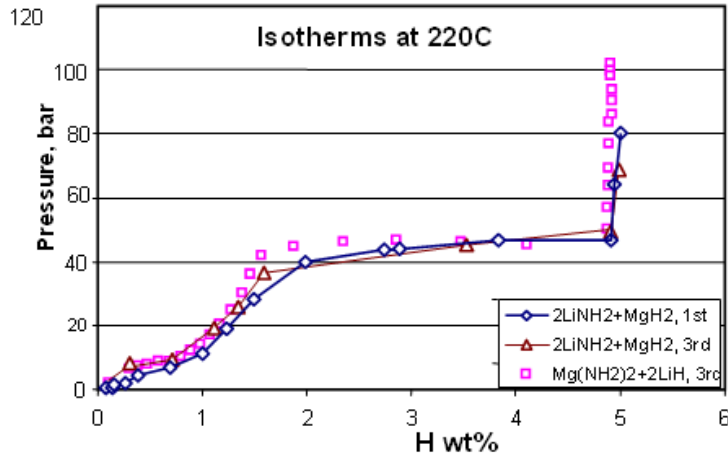
Figure 21. PCT measurement from $2LiNH_2 + MgH_2$, recorded at 220 ºC.

As indicated in Figure 21, hydrogen can be desorbed from $2LiNH_2 + MgH_2$ at 200 ºC with a pressure of 30 bar. This is a substantial increase in plateau pressure compared to the $LiNH_2$-LiH system. Figure 22 shows the results of extensive cycling studies of the $2LiNH_2 + MgH_2$ material, showing that the material could be cycled 264 times, albeit with a 23% loss of the storage capacity. The cause of this cycling-induced capacity loss was not determined, but clearly this material has significant potential for a reversible on-board material.
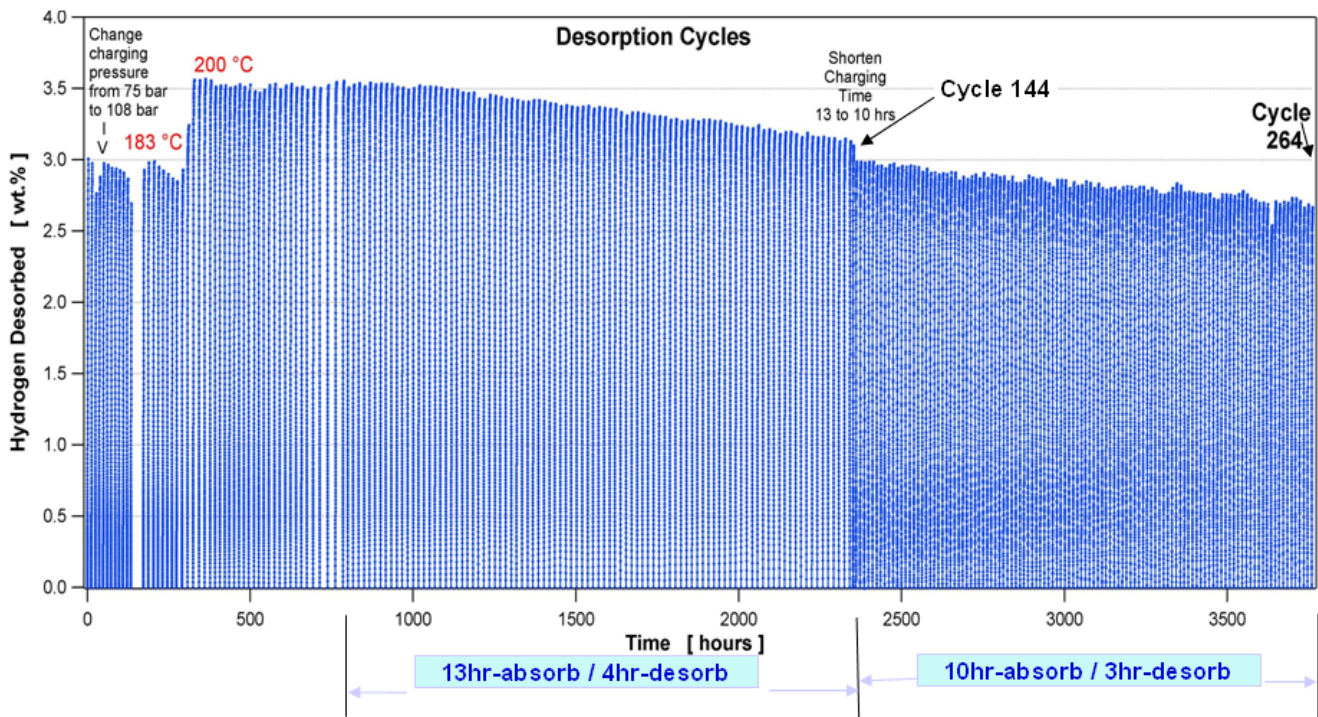
Figure 22. Cycling studies of $(2LiNH_2 + MgH_2)$.

A common difficulty of the general class of amide compounds is the release of ammonia, which is problematic for two reasons. First, nitrogen release represents an irreversible loss of the storage material that cannot be recovered. For practical matters, if the ammonia content in the hydrogen stream is ~200ppm or higher, one would have a 10% loss after 1000 cycles. A tighter requirement on the ammonia content arises from the need to keep the catalyst in PEM fuel cells from being poisoned by NH_3. This more stringent requirement requires that the NH_3 levels in the released H_2 be on order of 1ppm or less.

For the $(2LiNH_2 + MgH_2)$ system, measurements of the released ammonia content were made using "Draeger Tubes," an industry standard technology for measuring ammonia in gas streams. The results, shown in Figure 23, indicate that as the sample temperature is raised, so does the ammonia content in the hydrogen stream. At 200 ºC, the hydrogen stream is contaminated with ~300 ppm NH_3. Figure 23 indicates that if the desorption temperature could be reduced, then the ammonia content could drop.
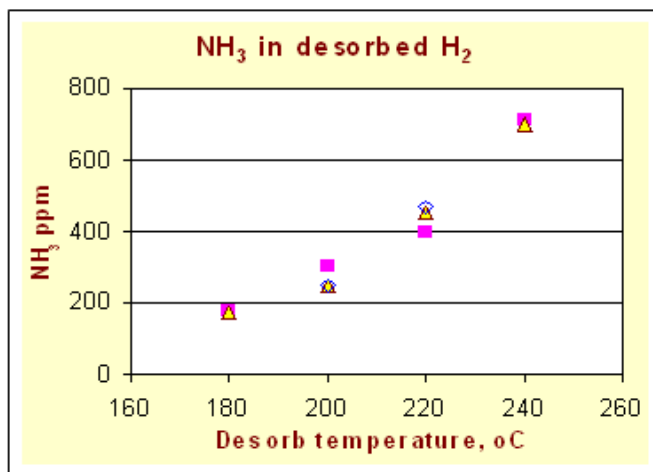
Figure 23. Measurements of NH_3 contamination in H_2 released from $(2LiNH_2 + MgH_2)$.

The mechanism for hydrogen release from this material was thoroughly investigated by XRD and FTIR. The results indicate that the following mechanism is operative for the $(2LiNH_2 + MgH_2)$ system:
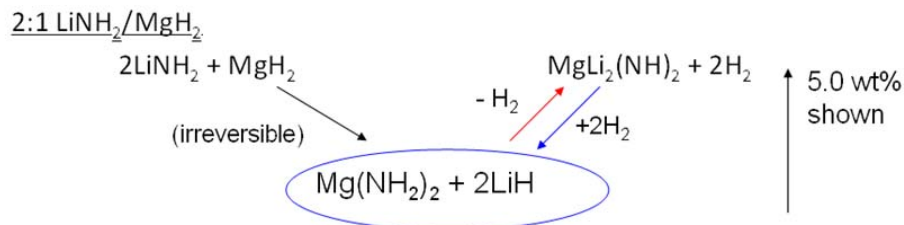
Figure 24. Pathways for hydrogen release from $(2LiNH_2 + MgH_2)$.

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Upon heating, the starting material ($2LiNH_2 + MgH_2$) undergoes an irreversible transformation to $Mg(NH_2)_2 + 2LiH$. This is the "hydrogenated" material that exists as this material undergoes hydrogen desorption/adsorption cycling. When ($Mg(NH_2)_2 + 2LiH$) is heated further, hydrogen is released to form $MgLi_2(NH)_2 + 2H_2$. The $MgLi_2(NH)_2$ material is a class of N-H materials called "imides." Generally imides are stable compounds and do not readily release the remaining hydrogen in the molecule. As a result, the final product produced by heating is $MgLi_2(NH)_2$ and the material system is limited to about 5 wt. % hydrogen. When the spent material is hydrogenated, the intermediate material formed is $Mg(NH_2)_2 + 2LiH$, and not the original lithium amide ($2LiNH_2 + MgH_2$). As a result, the system cycles between $Mg(NH_2)_2 + 2LiH$ and $MgLi_2 (NH)_2$ as shown in Figure 24.

During the course of the MHCoE program, work on this material was "paused" because the weight percent was limited to ~5 wt. %, and we sought new materials with higher capacity. However, toward the end of the MHCoE effort, the decision was made to recommend this material to the HSECoE as an important "near-term" material for subsystem engineering development. Dr. Luo performed additional experiments on this material to aid the kinetic performance. Confirming the original work of Chen, Luo found that KH had a strong catalytic effect on the kinetic performance of ($2LiNH_2 + MgH_2$). With faster kinetics, PCT data could be collected down to 180 ºC. These PCT data are shown in Figure 25:
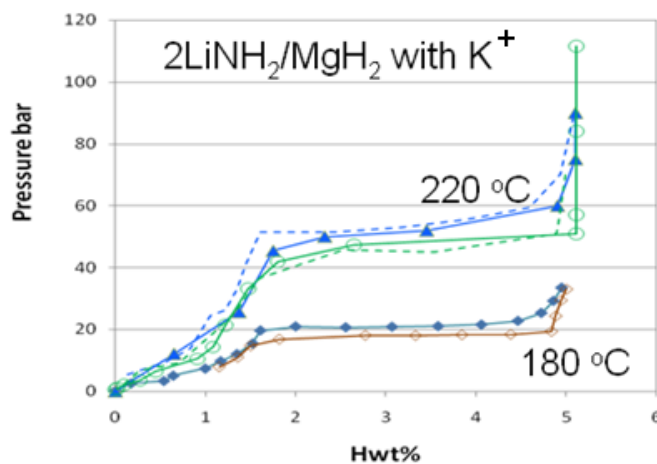
Figure 25. PCT studies of ($2LiNH_2 + MgH_2$) catalyzed with 2 mole % KH.

The vastly improved kinetics and reversibility allowed measurements leading to a van't Hoff plot of the system. The values of ΔH and ΔS for ($2LiNH_2 + MgH_2$) are 41.8 kJ/molH$_2$, and 99 J/moleH$_2$K, respectively. These can be compared with the corresponding values of ΔH and ΔS for LaNi$_5$H$_6$, which are 30.2 kJ/molH$_2$ and 104 J/moleH$_2$K, respectively. The ($2LiNH_2 + MgH_2$) material is now being examined by the HSECoE for subsystem testing of an engineered hydrogen storage vessel based on this material.

Investigations of LiMgN for Hydrogen Storage Applications

As indicated above, the (2LiNH$_2$ + MgH$_2$) system possesses limited hydrogen storage capacities. However, experience has shown that when the molar ratio of reactants changes, new reactions between lithium amide and simple or complex metal hydrides can take place, possibly opening up new reaction sequences with higher ultimate hydrogen production. At the University of Utah, an experimental program was launched by Prof. Zak Fang to re-evaluate the hydrogen desorption/adsorption properties of LiMgN.

LiMgN can be formed as the product of the reaction between LiNH$_2$ and MgH$_2$ when the molar ratio of LiNH$_2$ to MgH$_2$ is 1:1 as shown by the following reaction:

$$MgH_2 + LiNH_2 \rightarrow LiMgN + 2H_2 \qquad\qquad (1)$$
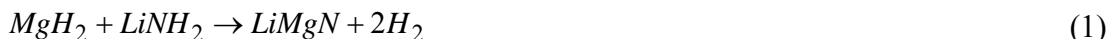
This system was first investigated theoretically by the MHCoE Theory Group partner David Sholl and co-workers [V. Alapati et. al. *Phys. Chem. Chem. Phys.,* **9**, 1438-1452 (2007)]. Theoretically, Reaction 1 was predicted to have a very attractive $\Delta H = 32$ kJ/moleH$_2$, with a hydrogen capacity of 8.2 wt. %. The high predicted weight percent of hydrogen is due to the full dehydrogenation all the way to LiMgN, bypassing the undesired imide intermediate. Because reaction 1 represents the complete dehydrogenation of the system, LiMgN would be an important candidate material for hydrogen storage if the dehydrogenation takes place at low temperature and if it is reversible.

To demonstrate the feasibility of reaction 1 experimentally, a mixture of MgH$_2$ and LiNH$_2$ with a molar ratio of 1:1 was prepared by ball milling for 24 h. Figure 26 shows the TGA profile of the as-milled MgH$_2$/LiNH$_2$ mixture as the sample is heated. The reaction starts at about 120 °C and the weight-loss accelerated at about 200 °C. The total weight loss was 8.1 wt. % of the initial weight after the sample was held at 220 °C for 20 min. Assuming all the weight losses were due to the release of hydrogen, the dehydrogenation process can be considered complete, confirming the theoretically predicted Reaction 1. Differential thermal analyses (DTA) of the hydrogen release were carried out. The results indicated that the dehydrogenation was completed in a one-step reaction, with a ΔH of 33.5 kJ/mol H$_2$, which is very close to the theoretically predicted reaction enthalpy of 32 kJ/mol H$_2$ found in the MHCoE work of Alapati et al. XRD studies of the reaction showed the presence of LiMgN in the fully dehydrogenated state, confirming Reaction 1.

Of course, the material must be reversible to be useful for automotive hydrogen storage. In order to investigate the reversibility of reaction 1, the dehydrogenated product of the reaction, LiMgN, was treated in a custom-made autoclave under 138 bar hydrogen pressure and 240 °C. The hydrogenated LiMgN was then analyzed using TGA, DTA, and XRD. Figure 27 shows TGA profile of the hydrogenated LiMgN sample. It shows that the sample took up H$_2$ amounting to about 5 wt. % of the hydrogenated product. The dehydrogenation reaction of the hydrogenated LiMgN sample appears to be a two-step process rather than a one-step process, as was shown by Figure 26. It is noted that the hydrogen capacity of the rehydrogenated LiMgN is less than that of the initial mixture of LiNH$_2$ + MgH$_2$ for reasons that are not currently understood.
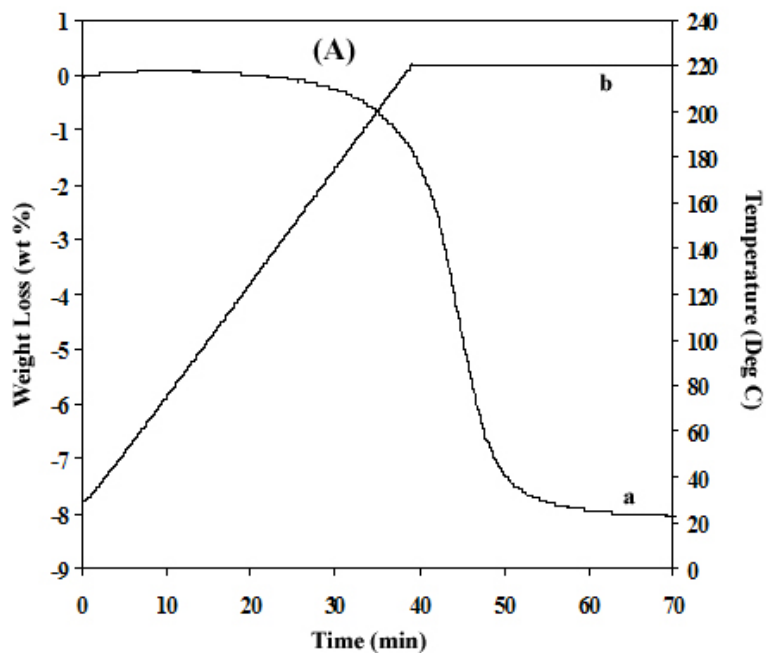
Figure 26. Thermogravimetric Analysis (TGA) data for desorption from ball-milled ($LiNH_2$ + MgH_2).
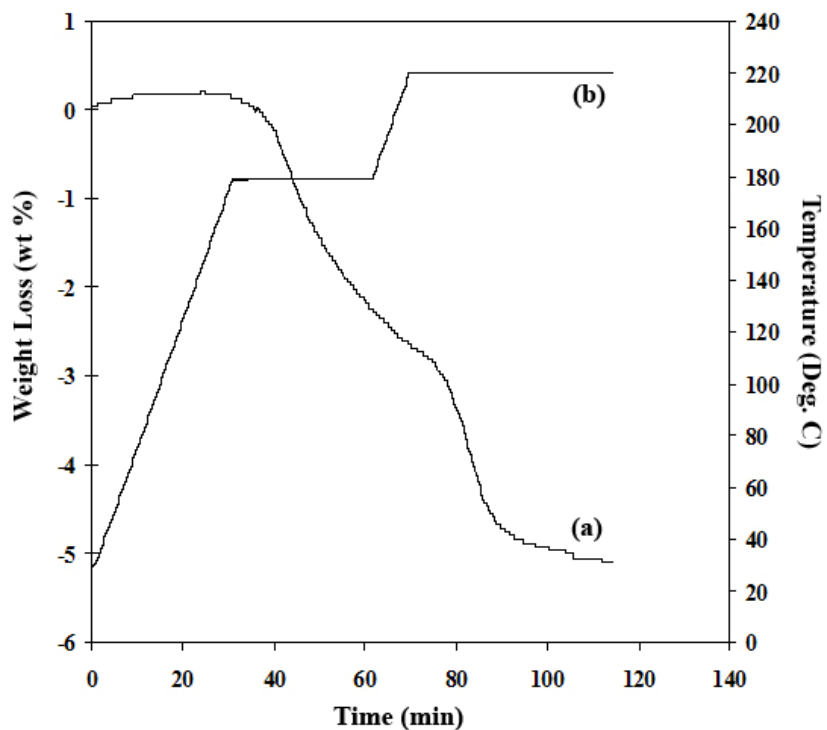
Figure 27. TGA curves for LiMgN after hydrogenation at 240 °C under 138 bar hydrogen pressure. Curve (a) shows the hydrogen release under argon and heating rate of 5 °C/min. Curve (b) shows the temperature profile.

The Utah team suspected that perhaps kinetic limitations were responsible for the poor reversibility. To improve the hydrogenation kinetics, a known catalyst for hydrogen storage reactions, 4 wt. % of $TiCl_3$, was added to the material. The LiMgN/Ti sample was then hydrogenated at 138 bar and 160 °C for 6 hours. After hydrogenation, the sample was heated to desorb H_2. Figure 28 shows that $TiCl_3$-doped LiMgN gained about 8.0 wt. % hydrogen from the rehydrogenation process, which is a significant improvement over the hydrogenation of LiMgN without catalyst. The TGA curve also shows that the dehydrogenation of the hydrogenated $TiCl_3$-doped LiMgN occurred in nearly identical temperature ranges as that of the hydrogenated LiMgN without catalyst. Compared to the hydrogenation temperature of LiMgN without doping, it is also noted that LiMgN with $TiCl_3$ doping can be hydrogenated at much lower temperatures (160 °C) than the material without $TiCl_3$ doping, which is further evidence that $TiCl_3$ significantly improves the hydrogenation kinetic of LiMgN.
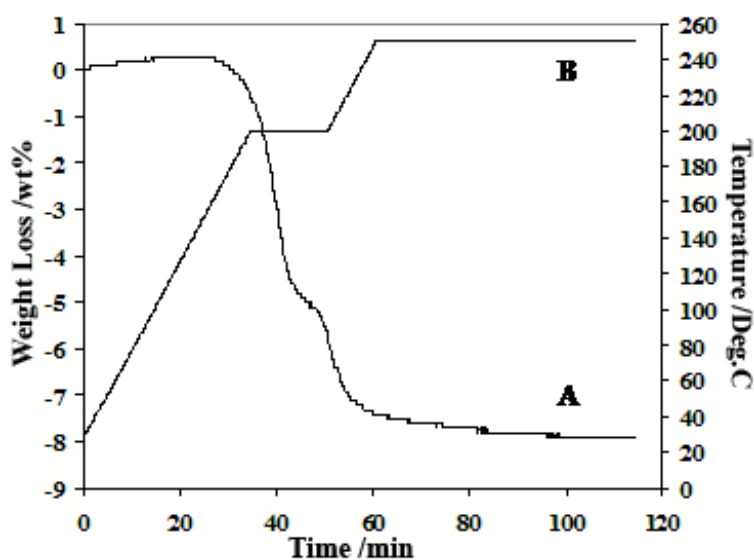
Figure 28. TGA curves for $TiCl_3$-doped LiMgN after hydrogenation at 160 °C under 138 bar hydrogen pressure for 6 h. Curve A shows the hydrogen release under argon and heating rate of 5 °C/min. Curve B shows the temperature profile.

Based on extensive XRD studies of this reaction, the following reaction mechanism is put forth to explain the hydrogen storage properties:
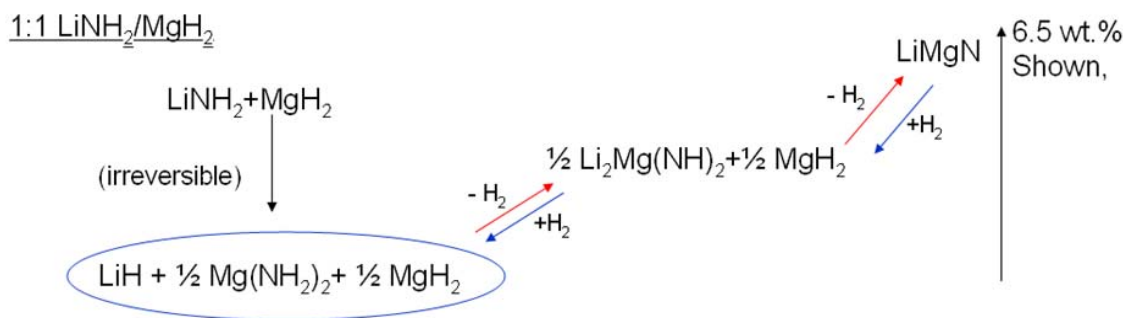
Figure 29. Proposed mechanism for hydrogen absorption/desorption involving 1:1 $LiNH_2/MgH_2$.

Extensive FTIR and XRD measurement support the assignment that upon hydrogenation, LiMgN converts to $LiH + \frac{1}{2} Mg(NH_2)_2 + \frac{1}{2} MgH_2$. The assignment of the imide in this reaction as an intermediate is speculative, as its detection as an intermediate in the cycling has not been confirmed, although the TGA data do show a multi-step behavior. The nature of the reaction pathway for the LiMgN system needs more work. Nonetheless, it is a material showing reversibility, with ~8 wt. % capacity, with dehydrogenation and hydrogenation temperatures in the range 160 ºC–220 ºC. The long term cycling behavior needs to be examined.

Effects of H_2 Impurities on Li_3N-H Cycling

Although materials may show excellent hydrogen storage properties in the pure state, for practical purposes, there may be impurities in the hydrogen stream that affect metal hydride performance. In the MHCoE, Prof. Dhanesh Chandra at UNR examined this phenomenon by placing 100 ppm levels of contaminants in the hydrogen stream and observing the effect on pressure cycling between LiN_3 and its hydrogenated state, which in these experiments was a mixture of Li_2NH and $LiNH_2$. The cycling experiments were performed with inexpensive industrial grade hydrogen (99.99% pure), and then with ultra-high purity (99.9999% pure) H_2 mixed with 100 ppm levels of individual impurity such as O_2, H_2O, CO, CO_2, CH_4, NH_3, and N_2. Cycling/aging of amide-imide, isotherms, and crystal structure analyses were evaluated.

The results are shown in Figure 30, which reports a pressure-composition measurement at 255 ºC for LiN_3 after a given number of cycles in the contaminated H_2 gas. The cycle labeled $^1H_2$ can be considered the "starting" unaffected material. Cycling over 500 times in O_2, H_2O and industrial grade hydrogen cause the greatest loss in hydrogen capacity, due to the formation of Li_2O and other contaminants. Cycling 100 times in 100ppm CH_4 also causes significant capacity loss. Interestingly, addition of 100ppm N_2 to H_2, actually improved the cycle life presumably due compensation for nitrogen lost during cycling. Increasing the N_2 concentration far beyond 100 ppm, to 20%, actually significantly improved the overall hydrogen cycling capacity to about 10.5 wt. %.
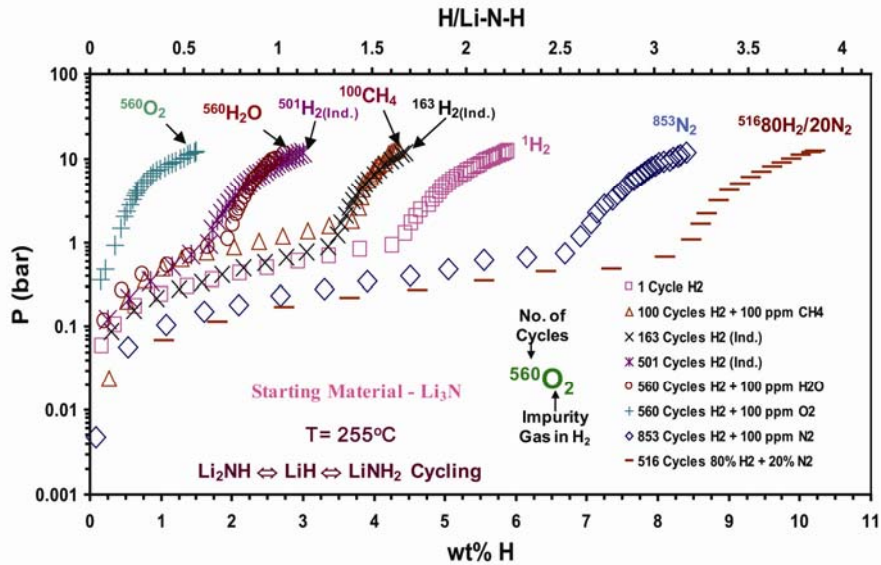
Figure 30. Summary of the effect of mixing impurity gases in UHP H_2. The $^{560}O_2$, $^{560}H_2O$, $^{110}CH_4$, $^{853}N_2$ data was taken at 100 ppm level impurity, $^{163}H_{2(ind.)}$ and $^{501}H_{2(ind.)}$ are industrial hydrogen, and $^{516}80H_2/20N_2$ has 20 mol.%N_2 premixed in H_2).

The increased capacity caused by adding N_2 to the hydrogen stream is explained by CALPHAD modeling that shows small amounts of pure liquid lithium metal form during cycling. Thus Li reacts with N_2 to form Li_3N and then eventually forms Li_2NH. In this way, Li metal, which would represent a loss in H_2 storage capacity, is recovered by eventual conversion to Li_2NH.

Summarizing, both ($2LiNH_2 + MgH_2$) and LiMgN have been extensively studied in the MHCoE, and both have been recommended to the HSECoE for further study and subsystem engineering for automotive hydrogen storage. In general, 100 ppm levels of impurites such as O_2 and H_2O can have dramatically deleterious effects on the cycling of amide based systems when the cycling is performed ~ 500 times. This indicates a practical consideration for the purity of hydrogen that must be achieved for a real hydrogen storage system.

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Summary and Highlights from Project D:
AlH$_3$ and Its Regeneration

Alane
(AlH$_3$)

- **BNL(POC)**
- SRNL
- U. Hawaii
- SNL
- UIUC
- UNB
- JPL
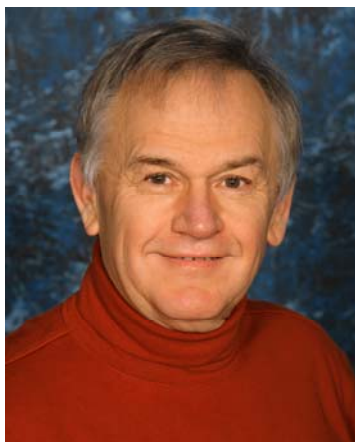
Dr. James Wegrzyn, Brookhaven National Lab, Project D Lead

In many ways, aluminium hydride (AlH$_3$), often referred to as "alane," represents a nearly ideal hydrogen storage material from a desorption point of view. AlH$_3$ has a gravimetric capacity of 10 wt. % and volumetric capacity of 149 g H$_2$/L, along with a hydrogen desorption temperature of ~60°C to 175°C (depending on particle size and the addition of catalysts). Due to aluminum hydride's low temperature of decomposition and its ability to store 10% hydrogen by weight, this material has been the subject of study for decades, as reviewed by Sandrock et al. [*J. Alloys and Comp.*, **421,** 185 (2006)]. More recently under the activities of the MHCoE, AlH$_3$ has been identified as a promising hydrogen storage material for low temperature fuel cell applications. Seven phases of AlH$_3$ are known. Early in the tenure of the MHCoE, BNL examined the thermodynamics, vibrational and crystal structures of the three most stable phases (α, β and γ) in order to better understand the storage material itself.

It was already appreciated that the difficulty with AlH$_3$ lies in its regeneration from the dehydrogenated state, namely Al metal. The heat of formation and the Gibbs free energy for the formation of α-AlH$_3$ directly from aluminum and hydrogen at room temperature is about 7 x 10^3 bar. Thus, the pressure to regenerate AlH$_3$ directly from aluminum and gaseous hydrogen is simply too high to be practical on a large scale. After the initial research phase characterizing the structure and hydrogen release properties of AlH$_3$, attention turned quickly to the problem of regeneration. It was already known that AlH$_3$ could be generated by reacting LiAlH$_4$ with AlCl$_3$ using organic solvents. This method produces stable salt by-products that are costly to recycle, and therefore is not useful for many applications.

In the MHCoE, we took a threefold approach to the problem of regeneration of AlH$_3$. All of these approaches are considered "off-board" regeneration strategies. AlH$_3$ differs from the other MHCoE materials in that for these other materials, we sought "on-board" reversibility. However, due to alane's nearly ideal hydrogen desorption characteristics, and the fact that "on-board"

reversibility seemed nearly impossible to achieve, we decided to extend the range of possibilities for regeneration to "off-board" methods.

One "off-board" method of AlH_3 regeneration considered regeneration of AlH_3 from Al and H_2 under supercritical fluid conditions. This method, developed by UNB, proved to be ineffective. This left two other methods, both of which proved successful. The first is regeneration of AlH_3 using a two-step organometallic process (conducted by BNL); the second is the regeneration of AlH_3 via electrochemical means (conducted by SRNL). These two approaches will be summarized below.

As the lead of the MHCoE Project D Alane Group, Dr. Jim Wegrzyn enjoyed a close working relation with all its members. Most notably JPL provided important NMR data on alane, University of Illinois did some excellent work on assessing the dispersion of Ti catalyst in AlH_3. Sandia provided high-level theoretical predictions on the thermochemistry of alane complexes.

Organometallic Approach to Regeneration of AlH_3

Early in the MHCoE, Dr. Jason Graetz, Dr. Jim Reilly, and Dr. Jim Wegrzyn of BNL investigated the synthesis and characterization of alane. Much foundational work was spent by BNL investigating the hydrogen release characteristics of the three AlH_3 polymorphs (α, β and γ). The measured H storage content for these polymorphs was better than 9.0 % by weight, but the decomposition kinetics failed to meet the DOE fuel delivery target at temperatures of 100°C or less. However, these initial results indicated that at slightly higher temperatures and with the addition of a catalyst, there should be no inherent barrier preventing alane from meeting most of the DOE 2010 storage targets.

The thermodynamics of AlH_3 were determined by BNL using differential scanning calorimetry and *ex situ* X-ray diffraction. A formation enthalpy of approximately -10 kJ/mol AlH_3 was measured for α-AlH_3, which is in good agreement with previous experimental and calculated results. The β and γ phases are less stable than the α phase for temperatures > 300K. The total heat evolved during the $\beta \rightarrow \alpha$ transition is 1.5 ± 0.4 kJ/mol AlH_3 and 2.8 ± 0.4 kJ/mol AlH_3 during the $\gamma \rightarrow \alpha$ transition. These transformations to the α phase are exothermic and are therefore favorable at room temperature.

The H_2 evolution rate for all the three AlH_3 polymorphs (α, β and γ) was later measured to be ~2 gH_2/s at 120 ºC, based on 100 kg of material. This H_2 rate is more than 3 orders of magnitude greater than that of $NaAlH_4$ (undoped) and exceeds the DOE full flow target of 1 gH_2/sec (the 0.02 gH_2/sec/kW DOE target applied to a a 50 kW fuel cell). The freshly synthesized α-AlH_3 had activation energy of 102.2 kJ/mol. This energy value was much less than the measured activation energy of 150.3 kJ/mol for the DOW "kinetically stabilized" material, as described by Sandrock [*J. Alloys and Comp.*, **421**, 185 (2006)]. DOW Chemical has shown that alane can be stabilized against thermal decomposition by the addition of protective surface coatings. At temperatures of 100 ºC and above, the decomposition of AlH_3 occurs at similar rates for all three α, β and γ polymorphs. This is because at temperatures above 100°C the less stable γ and β phases first transform to the α phase before decomposing to the elements. Therefore, above

100 ºC the H_2 evolution rates reflect the decomposition of the α phase. However, below 100 ºC there is a clear splitting of the kinetic plot showing much faster H_2 decomposition rates for the γ and β phases.

The remaining challenge was to identify a cost effective and energy efficient chemical pathway for regenerating α-AlH_3 from spent aluminum. In the BNL work, the general approach was to try to form AlH_3 in the presence of a stabilizing agent. Whereas forming AlH_3 directly from Al and H_2 in the gas phase is nearly impossible due to the instability of AlH_3, it was felt that through adduct formation, one could more easily form and stabilize AlH_3, and hopefully remove the stabilizing agent which is not wanted in the final material.

In early 2008, BNL demonstrated that this adduct-assisted formation of AlH_3 was possible. BNL demonstrated the regeneration of AlH_3 via a low-temperature, low-pressure, reversible reaction using Ti-doped Al powder and triethylenediamine (TEDA). The adduct is formed in a slurry of the Al powder and a solution of TEDA in THF in contact with H_2. The TEDA-AlH_3 product is insoluble and precipitates from solution.

The chief difficulty with forming the TEDA-AlH_3 adduct is that this particular adduct is too stable. If one attempted to recover pure AlH_3 by heating the TEDA-AlH_3 adduct (to desorb TEDA), too much H_2 is also lost from AlH_3 because the required temperatures are too high. On the other hand, it was not possible to stabilize the formation of AlH_3 with an adduct that could be easily removed, such as triethylamine (TEA). To circumvent this problem, BNL showed that one could successfully stabilize AlH_3 formation using one amine adduct, and then convert that adduct to a TEA-AlH_3 adduct whose TEA moiety could be more easily removed by thermal processing. That conversion of one amine adduct for another amine adduct is called "transamination." The overall strategy was therefore:

    Step 1: formation of NR_3-AlH_3 by direct hydrogenation

    Step 2: transamination exchange NR_3 with TEA

    Step 3: separation of TEA-AlH_3

One stabilizing agent investigated in detail by this technique was dimethylethylamine (DMEA). BNL demonstrated the direct hydrogenation of dimethylethylamine (DMEA) and catalyzed aluminum did indeed form DMEA-AlH_3, and that the DMEA-AlH_3 could be transaminated to TEA-AlH_3. Finally, they were able to separate and recover Ti-catalyzed AlH_3 from the TEA-AlH_3, thereby demonstrating a new low energy method to regenerate Ti-catalyzed AlH_3 from catalyzed aluminum and hydrogen gas. The results can be summarized in Figure 31:
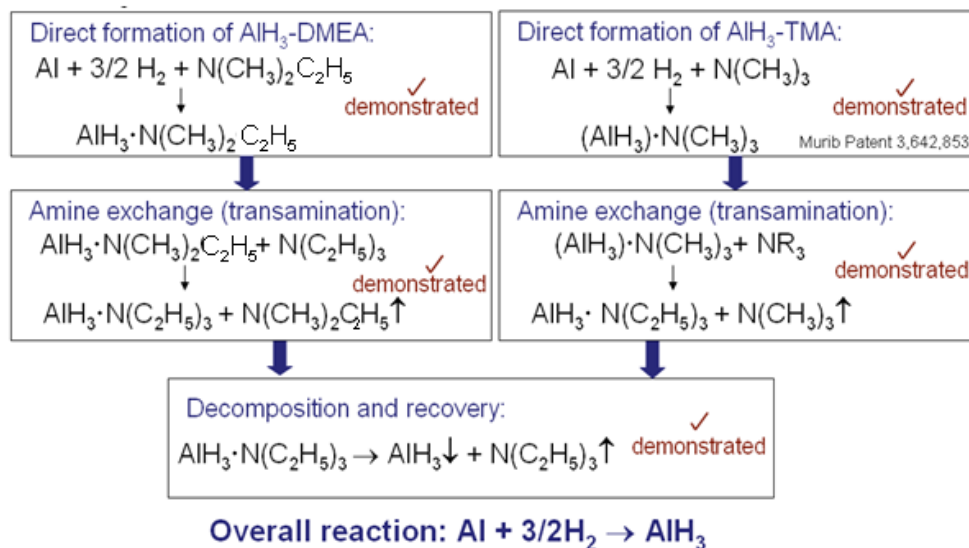
Figure 31. Regeneration of AlH₃ via demonstrated chemical routes. Although not indicated, catalytic levels of Ti are present in the original Al being processed.

As shown in Figure 31, direct formation of the stabilized AlH₃ moiety has been achieved using DMEA and also trimethylamine (TMA) as the stabilizing agents. Both DMEA and TMA bind too strongly to AlH₃ to allow facile removal of the stabilizing amine. However, both TMA-AlH₃ and DMEA-AlH₃ can be transaminated using TEA to TEA-AlH₃, which could then be easily thermally dissociated to produce pure AlH₃.

A major concern with such an "off-board" regeneration method is the energy required to execute these chemical steps. In 2008 an independent analysis of an AlH₃ storage system was conducted by R. K. Ahluwalia of Argonne National Laboratory. Argonne's analysis assumed a 70-wt. % aluminum hydride slurry, and used TMA as the stabilizing agent. The Argonne analysis indicated a well to tank (WTT) efficiency of 55% assuming 75% yields in the transamination step and 75% in TEA decomposition and recovery step, along with losses in producing hydrogen (73% efficiency) and compressing and recycling hydrogen. The WTT DOE target is 60%.

Further work on this organometallic approach should emphasize increasing the yield of the different chemical steps, and the purity of the products obtained. In general, the yields for forming DMEA-AlH₃ in the pressurized reactor were good. Difficulties occurred in the vacuum distillation transamination step, where trace amounts of metallic aluminum were observed. It is known that trace amounts of aluminum promotes the decomposition of AlH₃. This fact restricts the window for cleanly separating AlH₃ from TEA-AlH₃. Hence after repeated attempts in FY09-10 to recover pure AlH₃ from TEA-AlH₃, the final product always consisted of both AlH₃ and aluminum. This problem needs to be resolved experimentally.

Electrochemical Reversible Formation of AlH₃

During the tenure of the MHCoE, Dr. Ragaiy Zidan and colleagues at SRNL investigated the possibility of regenerating AlH₃ electrochemically. The general idea is to utilize electrolytic

potential to increase hydrogen activity and therefore drive chemical reactions to regenerate AlH$_3$. Hydrogen charging of metals has readily been accomplished through the utilization of electrical potential. The relatively low potential required to achieve high hydrogen pressure is illustrated in Faraday's equation as:

$$E = -\frac{RT}{2F} \ln P_{H_2} \qquad (1)$$

where E is the electrical potential, F is the Faraday's constant, R is the gas constant, and T is the temperature.

From the above equation it is evident that the driving potential is proportional to the logarithm of the hydrogen pressure, resulting in modest driving potential requirements. However, the use of electrochemistry has to take into account that Al and AlH$_3$ oxidize in aqueous environment, thereby prohibiting the use of all protic solvents as electrolytes. For this reason, SRNL developed a novel route using a non-aqueous solvent system. A polar aprotic solvent such as tetrahydrofuran (THF) is used in electrolytic cells. These cells are operated at ambient pressure and temperature. Following cell design and fabrication, a search for useful electrodes and operating conditions was conducted.

Details of the electrochemical regeneration route are beyond the scope of this summary, and can be found in the publication by Zidan [*Chem.Comm.*, **25**, 3717 (2009)]. However, the general idea can be shown in Figure 32.

Figure 32. Electrochemical Regeneration of AlH$_3$ from Al metal.

The anode in the cell is a pure aluminum electrode. The counter electrode is platinum foil or platinum coiled wire. The electrolyte in the cell is made of alanates such as $NaAlH_4$ or $LiAlH_4$ dissolved in anhydrous THF or diethyl ether. The electrolysis is carried out in an electrochemically stable, aprotic, and polar solvent such as THF or ether. $MAlH_4$ (M = Li, Na) is dissolved in this solvent, forming the ionic solution as shown in Figure 32, which is used as an electrolyte.

Starting with spent Al from the desorption of H_2 from AlH_3, the Al is removed from the vehicle, and processing begins. The Al is reacted with NaH and H_2 to form $NaAlH_4$. This $NaAlH_4$ is dissolved in THF and placed in the cell. Alternatively, Al from the vehicle can enter the electrochemical environment as the Al anode. When the cell is polarized, Al metal can be converted to Al^{3+}, which reacts with dissolved AlH_4^- ions to produce AlH_3 complexed with THF.

Once the AlH_3-THF adduct is formed as a white solid, the THF must be removed from the AlH_3. This proved to be problematic, as the temperatures required to remove the THF also led to some dehydrogenation of AlH_3, leading to a mixture of both Al and AlH_3 in the final product. Things improved dramatically when another proprietary adduct besides THF was introduced, which led to facile removal of the adduct, forming pure AlH_3 in gram quantities. XRD confirmation of AlH_3 as the product is shown in Figure 33 below:
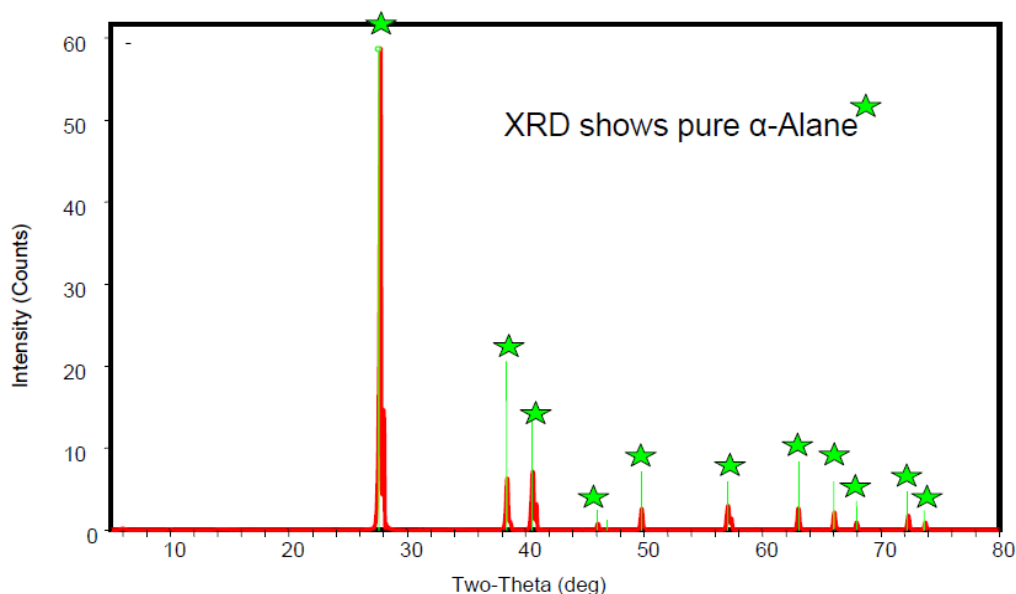
Figure 33. XRD confirmation that the electrochemically synthesized material is AlH_3.

In FY 2010 improvements in yield and efficiency were achieved by the use of $LiAlH_4$ in THF and the introduction of LiCl, which acts as an electro-catalytic additive (ECA). The use of LiCl greatly enhanced the electrochemical process, yielding a higher cell efficiency and higher amount of alane adduct produced.

Development of a Facile "Off-Board" Method for Regeneration of LiAlH$_4$

Lithium aluminum hydride (LiAlH$_4$) is a promising compound for hydrogen storage, with a high gravimetric and volumetric hydrogen density and a low decomposition temperature. Its hydrogen release is described by the following two-step reactions:

$$3LiAlH_4 \longrightarrow Li_3AlH_6 + 2Al + 3H_2 \qquad 5.3 \text{ wt.\%H} \qquad \Delta H = -10 \text{ kJ mol}^{-1} \qquad \textbf{Step 1}$$

$$Li_3AlH_6 \longrightarrow 3LiH + Al + 1.5H_2 \qquad 2.6 \text{ wt.\%H} \qquad \Delta H = +25 \text{ kJ mol}^{-1} \qquad \textbf{Step 2}$$

Similar to other metastable hydrides, LiAlH$_4$ does not form by direct hydrogenation at reasonable hydrogen pressures. Therefore, there is considerable interest in developing new routes to regenerate the material from the dehydrogenated products LiH and Al. In the course of MHCoE work, BNL demonstrated a low-energy route to regenerate LiAlH$_4$ from LiH and Ti-catalyzed Al. The initial hydrogenation occurs in a THF slurry and forms the adduct LiAlH$_4$•4THF. The thermodynamics of this reversible reaction were investigated by measuring pressure−composition isotherms, and the free energy was found to be small and slightly negative ($\Delta G = -1.1$ kJ/mol H$_2$), suggesting an equilibrium hydrogen pressure of just under 1 bar at 300 K. BNL also demonstrated that the adduct LiAlH$_4$•4THF can be desolvated at low temperature to yield crystalline LiAlH$_4$.

In a parallel MHCoE effort, Prof. Craig Jensen from UH and Prof. Sean McGrady from UNB discovered a remarkably mild process to generate LiAlH$_4$ from the dehydrogenation products LiH and Al.

$$LiH + Al[Ti] \xrightarrow[\text{r.t.; 24 h}]{\text{Me}_2\text{O/H}_2 \text{ (100 bar)}} LiAlH_4[Ti]$$
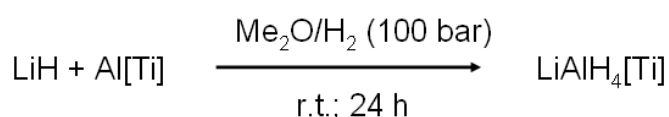
This process is remarkable for its mild conditions and convenience. The dehydrogenated products, LiH + Al + Ti catalyst, are dissolved in Me$_2$O at a hydrogen pressure of 100 bar. At this pressure, Me$_2$O is a liquid, and the LiH + Al [Ti] material dissolves. After 24 hours at room temperature, the hydrogen pressure is released. With venting of H$_2$, Me$_2$O also vents, and one is left with a quantitative conversion to catalyzed LiAlH$_4$. Studies of the hydrogen release properties of the LiAlH$_4$ (Ti catalyzed) thus formed shows that 7 wt. % of hydrogen is released from 80–180 ºC, with excellent kinetics, and only ~ 100 ppm of Ti is required for the catalysis. The material has been cycled up to 5 times with this process.

The prospects for this process to be a low-energy route to LiAlH$_4$ regeneration are considerable. A study by Argonne, shown in Figure 34, shows that as the relative amount of DME required for the process is minimized, and the WTT efficiency of the process can reach the 60% DOE target.
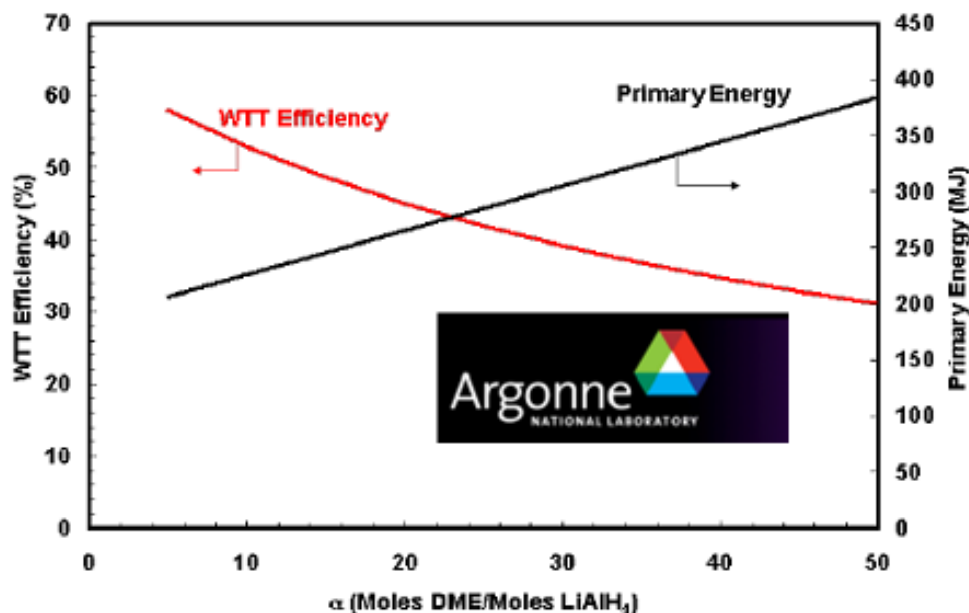
Figure 34. WTT efficiency of the Me$_2$O process for regenerating LiAlH$_4$.

Summarizing the results of Project D, a great deal of progress was made in developing "off-board" regeneration methods for AlH$_3$ and LiAlH$_4$ which both have desirable hydrogen desorption characteristics, but poor hydrogen reversibility. BNL developed an organometallic approach in which AlH$_3$ could be generated from H$_2$ in the presence of a stabilizing agent, with that stabilizing agent eventually removed to yield pure AlH$_3$. SRNL developed an electrochemical route in which spent aluminum could be converted to AlH$_3$ with high purity and in good yield. UNB and UH collaborated to develop a remarkably facile method to regenerate LiAlH$_4$. All of these methods provide for viable "off-board" regeneration of these metal hydrides.

Summary and Highlights from Project E: Engineering
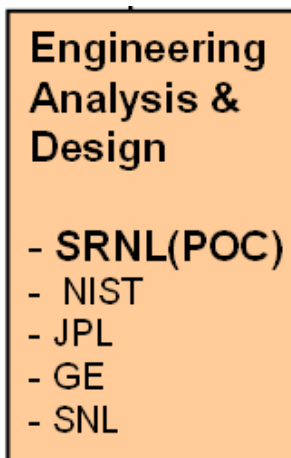
Dr. Don Anton, SRNL

As discussed in the Introduction, the original MHCoE Project E was discontinued in 2008 with the commissioning of the HSECoE. After that time, from 2008-2010, there was little engineering related work in the MHCoE, as the responsibility for that work fell on the HSECoE scientific program. For completeness, we review here some work that was conducted in the MHCoE during the timeframe 2005–2008. The Project E lead was Dr. Don Anton from SRNL.

The original mission for Project E was to perform subsystem engineering testing of promising metal hydride materials, and eventually construct a prototype hydrogen storage tank. A prototype tank was never constructed. However, there was very valuable "materials engineering" work performed in the MHCoE, including (1) studies at Sandia of the thermal conductivity of the amide system $2LiNH_2/MgH_2$, and (2) thermal modeling of hydrogen storage beds by SRNL. We review these activities in more detail below.

Thermal Conductivity of $2LiNH_2/MgH_2$

 Since most metal hydride systems need to absorb heat to release H_2, and release heat when the metal hydride is regenerated, there are significant thermal management issues with metal hydride hydrogen storage. Many metal hydrides are powders, and are poor thermal conductors. Additionally, the thermal conductivity can change with the state of hydrogenation of the bed. Thus, it is critically important to know the thermal conductivity, heat capacity and other materials engineering properties of solid-state hydrogen storage systems before a prototype bed is constructed.

At Sandia, measurements were made of the thermal conductivity of the amide system $2LiNH_2/MgH_2$. There are presented below in Figure 35.
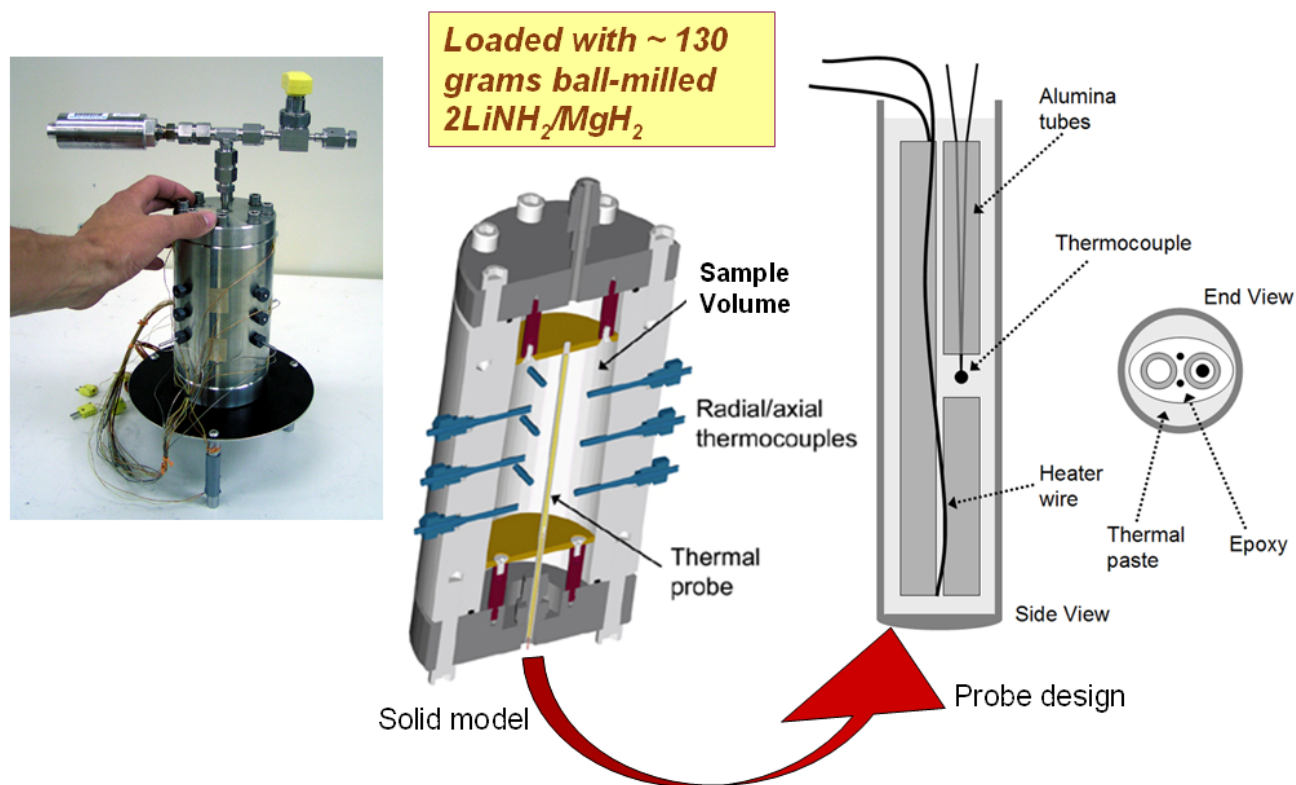
Figure 35. Apparatus for measuring thermal conductivity of $2LiNH_2/MgH_2$.

The apparatus of Figure 35 is a standard method of measuring thermal conductivity. The metal hydride is packed into the "sample volume" region shown in Figure 35. A probe is placed down the center that provides heating and can also measure temperature. A constant power is applied to the center probe. The time dependent temperature of the center probe depends on the thermal conductivity of the surrounding metal hydride. If the surrounding material has a poor thermal conductivity, the temperature of the central probe at constant power rises quickly. If the surrounding metal hydride has an excellent thermal conductivity, the temperature rises more slowly. There exists an analytical solution for the geometry of Figure 35, so that the time dependent temperature profile of the central probe yields the material thermal conductivity.

The results of the measurements are shown in Figure 36 below:
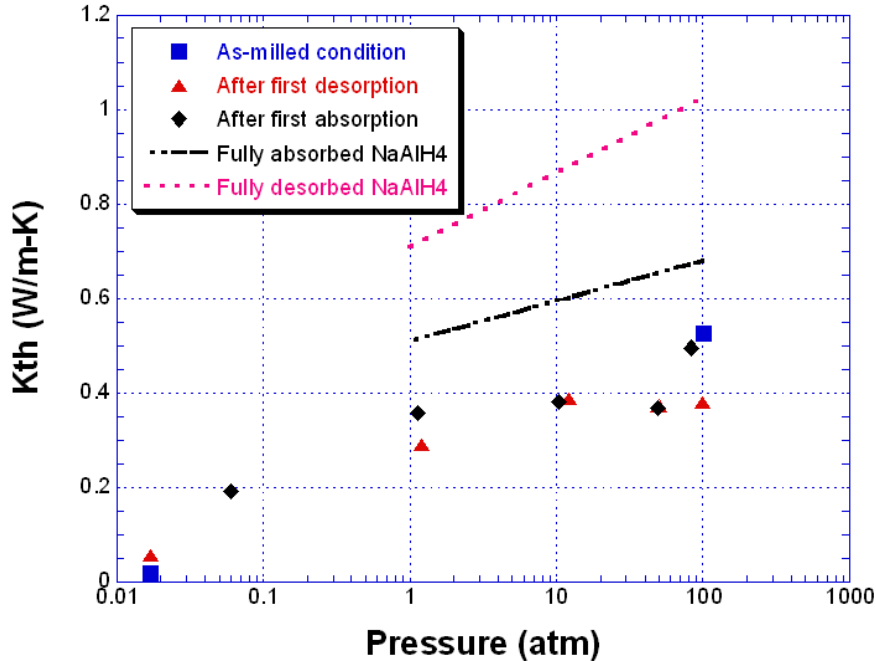
Figure 36. Results of thermal conductivity measurements for both hydrogenated and dehydrogenated forms of 2LiNH$_2$/MgH$_2$. Comparison is also made for fully adsorbed and desorbed NaAlH$_4$.

At any given pressure, Figure 36 shows that the thermal conductivity of 2LiNH$_2$/MgH$_2$ is the same whether the material is hydrogenated or dehydrogenated. In addition, the overall thermal conductivity of 2LiNH$_2$/MgH$_2$ is significantly less than the NaAlH$_4$ example. The enhanced thermal conductivity of the absorbed and desorbed states of NaAlH$_4$ is due to the presence of Al in those samples.

The overall increase of Kth with pressure observed in Figure 36 relates to the thermal conductivity of hydrogen gas filling the interstitial regions of the pores. This increase is not related to changes in composition caused by hydrogenation at these pressures, as the same increase is seen if He is used as the charging gas.

This thermal conductivity data is essential for any metal hydride bed to be accurately engineered with control of the thermal management issues associated with hydrogen release and recharging.

Hydrogen Storage Scoping and Integrated Modeling

In any practical storage system the rate of H$_2$ uptake will be governed by all processes that affect the rate of mass transport through the bed and into the metal hydride particles. These coupled processes include heat and mass transfer as well as chemical kinetics and equilibrium. These processes must be quantitatively understood through modeling to allow a full understanding of the behavior of hydrogen storage systems.

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At SRNL a detailed numerical model was constructed for a general metal hydride bed that couples reaction kinetics with heat and mass transfer, for both hydrogen release and hydrogen charging of the metal hydride. Scoping models for reaction kinetics, bed geometry and thermal conductivity were used to perform a quick assessment of storage systems and identify those bed geometries which have the potential to meet DOE performance targets. The operational characteristics of successful candidate systems were then evaluated with the more detailed models.

The engineered storage systems were modeled in either 2 or 3 dimensions via the general purpose finite element solver COMSOL Multiphysics®. The two-dimensional model serves to provide rapid evaluation of bed configurations and physical processes, while the three-dimensional model, which requires a much longer run time, is used to investigate detailed effects that are not accurately represented by two-dimensional analyses. The model is general and can be adapted to any geometry or storage media. In this study, the model was applied to a modified cylindrical shell and tube geometry for which the modification consists of radial fins perpendicular to the axis. The overall geometry is shown in Figure 37. Sodium alanate, $NaAlH_4$, was used as the hydrogen storage medium.
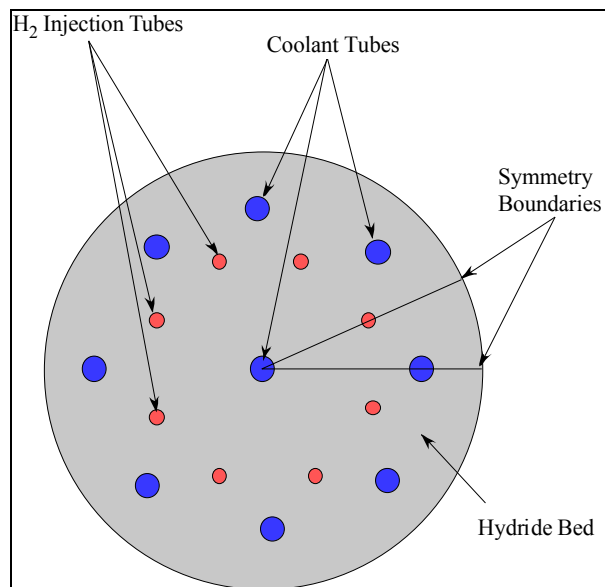
Figure 37. Schematic of cross-section for hydride bed.

The detailed finite element models indicated that the modified shell and tube heat exchanger, with fins normal to the axis, was very effective in allowing heat removal and thermal control of the system. For identical states of the coolant and feed hydrogen, the modified shell and tube system permits far better control of the bed temperature than the system without fins. This was clearly demonstrated by comparing the temperatures predicted by the 3-dimensional and 2-dimensional models, which represented storage systems with and without fins, respectively. Because the bed temperatures could be maintained below 120°C, the model indicated the hydrogen charging rate could be significantly improved for the modified shell and tube system.

The more uniform spatial temperatures in the modified storage system yielded smaller concentration gradients for the hexa- and tetra-hydrides formed from NaH. This resulted in more efficient utilization of the bed. Figure 38 shows that the charging rate for the modified system is essentially the same as that predicted by the 0-dimensional kinetics scoping model. This means that charging in the modified system is limited by kinetics alone, which represents an upper bound to the charging rate at a given temperature and pressure.
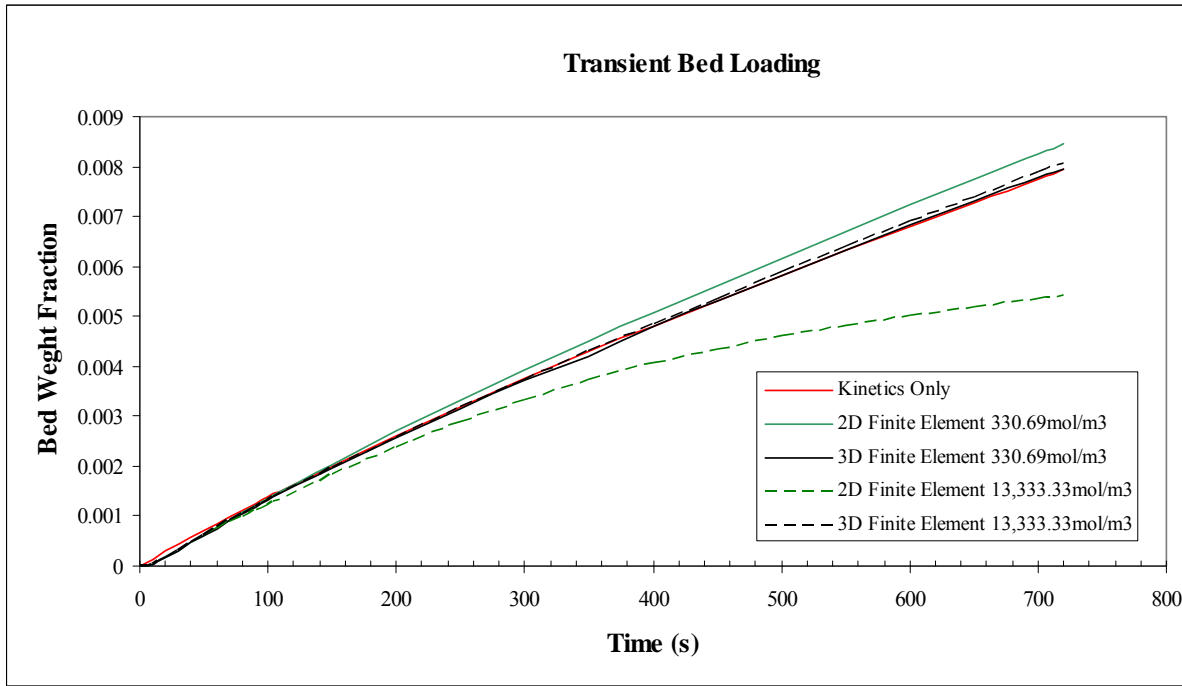
Figure 38. Comparison of the weight fraction of stored hydrogen for the kinetics scoping model and the 2 and 3-dimensional finite element bed models.

Summarizing these hydride bed modeling results, a combination of both scoping and integrated 2- and 3-d models were developed and found to be effective in modeling hydride hydrogen storage systems. The detailed finite element model showed the effectiveness of a modified shell and tube design versus a system without heat transfer fins. A kinetic scoping model of the hydrogen charging rate showed good agreement with the integrated model showing the value of using scoping models to save computation time and to gain preliminary information and insight into some complex processes.

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Summary and Highlights from Theory Group: First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems

Dr. Mark Allendorf, Sandia National Laboratories, Theory Group Coordinator

Although not a formal "project" in the MHCoE organizational sense, the MHCoE Theory Group (TG) was a vital and critical aspect of our Center operation. Indeed, the combination of theoretical capabilities being brought to bear on materials predictions in many ways set a new standard for how theory and experiment can work together in collaborative solid-state science. The overall approach of the TG was to use first-principles methods to conduct materials discovery, provide thermodynamic and kinetic data for use by engineering and modeling efforts, and suggest new directions for experimentalists and interpretation of their results. The TG consisted of theorists at the following institutions:

- Sandia National Laboratories (Mark Allendorf, TG coordinator)

- Georgia Institute of Technology (Prof. David Sholl)

- National Institute of Standards and Technology (Dr. Ursula Kattner).

- University of Illinois/Champagne-Urbana (Prof. Duane Johnson)

- University of Missouri, St. Louis (Prof. Eric Majzoub)

- University of Pittsburgh (Prof. Karl Johnson)

- UTRC (Dr. Susanne Opalka)

To make maximum use of the different areas of expertise, joint TG efforts were guided by SNL not only in terms of technical direction, but also to ensure that TG efforts were complementary and had an effective synergy with experimentalists, who interacted closely with the TG. The TG communicated through regular monthly conference calls involving all members of the team and several experimentalists.

Prior to the MHCoE, the state of metal hydride modeling and theory (circa 2005) can be summarized as:

1. Density functional theory (DFT) had been used to compute the thermodynamics of only a few individual metal hydride compounds. (e.g., Wolverton et al., *PRB*, **69**, 144109 (2004).

2. There was no way to predict phase diagrams/van't Hoff plots for metal hydrides.

3. Theory could not account for reaction complexities, for example meta-stable species and multi-step reactions, that can occur in solid-state H_2 desorption/absorption reactions.

4. Virtually no theoretical work had been done on amorphous MH materials or kinetics.

After the 5-year run of the MHCoE, the state of metal hydride theory and modeling (circa 2010) had advanced in many ways:

1. DFT is now routinely used to predict the ΔH and ΔG of complex metal hydrides.

2. We have developed the ability to predict reactions over wide ranges of P, T and composition, thereby focusing experimental efforts on promising compounds. Linear search methods have been implemented allowing the scanning of literally millions of different reaction conditions (composition, T, P).

3. Theory can now predict the existence of important and surprising reaction intermediates that are being confirmed by experiment (e.g. $[B_{12}H_{12}]^{2-}$ intermediates).

4. The Prototype Electrostatic Ground State (PEGS) method was developed for predicting crystal structures beyond the use of the ICSD database, thereby increasing accuracy and enabling thermodynamic predictions for new structural phases of materials.

5. We have a much deeper understanding of the thermodynamics of selected reactions.

6. Thermodynamic equilibrium calculations are now taking into account the role of non-H_2 species (impurity gases) in shaping the pathways for hydrogen release from metal hydrides.

7. Theory is taking on the problem of understanding metal hydride interactions with nanoconfined structures.

Here, we discuss some highlights from the Theory Group work listed above in 1, 2, 4 and 5. The TG published 22 papers on a wide variety of topics (those publications are listed separately in Appendix II). Interested readers may consult those publications for further details. Here we focus on selected results that convey some of the issues that were encountered theoretically, and how they relate to each other.

New Materials Discovery

New materials discovery can be aided by the use of first-principles (ab initio) computational modeling in two ways: (1) The properties, including mechanisms, of existing materials can be better elucidated through a combined modeling/experimental approach. (2) The thermodynamic properties of novel materials that have not been made can, in many cases, be quickly screened with ab initio methods. Although experiments are the final arbiter of a reaction's usefulness, it is not practical to systematically study every conceivable reaction mixture experimentally. Therefore, systematic thermodynamic calculations based on first-principles calculations have played a useful role in the search for desirable reaction mixtures. First-principles calculations have been shown to yield reaction free energies that are accurate within $\pm$ 10 kJ/mol H_2—a level of precision that is adequate for screening large numbers of potentially interesting reactions. We shall see that with more detailed consideration, the free energies of hydrogen storage reactions can be predicted with high accuracy.

The PITT/GT collaboration within the MHCoE TG employed state-of-the-art computational techniques to explore literally millions of possible reaction conditions consisting of different element spaces, compositions, and temperatures. The general approach is as follows:

1. Compute DFT total energies for an extensive number of compounds, collect into a database. These total energies are for T = 0 (E_{tot}(T=0).

2. Specify a set of elements to screen, e.g., Li, B, Na, Mg (H is always selected)—the program identifies all solid compounds having any of the elements.

3. Specify a pressure of H_2. Most often this was P_{H2} = 1 bar.

4. Scan the composition of the solid phase (amount of H_2 in system not specified).

5. Pick a starting and ending T and ramp the temperature in increments of dT.

6. At each T, minimize the grand potential, Ω, via linear programming to obtain equilibrium composition, using the DFT heats of formation and the chemical potential of H_2 at the specified T, P.

7. Chemical reactions are identified when the equilibrium composition changes between two successive temperatures.

8. Pick only reactions with hydrogen wt. % > 6 and with free energy changes between $15 \leq \Delta U_0 \leq 70$ kJ/mol H_2.

This method has been used to scan over 20 million different reaction compositions.

By 2008, the PITT/GT effort had optimized the crystal structures and computed energies of 212 solid materials having known (experimental or predicted) crystal structures comprised of Al, B, Ca, Li, Mg, K, Na, Si, C, N, Sc, Ti, V plus H. In 2008, these tabulations allowed the scanning of over 2 million reaction conditions (temperatures, compositions, elemental spaces), allowing predictions for equilibrium pressure P_{eq} and wt. % hydrogen. Reactions with hydrogen wt. % > 6, and with total energy changes $15 \leq \Delta U_0 \leq 70$ kJ/mol H_2 are considered interesting. These reactions are shown in Figure 39:
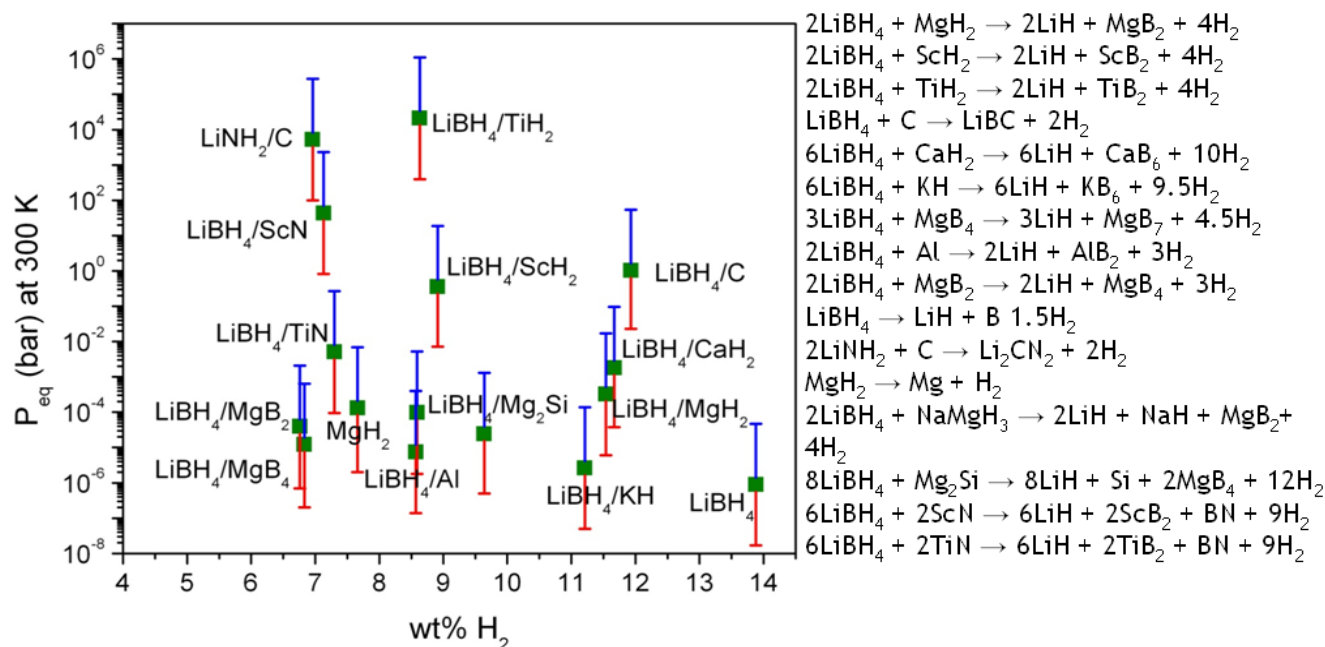
Figure 39. Theoretical predictions for reactions with weight percent hydrogen greater than 6 wt. %, and the desorption energy in the range $15 \leq \Delta U_0 \leq 70$ kJ/mol H_2 (Alapati et al., *J. Phys. Chem. C*, **112**, 5258 (2008).

In 2009, 147 new compounds were added containing Al, B, C, Ca, K, Li, Mg, N, Na, Sc, Si, Ti, V, H to the database, with structures taken from ICSD and recent literature. This new database allowed the prediction of 83 more reactions with wt. % > 6, $15 \leq \Delta U_0 \leq 70$ kJ/mol H_2.

Some of these reactions are shown in Figure 40 below:

Reaction	wt%	ΔU_0 (kJ/mol H_2)
$2MgH_2 + Mg(NH_2)_2 \leftrightarrow Mg_3N_2 + 4H_2$	7.4	26
$LiH + 2LiNH_2 + KBH_4 \leftrightarrow Li_3BN_2 + KH + 4H_2$	7.48	43.61
$56LiH + 21Mg(NH_2)_2 + 4V_2N \leftrightarrow 8Li_7N_4V + 7Mg_3N_2 + 70H_2$	6.75	47.87

Figure 40. Additional theoretical predictions for reactions with weight percent hydrogen greater than 6 wt. %, and the desorption energy in the range $15 \leq \Delta U_0 \leq 70$ kJ/mol H_2.

With the inclusion of $[B_{12}H_{12}]^{2-}$ compounds, whose role in borohydride reactions were not understood prior to the MHCoE, a number of interesting reactions were predicted with decent hydrogen storage capacity, as shown in Figure 41. In Figure 41 we list only those reactions with energy ΔU less than 44 kJ/mole H_2, for presentation purposes only.

Reaction	wt.%	ΔU_0 (kJ/mol H_2)
$10LiSc(BH_4)_4 + 4MgB_{12}H_{12} \rightarrow 10ScB_2 + 4Mg(BH_4)_2 + 5Li_2B_{12}H_{12} + 58H_2$	6.58	21.6
$5Si + 10Mg(BH_4)_2 + 4KBH_4 \rightarrow 5Mg_2Si + 2K_2B_{12}H_{12} + 36H_2$	8.1	37.3
$5Mg(BH_4)_2 + 2KBH_4 \rightarrow 5MgH_2 + K_2B_{12}H_{12} + 13H_2$	6.94	38.04
$4LiBH_4 + 5Si + 10Mg(BH_4)_2 \rightarrow 5Mg_2Si + 2Li_2B_{12}H_{12} + 36H_2$	9.46	40.96
$5Si + 10Mg(BH_4)_2 + 2Ca(BH_4)_2 \rightarrow 5Mg_2Si + 2CaB_{12}H_{12} + 36H_2$	8.85	41.18
$5Mg(BH_4)_2 + Ca(BH_4)_2 \rightarrow 5MgH_2 + CaB_{12}H_{12} + 13H_2$	7.72	43.09

Figure 41. Additional theoretical predictions for reactions involving $B_{12}H_{12}$ species, with weight percent hydrogen greater than 6 wt. %, and the desorption energy ΔU less than 44 kJ/mole H_2.

These predicted reactions are for "single-step" reactions, proceeding from reactants to products in a single step, without intermediates. The work of Siegel, Wolverton and Ozolins [*Phys. Rev. B*, **76,** 134102 (2007)] emphasized the importance of accounting for the fact that some reactions may be "multi-step" in nature. If there are multiple steps in a reaction, although the overall value of ΔU may be attractive, if one of the steps has an very unattractive ΔU, then the reaction will not proceed to the end product due to the system being "trapped" by the step that is thermodynamically unfavorable.

To account for the possibility that some of these single-step reactions may actually have multi-step character, a method was developed to allow the identification of metastable reactions that may lie near each other energetically. In other words, to account for possible intermediates, that would introduce a multistep nature to a reaction path, a method was developed to see if nearly degenerate reaction pathways may exist in reactions previously thought to be single-step.

To account for these possibilities, the process for assessing multiple step reactions involves:

- Run the linear program to identify the equilibrium reaction of interest.

- Exclude in turn each one of the possible solid products from the database and run the linear program again.

- By excluding one of the solid products, if the new run identifies a different reaction with a free energy within 10 kJ/mol H_2 of the original reaction, then the reaction is added to the metastable list.

- The process is repeated for excluding pairs, triples, etc. of compounds.

By this process, for a given single-step reaction, the space is scanned for possible nearby metastable reactions. The vast majority of reactions examined by the linear program have turned out to be solely "single-step" reactions in the sense above. Therefore, the thermodynamic

predictions are conceptually valid. However, a few reactions have turned out to have this multi-step character. An example is given below:

$$0.0300 \ Li_3AlH_6 + 0.0100 \ VH_2 \rightarrow 0.0900 \ LiH + 0.0100 \ Al_3V + 0.0550 \ H_2 \ (\triangle U_0 = 15.1 \ kJ/mol)$$

$$0.0686 \ Li_3AlH_6 + 0.0200 \ Al_3V \rightarrow 0.2057 \ LiH + 0.0029 \ Al_{45}V_7 + 0.1029 \ H_2 \ (\triangle U_0 = 27.2 \ kJ/mol)$$

$$0.1281 \ Li_3AlH_6 \rightarrow 0.3843 \ LiH + 0.1281 \ Al + 0.1921 \ H_2 \ (\triangle U_0 = 28.8 \ kJ/mol)$$
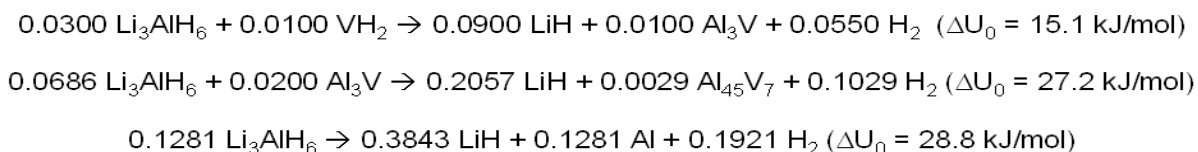
Net H_2 release is 14.44 wt.% (3.21% in step 1, 5.62% in step 2, and 5.62% in step 3)

Figure 42. Example of a potential multistep reaction arising from Li_3AlH_6 and VH_2 reaction.

A few caveats are in order. These calculations are based on a catalog of known compounds. If a reaction involves unknown compounds, these theoretical methods cannot describe it. For example, the earlier work of Alapati et al. [*Phys. Chem. Chem. Phys.,* **9**, 1438-1452 (2007)] did not include the metal closoboranes ($M_nB_{12}H_{12}$, for M=Li, Mg, Ca, or K), which since that time have been observed or predicted as intermediates in the decomposition reactions of the metal borohydrides. So, one of the results of the theory effort is to update the materials database used in the calculations. Another caveat: the results are based on thermodynamic analyses. There is no information in the results about chemical kinetics, nor do they contain information about chemical catalysis. Finally, the results are for stoichiometric compounds, so doped materials are not included as candidate hydrogen storage materials.

Prototype Electrostatic Ground State (PEGS) Theoretical Studies

As described above, computational modeling of the thermodynamics of hydrogen storage materials was used to narrow the search in composition space, and to guide experimental approaches used in the MHCoE. The success of this approach requires knowledge of the solid-phase crystal structures. Two approaches can generally be used and are shown in Figure 43 below for the example of $Ca(BH_4)_2$.

Early on in the MHCoE, interest turned to $Ca(BH_4)_2$ as a high weight percent material. However, the structure was unknown initially. To theoretically predict the thermodynamics of this material, there were two possible approaches. In the database method, a search is conducted of all materials with the same general formula as $Ca(BH_4)_2$, namely AB_2X_8. Of the ~80,000 structures in the database, there are ~30 with the formula AB_2X_8. At this point, a common but logically suspect assumption is made. The assumption is that the structure of $Ca(BH_4)_2$ is the same as one of the ~30 structures for the formula AB_2X_8. This assumption does not allow for possible new crystal structures that might exist. Regardless, for each of the 30 structures, a first principles DFT calculation using VASP is performed for the total energy (at T = 0). The structure with the lowest calculated ground state is presumed to be the ground state of $Ca(BH_4)_2$. This procedure is shown on the left hand side of Figure 43.

**Calculating Thermodynamics
When the Crystal Structure is Unknown**

$$3Ca(BH_4)_2 \longrightarrow CaB_6 + 2CaH_2 + 10H_2 \quad \text{(2006)}$$
9.6 wt. %
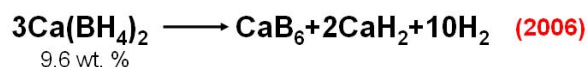
Database

- Inorganic crystal structure database
- ICSD data base contains 80,000 inorganic structures
- Looking for AB_2X_8 yields ~30 inequivalent test structures

"Breakthrough" Technique

PEGS
- Electrostatic interactions
- MH_x anion is a rigid unit
- Global energy minimization

VASP

b-initio
ackage
ienna imulation

PEGS Structure

(~ 30 times)   (1 time)

Energy of Structure at T=0K
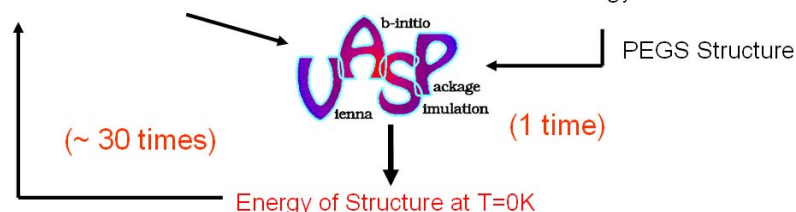
Figure 43. Comparison of two approaches (database searching and PEGS) for predicting the crystal structures of materials.

In some cases, there may not be many trial structures for the repetitive VASP calculations, or the true structure may be new. So, although database searching can yield the correct structure in many cases, there are also many exceptions. Dr. Eric Majzoub (formerly of Sandia) sought a more rigorous method to predict crystal structures by incorporating the understanding that these complex anionic materials are dominated by electrostatic interactions. By treating the complex anionic units (such as BH_4^-) as a rigid unit, and performing a global minimization of the electrostatic interactions, one obtains a structure that can then be the basis of one VASP calculation of the total energy. This PEGS procedure is shown on the right-hand side of Figure 43.

Describing the PEGS method in more detail, its important to note that in metal-hydrogen compounds containing complex anions, the metal atoms are frequently alkali or alkaline earth, and the complex anions one of $[NH]^{2-}$, $[NH_2]^-$, $[BH_4]^-$, $[AlH_4]^-$, and $[AlH_6]^{3-}$. Infrared and Raman vibrational spectra of existing alanates and borohydrides has established the nature of many of these compounds to be molecular ionic structures with the bending and stretching modes of the anions distinctly separated from the crystal modes involving motion of the cations. A simplified model of the structure of complex metal-hydrides consists of a rigid anion with appropriate charges on the center and vertex positions of, for example, the Al and H atoms, in AlH_4. These charges are conveniently provided by first-principles calculated Born effective charges from literature compounds. One may then simply optimize the total electrostatic energy of the crystal using a suitable optimization algorithm such as simulated annealing Metropolis Monte Carlo. Such a procedure has been developed for electrostatic interactions resulting in prototype electrostatic ground states (PEGS), the details of which can be found in the publication by Majzoub et al. [*Phys. Rev. B*, **77**, 104115 (2008)].

The Hamiltonian used in the PEGS approach consists of the electrostatic pair potential, with soft-sphere repulsion to prevent ion overlap as shown in Eqn (1), where the Z are the nominal ionic charges and r_{ij} is the distance between ions.

$$\sum_{i<j}\left(\frac{Z_i Z_j}{r_{ij}} + \frac{1}{r_{ij}^{12}}\right)$$

The method may be dramatically improved by incorporating potential energy smoothing. This remarkably successful method predicts ground state structures in many of the complex hydrides, including the sodium alanates, $NaAlH_4$, and Na_3AlH_6, and even quite complicated structures such as the bialkali alanate K_2LiAlH_6, and has been successfully applied to a very wide variety of materials. Below we highlight a few of the successes of the PEGS method as they apply to two materials investigated within the MHCoE, $Mg(BH_4)_2$ and $Ca(BH_4)_2$.

$Mg(BH_4)_2$

In the boron-containing hydrides, $Mg(BH_4)_2$ represents a compound with large hydrogen weight percent, and seemingly simple formula. However, two experimental determinations of the ground state structure indicate that the magnesium borohydride unit cell contains 330 atoms in the primitive cell in space group symmetry $P6_1$. The PEGS method produces a crystal structure prototype for $Mg(BH_4)_2$ in space group I-4m2, shown in Figure 44 below, with a first-principles total energy 5 kJ/mol formula unit below the experimentally observed crystal structure, suggesting that steric constraints during crystal growth, and the large volume change required to accommodate the I-4m2 structure may be important for the observation of the $P6_1$ structure.
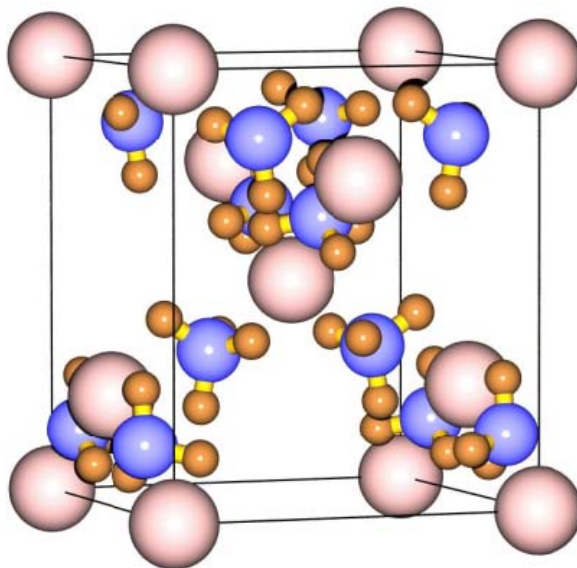
Figure 44. PEGS predicted structure for $Mg(BH_4)_2$ in symmetry I-4m2.

Ca(BH₄)

Depending on the preparation conditions and temperature, $Ca(BH_4)_2$ may be found in three or four different crystal structures. Two structures, the ground-state in symmetry *Fddd*, or *F2dd* and one elevated temperature polymorph in symmetry *P42/m*, were presumed known. PEGS identified several low energy crystal structure candidates for $Ca(BH_4)_2$. Two of the PEGS predicted crystal structures, *C2/c*, and *P-4*, appear to be observed in X-ray diffraction experiments and correspond to the ground state alpha phase and the beta phase. First-principles calculations indicate that *C2/c* is a competitive ground-state structure that is isoenergetic with the previously reported *Fddd*. The PEGS results correctly predict the phase stability as a function of temperature indicating a transition to symmetry *P-4* at elevated temperatures. Rietveld refinements of powder X-ray diffraction data confirm the reported beta phase structure has the predicted symmetry *P-4*.

Figure 45 shows the total free energy of competing phases of $Ca(BH_4)_2$ as a function of temperature, and indicates the alpha to beta phase transition, in agreement with experiment.
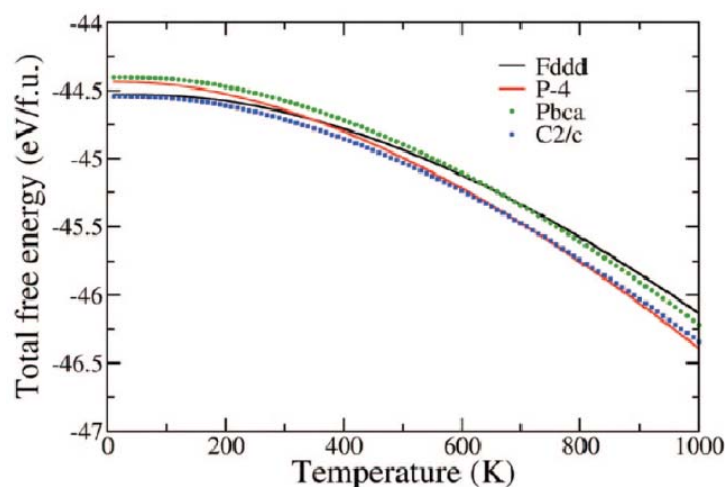
Figure 45. Total free energy of competing $Ca(BH_4)_2$ polymorphs as a function of temperature. The alpha to beta phase transition is indicated using PEGS-predicted structures.

Influence of Closoborane Salts on the Thermodynamics of Complex Borohydrides

Magnetic resonance studies within the MHCoE have shown that stable intermediates, in the form of B-H species, such as the closoborane $[B_{12}H_{12}]^{2-}$ salts are stable intermediates in the decomposition of many borohydride materials. Formation of closoboranes has a detrimental effect on the reversibility of these materials by effectively removing boron from the reaction and decreasing capacity. The crystal structures of these compounds were unknown. PEGS provided structure prototypes for Ca-, Mg-, Li-, and Na-$[B_{12}H_{12}]$ salts that were used in first-principles calculations to determine the resulting reaction pathways for decomposition in the borohydrides. The results indicated generally that formation of the closoborane salts is thermodynamically

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favored during decomposition, in agreement with experimental observation of these species. Additionally, crystal structure determination of several of these salts is in agreement with the PEGS-predicted structures.

The remarkable success of the PEGS method for structure determination of the complex hydrides indicates that the method captures the essential interatomic interactions in these compounds. The development of the method is one of the major successes of the MHCoE, and allowed for a theoretical understanding of the limitations of brute-force experimental compound searches, as well as addressing subtle structurally related thermodynamic properties.

More Detailed Consideration of the Factors Influencing Thermodynamics

All of the work discussed above relied on the use of DFT calculations for predictions of the thermodynamics of new material systems. However, early work in the MHCoE showed that DFT calculations were sometimes unable to *quantitatively* account for observed thermodynamics. Indeed, generally the errors associated with DFT values for ΔH were of order 10% or so. These quantitative difficulties were examined by Prof. Duane Johnson and colleagues at UIUC in order to provide an even greater accuracy to the theoretical prediction of new metal hydride hydrogen storage materials.

Molecular-based materials have significant contributions to the free energy arising from vibrations, of which there are two contributions, so-called harmonic vibrations and non-harmonic. For $LiBH_4$, the negatively-charged, tetrahedral $[BH_4]^-$ anions are charged balanced by Li^+ cations. The $[BH_4]^-$ anions are molecules that vibrate harmonically (e.g., typical molecular breathing and shear modes), whereas the Li^+ and $[BH_4]^-$ vibrate in response to each others motion and these are mostly anharmonic. For chemical reactions of interest in H-storage, the UIUC theorists showed that harmonic vibrations to thermodynamics mostly cancel out, whereas anharmonic vibrations do not.
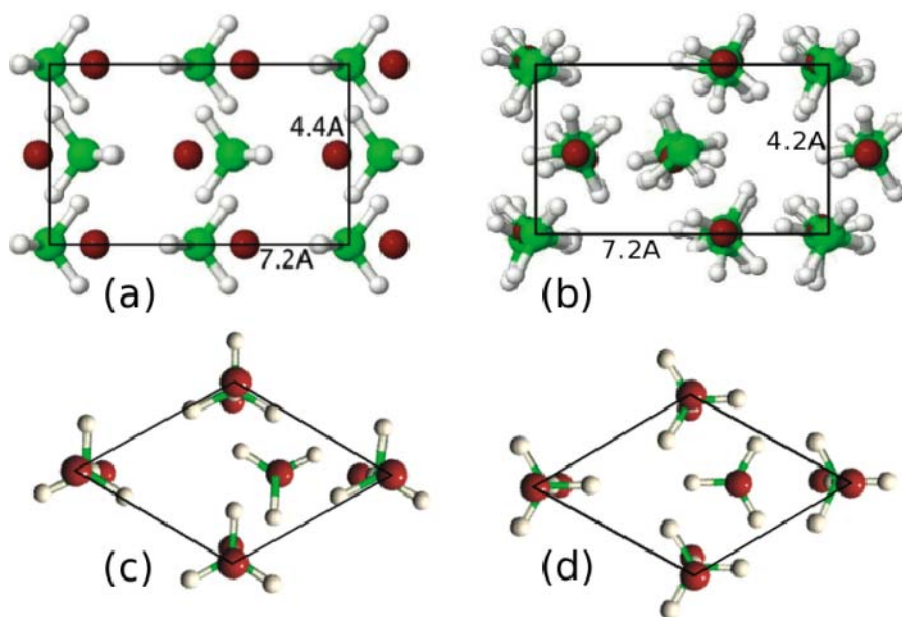
Figure 46. Bird's-eye view of possible LiBH$_4$ structures: (a) low-T orthorhombic (24-atom) cell; (b) our predicted new, high-T hexagonal structure showing the concerted BH$_4$ spiral-type rotations along the viewing axis that are the key low-energy anharmonic modes (which reduces to 12-atom cell by symmetry); (c) a 12-atom structure with BH$_4$ (symmetry-restricted) rotation due to electrostatic repulsion; (d) the ideal (P63mc) hexagonal structure assumed in experiment, but which cannot be correct due to electrostatic repulsion of protons on the H, as in (c). Note that structures (b-d) differ only by BH$_4$ orientation, which changes by the length they are correlated or, in calculations, is restricted due to choice of simulation cell.

The UIUC work detailed the origin and importance of such vibrational effects, reproducing all structural transformation in LiBH$_4$ versus temperature. Figure 46 shows structural properties of various phases of LiBH$_4$, including the predicted phase relevant for high-T adsorption (undetermined by experiment). This work provided an approximate but reliable means to include all vibrational effects, and yield quantitative predictions for the reaction enthalpies in all molecular-solid, H-storage materials.

The reaction 2LiBH$_4$ + MgH$_2$ ⟷ 2LiH + MgB$_2$ + 4H$_2$ was studied by HRL in the MHCoE and found to have an enthalpy of desorption of 41 kJ/mol-H$_2$ at 588-636 K. Previous theoretical calculation for this material gave up to 100% error for this desorption enthalpy. At 600 K, our theory gave 41 kJ/mol-H$_2$, in agreement with experimental data, as indicated in Figure 47 below. Note the highly exploded ordinate enthalpy scale and the small calculational errors. The theory indicated the melt phase appears at 600 K, in very good agreement with the observed H desorption studies. The proposed new first-principles-based method gave particularly accurate prediction of H-storage reaction enthalpies, required for thermodynamic assessment of potential candidate materials.
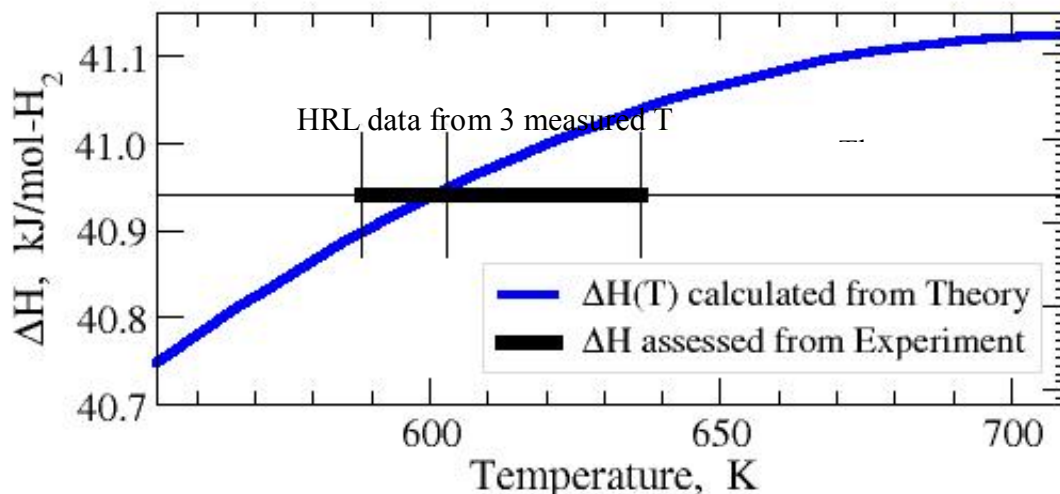
Figure 47. Reaction enthalpy ΔH versus T for $LiBH_4$ + MgH_2, both measured (van't Hoff average) and theory values (blue line). When the correct physics is incorporated, accurate theoretical estimates are made, including enthalpy for incongruent melting.

Summarizing the results for the Theory Group, we have now significantly advanced the use of DFT methodology to routinely predict promising materials systems based on their predicted ΔH and ΔG. These promising material reactions are predicted by assessing a wide range of P, T and composition, thereby focusing experimental efforts on promising compounds. Linear search methods have been implemented allowing the scanning of literally millions of different reaction conditions (composition, T, P). Theory can now predict the existence of important and surprising reaction intermediates that are being confirmed by experiment (e.g. $[B_{12}H_{12}]^{2-}$ intermediates). The Prototype Electrostatic Ground State (PEGS) method has been a breakthrough development for predicting crystal structures beyond the use of the ICSD database, thereby increasing accuracy and enabling thermodynamic predictions for new structural phases of materials. With more refined calculations, we have a much deeper understanding of the thermodynamics of selected reactions, and also the equilibrium thermodynamic properties.

Discontinued Materials and Materials Worthy of Further Work

Downselect Criteria

One of the primary tasks of the MHCoE has been to make sober assessments of the materials that have been discovered, and to assess if further work is really warranted on them, given the technical goals of the program. We call this process Materials Downselect. If a material is "downselected" we consider it worthy of further study, and work on it is continued. If a material is not "downselected," due to lack of promise, work on it is discontinued.. Although all of the DOE requirements indicated in Table 1 are required for a hydrogen-fueled light-duty automobile, within the MHCoE program particular attention has been paid to five technical targets because they are challenging and have a large influence on the successful engineered implementation of the technology. One of these is *system gravimetric density*. As indicated in Table 1, the 2010 system gravimetric target, indicating the mass of hydrogen stored per mass of the entire hydrogen storage system (including hydrogen storage material, tankage, and necessary plumbing) is 6%. A material's gravimetric storage density, indicating the mass of hydrogen stored per mass of hydrogen storage material (metal hydride) is intentionally not specified by the DOE to allow for different system designs. However, assuming at least a 50% weight penalty arising from the necessary system hardware, it is clear that the material's hydrogen storage capacity needs to be ~ 12% or higher to satisfy the 2010 targets. In our MHCoE research, we emphasize materials with a potential hydrogen storage weight percent exceeding the DOE system targets; however, materials with at least 5% that may serve as model systems for higher gravimetric capacity materials were also investigated.

A second system requirement specified by the DOE (and charged to the MHCoE) is that of *material reversibility*. The requirement for reversibility is implicit in the DOE requirement for cycle lifetime (2010 target: 1000 cycles). For a hydrogen-fueled auto to operate reliably, the hydrogen storage material must be able to take on hydrogen and release it many times over its lifetime. This is a challenging requirement from a materials perspective, and experience has shown that reversibility is especially challenging for the higher weight percent materials. From the MHCoE's perspective, we consider the threshold for reversibility to be 50% in the current phase of the R&D in which we are investigating new materials properties. The 50% reversibility criterion means that a material containing hydrogen must release hydrogen and then be capable of being regenerated with at least a 50% material yield after three hydrogen desorption/absorption cycles. Although the 50% material reversibility criterion was considered a suitable interim goal, from a practical perspective, the reversibility would need to be well in excess of 99% for a commercial storage system.

A third system requirement involves the *thermodynamic requirements*. It is desirable to use the waste heat from a fuel cell operating at 70–80 °C to drive off hydrogen from the metal hydride. Beyond the practical engineering issue of using waste heat from a fuel cell, if the material requires a high temperature to liberate hydrogen, the energy efficiency of the storage is reduced considerably. In a sense, the hydrogen storage material needs to be "metastable." The material

should be stable enough to store hydrogen near room temperature, yet be sufficiently unstable that only a modest amount of additional heat is required to liberate hydrogen completely and quickly. In the MHCoE R&D program, a material was not seriously considered if the temperature required to release hydrogen is above 350°C. For some experiments probing the effects of destabilization or nanoconfinement, materials with hydrogen desorption temperatures higher than 350 °C were considered. While it is understood that a hydrogen release temperature of 350 °C is significantly above the typical PEM fuel cell operating temperature of around 80 °C, important knowledge has been gained by R&D directed at reducing the temperature of metal hydride materials below 350 °C. We also came to appreciate that materials that may in fact be thermodynamically attractive may, by virtue of kinetic limitations, have high temperatures of hydrogen release.

A fourth material property considers *material stability and volatilization*. This material property is not explicitly called out in the DOE targets, but is implicit in the requirements for cycle lifetime and hydrogen purity (Table 1). Ideally, it is preferred that the hydrogen storage material liberates only hydrogen when heated and does not release volatile and reactive components such as NH_3, BH_3 or other gas-phase components. This requirement serves two purposes: preservation of the fuel cell (avoiding damage to catalysts and membranes); and maintaining hydrogen storage material integrity. If the storage material loses some of its components by volatilization as the material is heated, the hydrogen storage capacity will drop rapidly as the material is cycled. Certainly, if the material pathologically loses components by volatilization, and that volatilization cannot be prevented using additives or catalysts, the material will not be considered further. However, if there exists a low level of volatilization, such that the partial pressure of the component in the hydrogen gas stream is ~200 ppm, such a level would not produce a serious loss of material, although a 200 ppm level of contamination in the hydrogen stream could be a problem for the fuel cell itself. For fuel cell systems, the contamination target levels are less than 10 ppb sulfur, 1 ppm carbon monoxide, 100 ppm carbon dioxide, 1 ppm ammonia and less than 100 ppm non-methane hydrocarbons on a C-1 basis. Furthermore, oxygen, nitrogen and argon must not exceed 2%. In the MHCoE program, if a material volatilizes to less than the ~1000 ppm level for a single thermal cycle, it is still considered a viable hydrogen storage material worthy of further research, with the need for reductions in volatility clearly recognized.

Finally, *material kinetics* is critically important and forms the basis of the DOE target for fuel dispensing rate and hydrogen discharge. When the driver steps on the accelerator pedal, the storage system must deliver the required hydrogen flow rate. Perhaps even more challenging are the material's kinetics associated with refueling (rehydrogenation). In analogy with the current refueling operation of automobiles, a storage material must be capable of being recharged with hydrogen in approximately 3 minutes for a 5-kg hydrogen charge (2010 target). Both hydrogen delivery and hydrogen recharging of the material are severe technical challenges. In the MHCoE program, a criterion has been used that if a material takes longer than 24 hours to discharge or recharge, it is unlikely further R&D will bring the material into the practical kinetic realm, and work on the material is discontinued. It is clearly understood that charging and discharging in far less than 24 hours will ultimately be required.

Summarizing the MHCoE material performance metrics on which Go/No-Go decisions are based, the material's hydrogen storage gravimetric density should be at least 5 wt. %, the

material should be at least 50% reversible, the material should release its hydrogen for temperatures below 350 °C, the material's non-hydrogen volatilization products should not exceed 1000 ppm for a single thermal cycle, and the material should release hydrogen and reabsorb hydrogen in less than 24 hours. It is worth repeating that these criteria were used as guidelines in determining if specific material systems had sufficiently promising characteristics to warrant further work. They were not applied with absolute rigidity, nor do they substitute for the full DOE system targets for on-board hydrogen storage.

Using these guidelines, hydrogen storage R&D has been conducted within the MHCoE, and in the course of the work, many Go/No-Go decisions have been made on the viability of materials. These decisions are driven by the scientists doing the work, and are based on discussions of materials performance in individual MHCoE project meetings, MHCoE center-wide meetings held on a quarterly basis, and discussions within the Center's Coordinating Council. Such decisions are also based on feedback from DOE technical program management, from the FreedomCAR and Fuel Partnership Hydrogen Storage Technical Team meetings, and reviewer feedback from the annual DOE Hydrogen Program Merit Review and Peer Evaluation Meeting.

Over the course of the MHCoE work since the MHCoE inception in FY2005, 94 materials systems have been investigated in the 4 materials Projects (A-D) in the Center. Of these, research work on 84 materials was discontinued (not downselected) due to some shortcoming of the material. Ten materials have satisfied the 5 performance metrics listed above (i.e., show promise as a viable hydrogen storage material) and were thus downselected for further study, or represent materials for which insufficient information had been gathered to make the downselect decision.

Appendix I gives the list of materials considered by the MHCoE which were not downselected (were discontinued).. The materials are listed for Projects A–D, and within each project, roughly in time sequence (materials investigated early in the MHCoE listed first). Some selected examples of discontinued materials are now discussed.

For each system listed in Appendix I, the anticipated (going-in expectation) for the reaction is given, along with the partners involved, the theoretical hydrogen capacity, the standard enthalpy change per mole of hydrogen (ΔH) for the anticipated desorption reaction as written, the temperature for an equilibrium hydrogen pressure of 1 bar ($T_{1\,bar}$), and the temperature currently required for observable kinetics (T_K). When available, experimental data are used for ΔH and $T_{1\,bar}$; these entries are indicated as (exp). Otherwise, $T_{1\,bar}$ is obtained from the relationship $T_{1\,bar} = \Delta H/\Delta S$ where ΔH and ΔS are the changes in thermodynamic enthalpy and entropy (respectively) for the reaction as written. Values for ΔH and ΔS can be obtained from databases, including the Enthalpy (H)/Entropy (S)/Heat Capacity (C) (HSC) Chemistry Software Package for Windows, which give enthalpies and entropies for each species in the reaction. Such ΔH values are indicated by (db) in the tables. Alternatively, ΔH values obtained from density functional calculations performed by the MHCoE theorists are indicated by (DFT). Such DFT calculations typically include full vibrational contributions from the lattice. If a reaction is found to be not reversible, then an entry of N/A is given for $T_{1\,bar}$, since a true equilibrium does not exist. A dash (-) is entered in the tables if no information on that quantity is available.

The quantity $T_{1\,bar}$ is a purely thermodynamic construct, and does not convey information about reaction kinetics. To give a kinetic context for hydrogen adsorption/desorption from these materials, the Appendix I includes a "kinetic temperature" T_K. T_K is the temperature required for observable kinetics. It is subjectively defined from experimental data (e.g. thermogravimetric analysis, differential scanning calorimetry) as the temperature at which significant reaction occurs on the time scale of minutes up to an hour.

Examples of Discontinued Materials from Project A: Destabilized Materials

The primary focus of the Project A effort has been on high hydrogen capacity hydrides destabilized by additives that form new phases during dehydrogenation. The first system studied was MgH_2/Si, which forms Mg_2Si upon dehydrogenation. This material yields 5.0 wt. % hydrogen at 300°C and has an equilibrium hydrogen pressure at room temperature that is estimated to be near one bar. Formation of Mg_2Si during dehydrogenation was demonstrated experimentally. Unfortunately, rehydrogenation could not be achieved, presumable due to poor kinetics related to phase separation and segregation. The effort to achieve rehydrogenation included investigation of thin films, catalysts, nanoparticles, and mechanical activation. This work included contributions from all Project A members. As a result of the difficulty in achieving rehydrogenation, a No-Go decision on further work was made for this system at the end of FY2006, and work was discontinued. The MHCoE has also investigated $LiBH_4/MgX$ where X includes H, F, Cl, S, and Se, with $LiX + MgB_2$ being formed upon dehydrogenation. Full reversibility of ~10 wt. % hydrogen was demonstrated for $LiBH_4/MgH_2$ (i.e., X = H) before the start of the MHCoE program. However, the kinetics were slow and consequently temperatures >350 °C were necessary. The compounds X = F, S, Se were investigated beginning with the dehydrogenated phases $LiX + MgB_2$. For these three cases, it was not possible to hydrogenate the systems to $LiBH_4 + MgX$ and these reaction systems were discontinued.

Examples of Discontinued Materials from Project B: Complex Anionic Materials

The partners in Project B, Complex Anionic Materials, have been focussed on discovery and development of new high-capacity hydrogen storage materials. The first material that was under consideration was Ti-doped $NaAlH_4$, a material that is reversible at 100-150°C and 100-150 bar hydrogen pressure but with an ultimate capacity limited to 4.5 wt. % hydrogen. Thereafter, an effort was made to explore other potential bialkali alanates, which resulted in the discovery of K_2LiAlH_6. This material did not perform better than sodium alanate. Work was discontinued on the alanates because the hydrogen weight percent of the materials was limited to below ~ 5 wt. %.

A promising class of materials is the metal borohydrides with potential for up to ~16 weight percent capacity. $Ca(BH_4)_2$ was synthesized and extensively characterized, but it showed poor reversibility which did not improve with additives. In addition the desorption temperature was about 350 °C, which is too high for a practical material. Therefore, $Ca(BH_4)_2$ was discontinued. Alkali transition metal borohydrides of more than 10 weight percent capacity were also under consideration. The $A_xZn(BH_4)_y$ and $A_xMn(BH_4)_y$ materials (A = Li, Na, K) release hydrogen

below ~150 °C, but could not be reversed. The Zn-containing borohydrides also have a strong tendency to release diborane, B_2H_6. So, the Zn and Mn borohydrides were downselected.

Examples of Discontinued Materials from Project C: Amide/Imide Hydrogen Storage

The focus of the MHCoE Project C has been on the discovery and synthesis of amide ($-NH_2$) containing materials and their reactions with other metal hydrides (alanates, MgH_2) for hydrogen storage applications. The interest on amide containing materials was first prompted by the published work from Chen et al. [*Nature*, **420** 302 (2002)] on the potential of using Li_3N as a hydrogen storage material. This reaction was considered originally by Project C, but was not pursued due to its poor dehydrogenation kinetics.

Studies were initiated of the reaction between lithium amide with lithium alanate. The $LiNH_2/LiAlH_4$ system was found to release considerable amounts of hydrogen (~8 weight percent) at temperatures of ~300°C. However, this material system is not sufficiently reversible, so was given a No-Go status in FY 2006.

The amide material system $Li_3AlH_6 + 2LiNH_2$ was investigated for its hydrogen storage properties. Unfortunately, this material showed poor reversibility, and was also discontinued.

Materials Examined Near Program End In the last year of the MHCoE, a number of materials were investigated. In some of these, sufficient promise was shown, but when the MHCoE effort ended, there was not enough data to make the "downselect" decision. Some of these materials are described below.

$Mg(BH_4)_2(NH_3)_2$

$Mg(BH_4)_2(NH_3)_2$ was synthesized by reacting $Mg(BH_4)_2$ with NH_3. The properties of $Mg(BH_4)_2(NH_3)_2$ are very sensitive to how it is made. If not processed properly, the desorption of this compound gives significant amount of NH_3. When it is synthesized properly, as demonstrated by the GE group, it desorbs hydrogen without much NH_3 formation. Presumably the dihydrogen bonds between the NH_3 group and the BH_4 group significantly facilitate the hydrogen desorption, reducing the desorption temperature from ~290 °C of $Mg(BH_4)_2$ to ~100 °C for $Mg(BH_4)_2(NH_3)_2$. Partial reversibility is observed at mild conditions after partial desorption.

$(NH_4)_2B_{10}H_{10}$

$(NH_4)_2B_{10}H_{10}$ was synthesized from $(NH_4)_2B_{10}H_{10}\cdot1.5H_2O$. It contains 11 wt. % H and it is a crystalline compound. TGA shows hydrogen desorption started ~190°C and ~ 9% weight loss was observed up to 400 °C. The low temperature onset is particularly interesting. Mass spectroscopy analysis of the desorbed gases shows a sizeable amount (~3.3 mole %) of ammonia is released although no diborane was observed. Rehydrogenation of 1.8 wt. % was observed at a mild condition (240 °C and 93 bar hydrogen pressure) even without any catalyst, which is quite

promising. Given the attractive aspects of this material, more data is needed to fully understand its hydrogen storage potential.

$ANH_2/B(BH_4)_x$

There is potential advantage of having both B and N in the same molecule because of the presence of both 'hydridic' B-H and 'protic' N-H bonds. Solid state structures of a number of structurally characterized B and N-containing hydrides exhibit short B-H···H-N intermolecular interactions believed to favor the formation of the dihydrogen bond. Sandia investigated $Ca(Mg)(BH_4)_2$-$LiNH_2$ and $Ca(Mg)(BH_4)_2$-$NaNH_2$ systems and found new phases were formed upon ball milling at room temperature. TGA/DSC and RGA analyses indicate that significant amount of ammonia is released upon heating, typically starting <100 °C. Additional residual gas analysis (RGA) study of $Ca(BH_4)_2$-$LiNH_2$ showed that the amount of ammonia can be significantly reduced (up to 50 times) when a third component (namely LiH or MgH_2) is added before the ball-milling step. This offers promise for these materials, especially the tri-component mixtures borohydride-amide-hydride and justifies additional investigations in this area.

AlB_4H_{11}

For this material, thermal decomposition starts around 125°C and the desorbed gas is H_2 with less than 1% diborane. PCT measurement shows ~ 8 wt.% and ~11.5 wt. % H desorption at 250 °C and 400°C, respectively, indicating a very promising hydrogen capacity. PCT experiments show that up to 2.5 wt.% H was re-absorbed during charging at ~220°C and ~100 bar H_2, relatively mild conditions for rehydrogenation. Overall, we feel that further study of this material is warranted because this compound is one of the very few boron hydrides that show reversibility at mild conditions. It is highly recommended to continue the exploration of this very interesting compound.

$Al(BH_4)_3/NH_3$

The products from the reaction of NH_3 with $Al(BH_4)_3$ depend on stoichiometry, solvent (or absence thereof), and other reaction conditions. To date ORNL has prepared and identified diammine, triammine, and hexamine adducts as well as a dialuminum species in which partial decomposition of borohydride has occurred. Hydrogen evolution from the diammine adduct, $Al(BH_4)_3(NH_3)_2$, occurs at a lower temperature than the parent compound, $Al(BH_4)_3$, beginning at 100 °C and ultimately yielding 15.1% hydrogen. Decreased H_2 evolution under 100 bar hydrogen pressure indicates potential reversibility although H-1 NMR does not indicate any H_2 uptake when the rehydrogenation reaction is conducted at 200 °C.

The triammine adduct, $AlBH_4)_3\cdot3(NH_3)$, is formed from the reaction of NH_3 with $Al(BH_4)_3$ in toluene. This material also begins H_2 evolution around 100 °C, ultimately evolving 15.9% hydrogen with almost no observed evolution of ammonia or diborane. We have no direct evidence of reversibility in the hydrogen evolution reactions of the diammine and triammine materials to date, but the quantity of hydrogen evolved by 150 °C (~12-13 %) is quite high. Furthermore ammonia and diborane are essentially absent as reaction products. Reaction schemes in which AlH_3 (formed from the reaction of Al metal with H_2) reacts with a $(BHNH)_2$ polymer product are

plausible for a regeneration pathway if an effective catalyst can be discovered. It is recommended that exploration of this very interesting series of compounds be continued.

High-Priority Materials Requiring Further Work

In the final year of the MHCoE, an emphasis was given to identifying high-priority materials that the HSECoE could work on, and also to give guidance to the community at large which materials classes were most worthy of further study. These materials have already been discussed in the MHCoE highlights from each of the projects, and include $Mg(BH_4)_2$, LiMgN, $2LiNH_2/MgH_2$, Al regenerated by organometallic approaches and electrochemical means, and $LiAlH_4$ regenerated with hydrogen in DME.

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Comparison of Materials to DOE Targets

In this section we take a step back and assess the best materials the MHCoE has produced and compare them against the targets set forth by the DOE at the beginning of the MHCoE. The DOE storage system targets are reproduced in part in Figure 48 (A). These targets are for the entire storage system that would be placed inside a light duty vehicle, including not only the metal hydride material, but also the tankage holding the metal hydride, the heat exchange hardware inside the tank to allow thermal management of the system, all associated plumbing, regulators, pressure relief devices, and other pieces of hardware. However, in our materials work, most of our information arrives in the form of materials properties, for example the material gravimetric capacity, and material volumetric capacity, and so on. In order to compare to the DOE targets, it is most convenient to translate the system "targets" into materials "goals."

(A)

Storage System Parameter	2010 DOE Target (New)
System Grav.: kgH$_2$/kg-system	4.5%
System Vol.: gH$_2$/L system	28
System Fill Time (5kg H$_2$): mins	4.2
Operational Cycle Life: cycles	1000
Hydrogen Purity	99.97% (dry)

Convert to inferred materials properties for making Spider Charts

(B)

Storage Material Parameter	"Goal"
Material Grav.: kgH$_2$/kg-material	9.0%*
System Vol.: gH$_2$/L material	56**
1/(Fill Time) Min^{-1}	0.238
Operational Cycle Life: cycles	1000
1/(Fuel Impurities) ppm^{-1}	0.01

* Assumes 50% system gravimetric penalty

** Assumes 50% system volumetric penalty (including packing density penalty)

Figure 48. Conversion of DOE Hydrogen Storage System Parameters and Targets (A) to Hydrogen Storage Material Parameters, and "Goals" (B), assuming 50% system gravimetric and volumetric penalties.

To perform this translation, some assumptions must be made about the engineering gravimetric and volumetric penalties that would exist if a metal hydride were actually deployed in a real system. We will assume that the hardware imposes a 50% volumetric penalty and a 50% gravimetric penalty on the materials properties. It's possible that these penalties could be somewhat less in a cleverly designed storage system, which would then place fewer demands on the materials gravimetric and volumetric density goals. Another caveat is that the gravimetric and volumetric penalties may vary somewhat from material to material. Using the 50% penalty

assumptions, Figure 48 (B) shows the storage material "goals" that are in support of the DOE targets.

In anticipation of presenting the results in the form of "Spider Charts," it is visually more straightforward to cast several of these parameters in a form such that smaller numbers are worse and bigger numbers are better. For example, in Figure 48 (B), we recast "Fill Time" as 1/(Fill Time), so that if excessively long fill times are required (Fill Time large), then 1/(Fill Time) becomes a smaller number which appears worse when plotted on a spider chart. Similarly, for Fuel Impurities, if the material produces large impurites in the hydrogen stream, we recast this property as 1/(Impurities) so that 1/(Impurities) becomes a smaller (worse) number when plotted on a spider chart.

Of the 94 material systems which were investigated in the MHCoE, only two were considered for "off-board" regeneration, namely AlH_3 and $LiAlH_4$. We accepted the premise of off-board regeneration for these two materials because they possessed very attractive hydrogen release properties, but were problematic in their reversible behavior. For "off-board" regeneration materials, the Fill Time becomes a less urgent issue. What becomes a very important issue is the well-to-tank (WTT) energy efficiency. The WTT efficiency indicates how much of the hydrogen energy content contained in the metal hydride is required to regenerate the metal hydride itself. The DOE target for WTT efficiency is 60%.

Figure 49 below shows a number of the materials goals, along this the WTT goal, and compares them to the properties observed for $LiAlH_4$ and AlH_3. We note here that the "Minimum Delivery Pressure" and the "Minimum Flow Rate" targets are for operation at 85 ºC, the temperature of waste heat from a Proton Exchange Membrane (PEM) fuel cell. There are actually wide-ranging requirements on the purity of the hydrogen stream, with extremely stringent limits on H_2S, and less stringent on for example CO_2. For the purposes of the spider charts, we assume that the needed purity in the hydrogen stream is set at 100ppm, thereby making the goal 1/(Fuel Impurity) = 0.01 for the Spider Charts.

Materials "Goals"		LiAlH$_4$	AlH$_3$
Gravimetric Density (wt. %)	9%	7.5%	9.8%
Volumetric Density (gH$_2$/L)	56	74	139
Min. Delivery Pressure @ 85°C (PEMFC) (bar)	5	5	>5
Cycle Life	1000	5	1
WTT Efficiency	60	60	55
Minimum Flow Rate (gH$_2$/sec) @ 85 °C	1	0.2	1
1/(Fuel Impurities = 100 ppm) ppm^{-1}	0.01	∞	∞

Figure 49. Measured values of "Material Goals" for "Off-board Regenerated Metal Hydride Systems LiAlH$_4$ and AlH$_3$

It is quite common to make such comparisons between properties and goals in the form of a "Spider Chart." Such a chart is shown in Figure 50 (A), which gives a spider chart for a hypothetical material whose properties meet all of the material goals of Figure 49. The material properties are located along axes issuing radially from the center point, with the endpoint of each axis marking the material goal as listed in Figure 49. Each axis possesses a <u>linear</u> scale along which the observed material property is plotted. The axes are demarcated every 20%, the visual effect producing a spider web. Lines are drawn between the points on the axes marking the observed material property, with the area inscribed within filled in with color. While it is natural to react to the area of the enclosed shape, it must be pointed out that the plots only have definition along the radial axes.
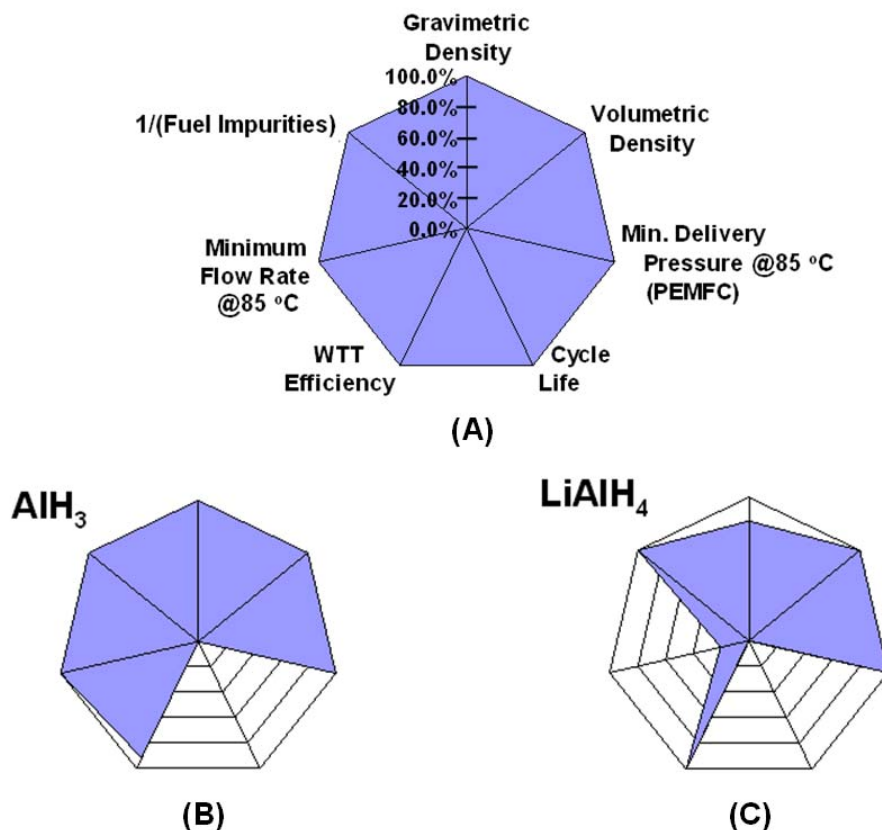
Figure 50. Spider charts for a hypothetical material that fully satisfies the material goals (A) and for AlH₃ (B) and LiAlH₄ (C).

AlH₃ and LiAlH₄: "Off-Board" Reversible Materials

Two materials, AlH₃ and LiAlH₄, were investigated separately for "off-board" generation due to their exceptionally high performance in hydrogen release. In Figure 50 (B) and Figure 50 (C) we plot the properties for AlH₃ and LiAlH₄, respectively. For plotting purposes, if the material property exceeds the goal, we plot the property as being equal to the goal to maintain the integrity of the spider chart.

Figure 50 (B) shows the materials properties for AlH₃ meet or exceed the materials goals in five of the materials property categories. The WTT efficiency is slightly less than the goal, and the cycle life requirement is far from being met. Although the organometallic and electrochemical approaches to regeneration have shown success for a single cycle, these processes have not yet demonstrated success for many repeated cycles. Success for many repeated cycles requires very high efficiency for a single step. So, the spider chart indicates a big gap between the AlH₃ cycling goal, and the observed cycling which is experimentally limited to one cycle to date. It is important to note that the plotted material property for cycle life only represents what's been demonstrated in the laboratory. It is not a projection of what we think could be achieved; rather it shows what has been achieved thus far.

Figure 50 (C) shows the spider chart for LiAlH$_4$ using the values listed in Figure 49. This material falls a bit short on gravimetric capacity. There is an order of magnitude gap in the Minimum Hydrogen Flow Rate that would be observed at 85° C, indicating that more work needs to be done to improve the kinetics of this material. There is a very large gap on demonstrated cycle life. LiAlH$_4$ has in fact been reversed 5 times using the low temperature low pressure DME process developed by UNB and UH. However, some degredation was observed in the hydrogen capacity as the material was sequentially rehydrogenated. As indicated by Figure 50 (C), more work needs to be done on dehydrogenation kinetics, and understanding the cause of the drop off in material hydrogen capacity with cycling.

Summarizing the comparisons of the "off-board" MHCoE materials AlH$_3$ and LiAlH$_4$ with the materials goals, these materials show great promise for constituting a viable hydrogen storage material. However, the repeated reversibility of these materials (i.e., cycling) needs to be demonstrated while maintaining a high WTT efficiency.

We turn now to consideration of the vast majority of the MHCoE materials which were considered for "onboard" reversible regeneration. For these materials, we do not plot the WTT efficiency, but rather plot 1/(Fill Time), as this is particularly important for an onboard reversible system. Figure 51 (A) shows the spider chart for a hypothetical material whose material properties meet all of the materials goals in Figure 48 (B). Figure 51 (B) and 51 (C) show spider charts for two materials that represented the state-of-the-art in solid-state hydrogen storage in 2005 when the MHCoE began its work. Figure 51 (B) shows a spider chart for Ti-catalyzed sodium alanate (NaAlH$_4$), which remains probably the best characterized complex anionic metal hydride material in existence. Figure 51 (C) shows a spider chart for a commercial interstitial metal hydride sold by Ovonic Hydrogen Systems, a proprietary AB$_2$H$_3$ alloy in which A is a mixture of Ti and Zr and B is a mixture of V, Cr and Mn. For our purposes this AB$_2$H$_3$ alloy represents the general class of interstitial metal hydrides that have been studied for decades.

It is clear from Figure 51 (B) that NaAlH$_4$ falls short of the goals in gravimetric capacity, minimum flow rate, cycling and a bit short on recharge time. However, NaAlH$_4$ yields very pure hydrogen with excellent volumetric density and an equilibrium pressure at 85 ºC that satisfies the material goal. It turns out that NaAlH$_4$ has only been demonstrated to cycle for ~ 100 cycles. Longer tests of cycling are needed. The ability to produce the acceptable equilibrium pressure at the low temperature of the PEM fuel cell waste heat is a remarkable property of this material.
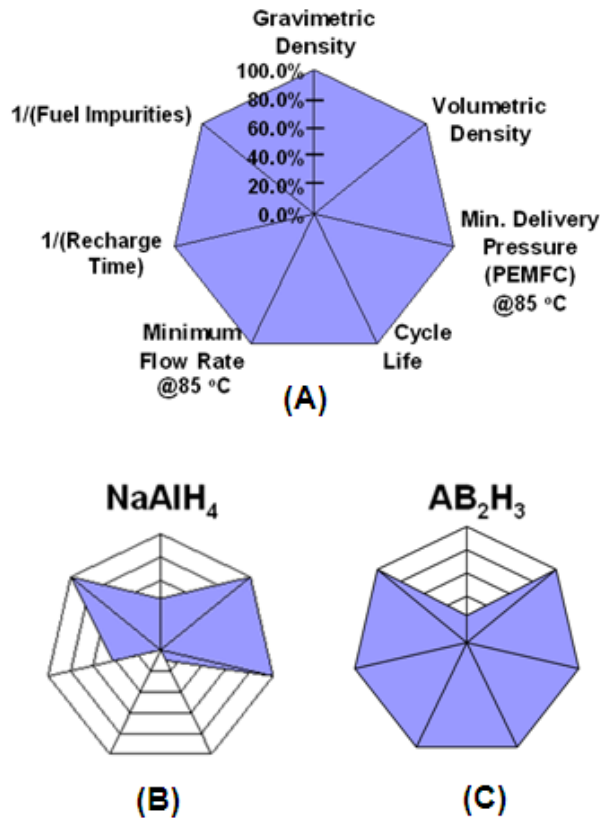
Figure 51. Spider charts for a hypothetical material that fully satisfies the material goals (A) and for NaAlH₄ (B) and a proprietary Ovonic commercial alloy (C) where A= Ti, Zr and B= V, Cr, and Mn (bottom right).

Turning attention now to the interstitial metal hydride from Ovonic, it is clear that this material actually performs quite well in many of the categories. However, as is true for all interstitial metal hydrides, this material falls short in the gravimetric capacity when compared to the material goal. Figure 51 (A) and 51 (B) indicate the approximate state of the art when the MHCoE began its work in 2005.

We show in Figure 52 spider charts for selected materials we have found in the MHCoE work, namely LiBH$_4$/MgH$_2$, LiBH$_4$/Mg$_2$NiH$_4$, Mg(BH$_4$)$_2$, 2LiNH$_2$/MgH$_2$ and LiNH$_2$/MgH$_2$. Figure 53 tabulates the observed materials properties of these five systems in comparison to the materials goals of Figure 48.
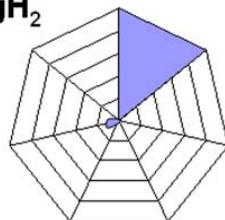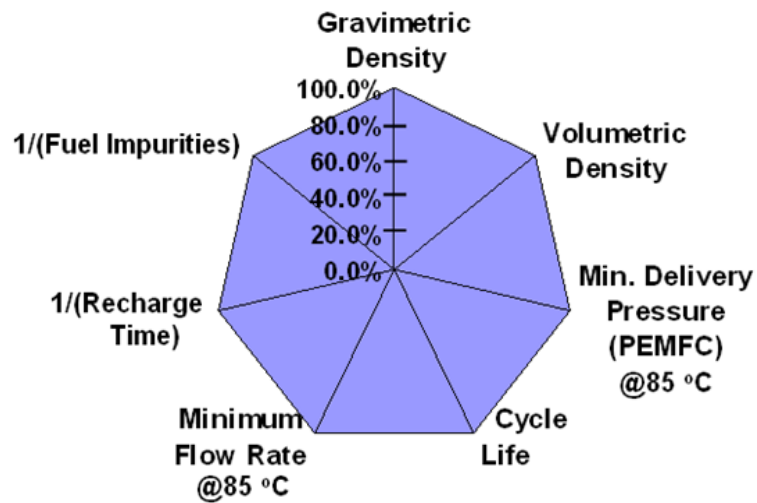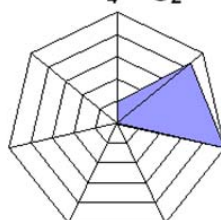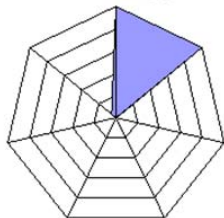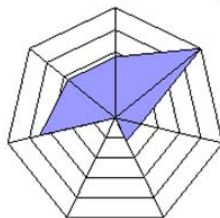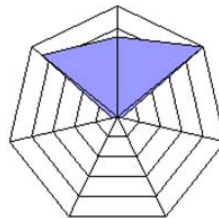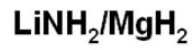
Figure 52. Spider charts for LiBH$_4$/MgH$_2$ (A), LiBH$_4$/Mg$_2$NiH$_4$ (B), Mg(BH$_4$)$_2$ (C), 2LiNH$_2$/MgH$_2$ (D) and LiNH$_2$/MgH$_2$ (E)

2010 Materials "Goals"		$LiBH_4/$ MgH_2	$LiBH_4/$ Mg_2NiH_4	$2LiNH_2/$ MgH_2	$Mg(BH_4)_2$	$LiNH_2/$ MgH_2	AB_2H_3 A = Ti, Zr B = V, Cr, Mn	$NaAlH_4$
Gravimetric Density (wt. %)	9%	10%	1.7%	5%	11%	6.5%	2.1%	4%
Volumetric Density (gH_2/L)	56	95	48	70	147	107	110	80
Min. Delivery Pressure @ 85 °C (PEMFC) (bar)	5	0.022	10	1.2	0.035	0.2	70	0
Cycle Life	1000	10	10	235	2	10	1000	100
Minimum Flow Rate (gH_2/sec) @ 85 °C	1	~0	~0	~0	~0	~0	1.5	~0
1/(Recharge Time = 4.2 min), min^{-1}	0.238	0.0333	0.0083	0.1667	0.0028	0.0110	0.0660	0.1
1/(Fuel Impurities = 100 ppm), ppm^{-1}	0.010	unknown	unknown	0.0056	0.0005	0.0088	∞	∞

Figure 53. Measured values of "material goals" for "on-board regenerated" metal hydride systems $LiBH_4/MgH_2$, $LiBH_4/Mg_2NiH_4$, $2LiNH_2/MgH_2$, $Mg(BH_4)_2$, $LiNH_2/MgH_2$, $NaAlH_4$ and AB_2H_3 (A = Ti, Zr; B = V, Cr, Mn).

$LiBH_4/MgH_2$

$LiBH_4/MgH_2$ existed prior to the MHCoE as reported by Vajo and Olson [*Scripta Materialia*, **56,** 829-834 (2007)], although its incorporation into carbon aerogels was intensively investigated by HRL during the tenure of the Center. The bulk material still represents one of the highest gravimetric capacity reversible metal hydrides in existence. As can be seen from Figure 53 (A), this material has excellent gravimetric and volumetric hydrogen storage density. However, the purity of the hydrogen emitted from this material has not been measured, and there is some concern that diborane (B_2H_6) may accompany hydrogen release from this material. Because the purity of the hydrogen release is unknown, we assign it a 1/(fuel impurity) value of 0. Although the $LiBH_4/MgH_2$ ΔH is 40.5 kJ/mole H_2, a very attractive value, the material appears to be severely kinetically limited, causing the practical H_2 desorption temperature to be ~400° C. Thus, the equilibrium hydrogen pressure and hydrogen flow rates at 85° C are practically nonexistent.

$LiBH_4/Mg_2NiH_4$

Recently, HRL has extensively characterized the $LiBH_4/Mg_2NiH_4$ system, as described in the Project A Summary. This is a very interesting system that in many ways displays the full power of the "destabilization" strategy. Although the weight capacity of this material is not as good as

$LiBH_4/MgH_2$, $LiBH_4/Mg_2NiH_4$ possess superior thermodynamics that allow for much improved kinetics at lower temperature, thereby providing good equilibrium hydrogen delivery pressure at 85° C. The possible contamination of the hydrogen stream with B_2H_6 is unknown, although it may not be too bad given that the system is highly reversible (indicating material volatilization is not a major problem).

$Mg(BH_4)_2$

$Mg(BH_4)_2$ represents the highest hydrogen capacity reversible material that we have discovered, albeit the reversibility is achieved at much higher temperatures and pressures than is desired. This material was discussed extensively in the Project B Summary. The delta ΔH for hydrogen desorption for this material is ~40 kJ/mole H_2. However, the material is apparently severely kinetically limited, and the temperatures required for significant hydrogen desorption are ~300 ºC. Because of this kinetic limitation, the hydrogen desorption observed at 85°C would be virtually zero, leading to negligible H_2 equilibrium pressure and H_2 flow rate at the temperatures associated with PEM fuel cell waste heat. $Mg(BH_4)_2$ possesses a very high volumetric density and sets the record (12 wt. %) for the gravimetric capacity of a reversible metal hydride system.

$2LiNH_2/MgH_2$

The material $2LiNH_2/MgH_2$ is one of the more practical materials that were discovered in the MHCoE, and was discussed in the Project C Summary. Although its gravimetric capacity is limited to ~ 5wt. % (falling short of the material goal), its recharge time nearly satisfies the goal, and its volumetric storage density meets the goal. In addition, it is unusual in comparison to most of the complex anionic metal hydrides in that it has been very extensively cycled, 264 times in experimental tests. More cycling would be required to satisfy the material cycling goal. The hydrogen purity has also been measured, with ~200ppm NH_3 found at 200 ºC, which is almost 60% satisfaction of the material goal.

1:1 $LiNH_2/MgH_2$

This material is closely related to its cousin $2LiNH_2/MgH_2$, and was also discussed in the Project C Summary. The larger proportion of magnesium hydride in this material allows it to reach a more fully dehydrogenated state (LiMgN), thereby allowing the system to move past the "imide" intermediate which limits the $2LiNH_2/MgH_2$ material to 5 wt %. The 1:1 material has shown a reversible hydrogen capacity of 6.5 wt. %, a significant improvement beyond $2LiNH_2/MgH_2$, but the reversibility has only been demonstrated for a few cycles. This material still needs work to improve its kinetics, and catalytic studies were only just beginning when the MHCoE came to an end. The equilibrium plateau pressure is significantly lower than for $2LiNH_2/MgH_2$. The amount of NH_3 impurity in the hydrogen released from this material shows a complicated dependence on heating rate.

Summarizing the comparisons for the "on-board" MHCoE materials with the materials goals, the H_2 capacity (wt. %) was significantly improved with high volumetric density and good H_2 purity. However, the "on-board" materials have poor kinetics at 85 ºC, and robust cycling has not been demonstrated.

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Recommendations from the MHCoE on Future High-Priority R&D Directions

Summarized here are recommendations from the MHCoE to the international hydrogen storage community on high-priority future R&D directions for metal hydride hydrogen storage materials.

Destabilized Materials

The work in the MHCoE has established that metal hydride systems can be destabilized by addition of a second compound to provide lower thermodynamic thresholds for releasing hydrogen. It is clear from the studies that much more fundamental work is needed on the mechanism of the destabilization and how the kinetics can be improved. The work of HRL on the $LiBH_4/Mg_2NiH_4$ material showed that entirely new reaction pathways can emerge in these multicomponent metal hydride systems. The detailed mechanistic route by which destabilization is achieved needs to be examined in much greater detail for existing promising destabilized systems and those yet to be discovered.

It is also clear from the studies that the destabilized systems are severely kinetically limited. This kinetic limitation may be due to the fact that by introducing a second component into a metal hydride system, one is introducing a second material phase. In the "initial state" of the reaction, these phase-phase interactions can determine how fast hydrogen is released. Certainly improvements can be made on how intimately these phases are intermixed in the starting (hydrogenated) compound. Upon hydrogenation, it seems logical that two separate materials phases need to be generated to get back to the initial hydrogenated state. This phase separation must introduce kinetic barriers for the rates of hydrogenation. However, we do not understand these phase-induced kinetic limitations in any real way, and the thoughts above are largely speculative.

Therefore, based on this situation, we recommend future fundamental studies be directed towards understanding the role of solid-solid interfaces on the kinetics of hydrogen desorption and absorption. In particular:

1. More studies are needed to characterize the interface area and structure of destabilized systems. Ultimately, these studies should include how additives affect the interfacial areas and structures, and how processing can affect them as well.

2. Studies are needed that can correlate the structure and area of the interfaces between the two destabilized components with the kinetics which are actually observed. In other words, more study is needed to understand the role of the phase separation problem in the observed kinetics of hydrogen desorption and absorption.

3. The interfaces between the two materials phases need to be understood theoretically, and hopefully correlated with the observed kinetics.

Nanoscaffolds/Nanoporous Materials

Research in the MHCoE has demonstrated several advantages may accrue when incorporating a metal hydride into a nanoporous material. For example, the kinetics of hydrogen release can be enhanced greatly ($LiBH_4$, MgH_2), the reversibility can be improved ($LiBH_4$), and in some cases precursor stability can be improved as well ($NaTi(BH_4)_2*DME$). The going-in assumption of why the kinetics might be improved are based on the general idea that diffusion times follow the relationship $t \sim l^2/D$ where t is the diffusion time, D is the diffusion coefficient, and l is the required diffusion distance. So, if nanoporous materials reduce the required diffusion distances, diffusion time should be reduced and reaction rate should increase. This is only a very general concept, and in fact, the real atomistic mechanism for why the kinetics of the studied systems are being so dramatically improved remains unknown.

In the MHCoE, these nanoscaffold, or nanoporous materials are being investigated not so much as practical storage materials, but as model systems in which to understand the prospects of nanoconfinement to enhance thermodynamics and kinetics. In order for these nanoconfined materials to serve as practical hydrogen storage materials, the gravimetric and volumetric penalties associated with the nanoscaffold need to be significantly reduced, as reviewed previously in the Project A Summary.

Therefore, based on this situation, we recommend future fundamental studies be conducted on metal hydrides confined to nanoporous structures. In particular, we recommend that:

1. Fundamental studies be performed on understanding the nature and origin of fast diffusing species presumed to exist in these nanoconfined systems. NMR will be a key analytical tool in these studies.

2. The nature of the scaffold-hydride interactions needs to be understood in much greater detail. Within the MHCoE, UTRC has provided the first theoretical understanding of these interactions which are likely to drastically affect the stability and reversibility of the hydrogen storage system. These and future theoretical studies of nanoconfinement need to be combined with careful experimental investigation to fully understand the scaffold hydride interactions.

3. Much more work is needed to understand the effects of scaling particle dimensions down to the nanoscale on hydrogen storage. The work in the MHCoE focused on nanoscaffolds with a minimum pocket size of ~ 13 nm. However it's possible to incorporate metal hydrides into even smaller nano pockets, and the effect on thermodynamics should be understood better.

4. Nanomaterials with ~ 5–10 nm pore dimensions, with greater than 3 cm^3/g pore volume, need to be developed to reduce the gravimetric penalty associated with using nanoconfinement. More fundamental synthetic and structural study needs to be performed on nanoscaffolds, (both C-based and inorganic), with an emphasis on reducing the wall thicknesses between nanopockets.

Kinetics of Solid-State Reactions

Almost all of the complex anionic materials that were developed in the MHCoE were severely kinetically limited. Our theoretical understanding of the kinetics of solid-state reactions in the hydrogen storage arena is almost nonexistent. In addition, a detailed exploration of this fundamental research topic was not really appropriate for the more applied EERE MHCoE research and development program.

Clearly, being able to address quantitatively the kinetics of these hydrogen desorption and absorption reactions requires detailed understanding of the mechanistic pathways, the intermediates involved, and understanding the activation barriers that the reactions must must overcome. The development of a robust theory of solid-state reaction kinetics is an extremely challenging problem, and is worthy of the title "Grand Challenge."

Therefore, we recommend for the future that detailed theoretical methods be developed to predict and account for kinetics of model solid phase hydrogen storage reactions. Furthermore, we recommend these theoretical studies be conducted in concert with experiments needed to validate the theory.

Catalysis of Solid-State Reactions

It is well known in hydrogen storage materials science that catalyst can play a very important role in the kinetics of these reactions. The most famous of these is the discovery that ~ 2-4 mole % of Ti, drastically improves the properties of $NaAlH_4$, particularly in hydrogenation. Over 10 years of effort have been invested by the community on trying to understand the role of this one elemental catalysts on the behavior of $NaAlH_4$ and the situation is still not completely understood.

In the MHCoE, there have been a number of examples where catalysts are observed to play dramatic roles in the hydrogen storage reactions. For example, it was found that 4 mole % of KH increases the hydrogen absorption rate for the $2LiNH_2/MgH_2$ system by ~ 2-3 times. In general, we have very little theoretical understanding of how these catalysts work. As a result, we have no guiding understanding to develop a strategy for choosing catalysts for a particular hydrogen storage reaction. Given the importance of kinetics in these systems, it's very important to improve our understanding of how catalysts aid the kinetics of both hydrogen desorption and absorption reactions.

Therefore, we recommend for the future that, although it will be a very challenging task, detailed theoretical approaches need to be developed that will elucidate how specific catalytic agents are improving the kinetics of well-documented experimental hydrogen storage systems. This will require concerted theoretical and experimental work. A theoretical method, thus validated by experimental work, could then be used to predict new catalysts for enhancing the kinetic performance of the high priority metal hydride storage systems.

Borohydrides

The borohydrides offer the potential for 12–14 wt.% materials, and their properties can vary widely. We need to gain a fundamental understanding of the "knobs" that control borohydride properties, such as: reversibility, diborane release, ammonia release, temperature for H_2 release. With this understanding, a truly remarkable material might be found.

Therefore, we recommend for the future that much more emphasis, particularly fundamental work, be applied to the borohydride materials. Although over 50 borohydride systems were investigated in the MHCoE, many more systems remain to be discovered. Combined theoretical and experimental studies of borohydride stability, and their tendency to release diborane needs further work. Combined with these future borohydride studies would be more investigation of the role of $[B_{12}H_{12}]^{2-}$ species, and how these enter into the reaction pathways for borohydride hydrogen desorption and absorption reactions.

Prospects for a Truly Remarkable Metal Hydride Hydrogen Storage Material

As described in this Final Report, many materials were investigated in the MHCoE, and great advances were made in synthesizing new materials, understanding their properties, and developing theory to account for their behavior. Although a great deal of progress was made, the MHCoE effort did not find a material that simultaneously satisfies all of materials goals consistent with the DOE targets. What are the prospects for finding a truly remarkable material that *can* meet all of the goals?

We believe that such a material may lie in the family of the borohydrides. The borohydrides offer the potential for 12–14 wt. % hydrogen storage capacity, exceeding the materials goals for gravimetric capacity. Furthermore, their properties can vary widely, thereby providing chemical "knobs" that can be adjusted to provide the desired properties.

Figure 54 gives some examples of the type of chemical variability seen in the borohydrides:

$Mg(BH_4)_2$ releases H_2 at 295 ºC,
yet $Na_2Zr(BH_4)_6$ releases H_2 at 40-110 ˚C

$Li_2Zn(BH_4)_4$ releases H_2 with 30% B_2H_6 contamination,
yet $Na_2Zr(BH_4)_6$ releases H_2 with no detectable B_2H_6

$Ca(BH_4)_2$•$2NH_3$ only releases NH_3 upon heating
yet, $Mg(BH_4)_2$•$2NH_3$ only releases H_2 upon heating

$Mg(BH_4)_2$ is ~ 90% reversible (with high T, P),
yet $Mn(BH_4)_2$ is not reversible at all.

Figure 54. Property variability seen amongst borohydride materials investigated in the MHCoE.

As seen in Figure 54, there is a large range in the temperature required to remove hydrogen from borohydrides. $Na_2Zr(BH_4)_6$ can release hydrogen at very low temperatures, 40–110 ºC. Yet, $Mg(BH_4)_2$ releases hydrogen only at temperatures of ~ 295 ºC. This is a dramatic variation in the thermal requirements.

Similarly $Li_2Zn(BH_4)_4$ releases hydrogen, only with a pathological amount (30%) of diborane contamination. In contrast, $Na_2Zr(BH_4)_6$ releases H_2 with no detectable B_2H_6. What is governing this difference in B_2H_6 release? We currently don't know, but there is clearly a large range of behavior with respect to B_2H_6 release.

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In the last year of the MHCoE, we investigated ammonia adducts of borohydrides. This was prompted by the finding by OSU that $Mg(BH_4)_2 \cdot 2NH_3$ released hydrogen with no detectable NH_3 emission. However, further studies showed that $Ca(BH_4)_2 \cdot 2NH_3$ only releases NH_3 with heating. This is a striking change in behavior for two compounds so similar to one another in other ways.

Finally, $Mg(BH_4)_2$ has been successfully reversed, yet $Mn(BH_4)_2$ is not reversible at all. Again, two very similar materials at least with regard to intrinsic composition, yet with strikingly different chemical behaviors with regard to reversibility. What is it about $Mg(BH_4)_2$ that makes it reversible, while the manganese analog is not? The answer to that question may allow the design of a fully reversible borohydride with overall better performance than $Mg(BH_4)_2$.

We need to gain a fundamental understanding of the these variations, because if we can understand what controls these properties of reversibility, diborane release, ammonia release and temperature for H_2 release, we should then have a reasonable chance for controlling these properties to produce a truly remarkable hydrogen storage material. When viewed in this light, the prospects for finding a remarkable material that satisfies all the material goals are hopeful, as the material for which we seek has properties intermediate to those listed in Figure 54. In a sense, our work has "bounded" the chemical problem, finding materials that have determined a "property space" which contains the properties of the material we seek. Thus, finding that material is in a sense a problem of "interpolation," which is inherently much less risky than "extrapolation." In addition, given the richness of the borohydride chemistry, for example the possibility to form multiple metal compounds such as $NaTi(BH_4)_4$, there is a high level of discreteness in the "property space," suggesting that a remarkable material can in fact be found.

DOE Awards and Honors

A number of DOE Awards were given both to the MHCoE as a whole, and to MHCoE participants during the 5-year tenure of the MHCoE. These DOE awards are listed below.

1. DOE Hydrogen Program 2010 "Special Recognition Award," presented to Director Lennie Klebanoff on behalf of the entire Metal Hydride Center of Excellence, in recognition of outstanding contributions to the Department of Energy, awarded June 8, 2010.

2. DOE Hydrogen Program 2010 R&D Award to Dr. Ragaiy Zidan and his team at Savannah River National Laboratory for their outstanding contribution to the development of electrochemical methods to regenerate alane (AlH_3), awarded June 8, 2010.

3. DOE Hydrogen Program 2009 Special Recognition Award to Jay Keller, MHCoE Deputy Director and Sandia Hydrogen Program Manager, for years of outstanding contributions to the DOE Hydrogen Program, awarded May 19, 2009.

4. DOE Hydrogen Program 2008 R&D Award to Dr. J. Karl Johnson (PITT), Dr. David Sholl (Georgia Tech), and Bing Dai (Georgia Tech), in recognition of outstanding theoretical contributions to hydrogen storage technologies, awarded June 10, 2008.

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Appendix I:
Materials Investigated in the MHCoE
That Were Discontinued

Description of Appendix I

Appendix I lists materials investigated in the MHCoE for which work was discontinued due to one or more unacceptable properties, making these materials unsuitable for a practical hydrogen storage system. For each system listed in Appendix I, the initially anticipated character (going-in expectation) for the reaction is given, along with the partners involved, the theoretical hydrogen capacity (for the starting material as written), the standard enthalpy change per mole of hydrogen (ΔH) for the anticipated desorption reaction as written, the temperature for an equilibrium hydrogen pressure of 1 bar ($T_{1 \text{ bar}}$), and the temperature currently required for observable kinetics (T_K). When available, experimental data are used for ΔH and $T_{1 \text{ bar}}$; these entries are indicated as (exp). Otherwise, $T_{1 \text{ bar}}$ is obtained from the relationship $T_{1 \text{ bar}} = \Delta H/\Delta S$ where ΔH and ΔS are the changes in thermodynamic enthalpy and entropy (respectively) for the reaction as written. Values for ΔH and ΔS can be obtained from databases, including the Enthalpy (H)/Entropy (S)/Heat Capacity (C) (HSC) Chemistry Software Package for Windows, which give the standard enthalpies and entropies for each species in the reaction. Such ΔH values are indicated by (db) in the tables and are for 300K. Alternatively, ΔH values obtained from density functional calculations performed by the MHCoE theorists are indicated by (DFT). Such DFT calculations give ΔH values for 0K. If a reaction is found to be not reversible, then an entry of dash (-) is given for $T_{1 \text{ bar}}$, since a true equilibrium does not exist. A dash (-) is entered in the tables if no information on that quantity is available. The final column of Appendix I gives a brief reason why the dowselect decision was made.

The quantity $T_{1 \text{ bar}}$ is a purely thermodynamic construct, and does not convey information about reaction kinetics. To give a kinetic context for hydrogen adsorption/desorption from these materials, the Appendix I includes a "kinetic temperature" T_K. T_K is the temperature required for observable kinetics. It is subjectively defined from experimental data (e.g., thermogravimetric analysis, differential scanning calorimetry) as the temperature at which significant reaction occurs on the time scale of minutes up to an hour.

The final column of Appendix I lists the principle reasons why the materials were discontinued.

System	Anticipated Reaction	Partners Involved	Theoretical Hydrogen Capacity	ΔH (kJ/mol-H$_2$)	T$_{1bar}$ (°C)	T$_K$ (°C)	Reasons for Discontinuing Work
Project A							
MgH$_2$/Si	2MgH$_2$ + Si→ Mg$_2$Si + 2H$_2$	HRL, Caltech, JPL, Stanford, SNL, Intematix, U. Hawaii, NIST, U. Pitt., U. Illinois	5.0 wt. %	36 (db) 35 (dft)	~20 (db) -30(dft)	~200	No longer considered because the reaction is not reversible.
MgSiN$_2$	MgSiN$_2$ +2H$_2$→ Mg(NH$_2$)$_2$ + Si	HRL	4.7 wt. %	-	-	-	No longer considered because no hydrogenation was observed (system not reversible)
Li$_2$SiN$_2$	Li$_2$SiN$_2$ + 2H$_2$→ 2LiNH$_2$ + Si	HRL	5.4 wt. %	-	-	-	No longer considered because of difficulty synthesizing Li$_2$SiN$_2$
LiF/MgB$_2$	2LiF + MgB$_2$ + 4H$_2$→ LiBH$_4$ + MgF$_2$	HRL	7.6 wt. %	45 (db)	150 (db)	~300	No longer considered because the reaction is not sufficiently reversible.
LiCl/MgB$_2$	2LiCl + MgB$_2$ + 4H$_2$→ 2LiBH$_4$ + MgCl$_2$	HRL	5.8 wt. %	29 (db)	-10 (db)	-	No longer considered because no hydrogenation was observed
Li$_2$S/MgB$_2$	2Li$_2$S + MgB$_2$ + 4H$_2$→ 2LiBH$_4$ + MgS	HRL	8.0 wt. %	47 (db)	170 (db)	~300	No longer considered because the reaction is not sufficiently reversible.
Li$_2$Se/MgB$_2$	2Li$_2$Se + MgB$_2$ + 4H$_2$→ 2LiBH$_4$ + MgSe	HRL	5.4 wt. %	36 (db)	70 (db)	~300	No longer considered because the reaction is not sufficiently reversible
Li$_2$CO$_3$/MgB$_2$	Li$_2$CO$_3$ + MgB$_2$ +4H$_2$ → 2LiBH$_4$ + MgCO$_3$	HRL	6.3 wt. %	42 (db)	110 (db)	-	No longer considered because the CO$_3$ anion decomposes.
LiBH$_4$/Mg$_2$Cu	4LiBH$_4$ + Mg$_2$Cu→ 4LiH + 2MgB$_2$ + Cu +6H$_2$	HRL, BNL	6.0 wt. %	41 (db)	150 (db)	-	No longer considered because no coupling between LiBH$_4$ and Mg$_2$Cu was observed.
LiH/B$_4$C	4LiH + B$_4$C→4LiBH$_4$ + C	HRL	12.0 wt. %	55 (db)	290 (db)	-	No longer considered because no hydrogenation was observed

System	Anticipated Reaction	Partners Involved	Theoretical Hydrogen Capacity	ΔH (kJ/mol-H_2)	T_{1bar} (°C)	T_K (°C)	Reasons for Discontinuing Work
$LiBH_4$/Si	$3LiBH_4 + Si \rightarrow$ $3LiH + B_3Si + 4.5H_2$	HRL	9.5 wt. %	-	-	-	No longer considered because no B_3Si was observed
$LiBH_4$/MgH_2 catalyzed with Ti	$2LiBH_4 + MgH_2 \rightarrow$ $2LiH + MgB_2 + 4H_2$	UH	11.4 wt. %	46 (db) 41 (exp) 66 (dft)	170 (db) 225 (exp)	300-350	No longer considered because $TiCl_3$ did not improve the unacceptably slow kinetics of the dehydrogenation of $2LiBH_4$/MgH_2 to MgB_2/2LiH
LiH/Si	$x\,LiH + y\,Si \Leftrightarrow$ $Li_xSi_y + (x/2)\,H_2$	JPL, HRL, Caltech, NIST	2.8-7.0 wt. %	106, 120 (2 plateaus, exp)	480, 550	425	Destabilized & partially reversible, but no longer considered due to low pressure, slow kinetics, & Li_4Si_2H phase formation reducing capacity
LiH/Ge	$x\,LiH + y\,Ge \Leftrightarrow$ $Li_xGe_y + (x/2)\,H_2$	JPL, HRL, Caltech, NIST	1.2-4.1 wt. %	-	420, 660, 700	400	Destabilized system, but no longer considered due to low capacity, slow kinetics, & Li_4Ge_2H phase formation
$LiBH_4$/MgH_2 (catalyst study)	$2LiBH_4 + MgH_2 \rightarrow$ $2LiH + MgB_2 + 4H_2$	Intematix, HRL, SNL	11.4 wt. %	46 (db) 41 (exp) 52 (dft)	170 (db) 225 (exp)	300 - 350	Poor thermodynamics
$LiBH_4$/MgH_2 @ aerogel	$2LiBH_4 + MgH_2 \rightarrow$ $2LiH + MgB_2 + 4H_2$	HRL, LLNL, Caltech, JPL, NIST, Stanford	11.4 wt. %	52 (dft)	-	-	Difficulty achieving simultaneous incorporation of two substituents in aerogel
$LiBH_4$/ScH_2	$ScH_2 + 2LiBH_4 \rightarrow$ $2LiH + ScB_2 + 4H_2$	JPL, Caltech, U. Pitt, CMU, NIST	8.9 wt. %	50 (dft)	60 (dft)	-	Reactants did not couple; no destabilized reaction
C/ $Mg(BH_4)_2$	$2\,C + Mg(BH_4)_2 \rightarrow$ $MgB_2C_2 + 4\,H_2$	U. Pitt/CMU	10.3 wt. %	43 (dft)	-	-	Theory predicts excellent thermodynamics and hydrogen storage capacity. System was not reversible experimentally
B/$Mg(BH_4)_2$	$5\,B + Mg(BH_4)_2 \rightarrow$ $MgB_7 + 4\,H_2$	U. Pitt/CMU	7.5 wt. %	42 (dft)	-	-	Theory predicts excellent thermodynamics and hydrogen storage capacity. System was not reversible experimentally.
C/$LiNH_2$	$2\,LiNH_2 + C \rightarrow$ $Li_2CN_2 + 2H_2$	U. Pitt/CMU	7.0 wt. %	31 (dft)	-100 (dft)	-	Theory predicts excellent thermodynamics and hydrogen storage capacity. System was not reversible experimentally.

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System	Anticipated Reaction	Partners Involved	Theoretical Hydrogen Capacity	ΔH (kJ/mol-H_2)	T_{1bar} (°C)	T_K (°C)	Reasons for Discontinuing Work
LiH/Mg(NH_2)/VN	28 LiH + 9 Mg(NH_2)$_2$ + 4VN → 4 Li_7N_4V + $3Mg_3N_2$ + 32 H_2	U. Pitt/CMU	6.5 wt. %	47.5 (dft)	-	-	Theory predicts excellent thermodynamics and hydrogen storage capacity. Experimental investigation was inconclusive
$4LiBH_4$/$5Mg_2NiH_4$	$4LiBH_4$ + $5Mg_2NiH_4$ → $2MgNi_{2.5}B_2$ + 4LiH + $8MgH_2$ + $8H_2$	HRL	5.6 wt. %	15	-25	270	Low Wt. % hydrogen storage
Project B							
Ti-$NaAlH_4$	$NaAlH_4$ → NaH + Al + 3/2H_2	UH, SNL	5.5 wt. %	37 (exp)	33	120	No longer considered because the reversible storage capacity is too low
K_2LiAlH_6	K_2LiAlH_6 → 2KH + LiH + Al + 3/2H_2	SNL	5.0 wt. %	-	-	~ 250	No longer considered because the reversible storage capacity is too low and kinetics too slow
$A_xZn(BH_4)_x$ A=Li, Na,K	$A_xZn(BH_4)_2$ → $[A_x-Zn-B]$ + $2xH_2$	UH	~11 wt. %	-	-	100-150	Desorbs H_2 below 150 °C. No longer considered because of significant release of B_2H_6 upon decomposition
$NaK(BH_4)_2$	$NaK(BH_4)_2$ → [Na-K-B] + $4H_2$	USML, SNL	8.7 wt. %	-	-	-	This compound is unstable and decomposes into the constituent MBH_4 at room temperature without releasing hydrogen
$Mg(BH_4)(AlH_4)$	$Mg(BH_4)(AlH_4)$ → [Mg-B-Al] + $4H_2$	GE	11.4 wt.%	-	-	120	Could not make material in pure form
$Mg(BH_4)_2$ in C aerogel	$Mg(BH_4)_2$ → MgB_2 + $4H_2$	UTRC, UH	-	-	-	-	$Mg(BH_4)_2$ is incorporated into aerogel via diethylether solution. Cannot find method to desolvate without decomposing borohydride
$Al(BH_4)_3$	$Al(BH_4)_3$ → Al + 3B + $6H_2$	ORNL	16.8 wt. %	-	-	-	Too much diborane release
$LiM(BH_4)_4$ (M=Ti or Al)	$LiM(BH_4)_4$ (M=Ti or Al) → Li + M + 4B + $8H_2$	ORNL	14-17 wt. %	-	-	-	Could not synthesize the material
$Mn(BH_4)_2$	$Mn(BH_4)_2$ → MnB_2 + $4H_2$	UH	9.5 wt.%	-	-	-	Not reversible

System	Anticipated Reaction	Partners Involved	Theoretical Hydrogen Capacity	ΔH (kJ/mol-H_2)	T_{1bar} (°C)	T_K (°C)	Reasons for Discontinuing Work
$A_xMn(BH_4)_x$ A=Li, Na, K	$A_xMn(BH_4)_x \rightarrow$ $[A_x\text{-Mn-B}] + 2xH_2$	UH, SNL	~12.0 wt. %	-	-	100 (A=Na)	Not reversible
$LiK(BH_4)_2$	$LiK(BH_4)_2 \rightarrow$ $[\text{Li-K-B}] + 4H_2$	SNL, UH	10.6 wt. %	-	-	~380	Desorption T too high
$Ca(BH_4)_2$	$3Ca(BH_4)_2 \rightarrow CaB_6 +$ $2CaH_2 + 10H_2$ OR $3Ca(BH_4)_2 \rightarrow (5/6)CaH_2 +$ $(1/6)CaB_{12}H_{12} + (13/6)H_2$	SNL, UNR, UMSL	9.6wt. %	59 (dft) OR 57 (dft)	350	300	Poor reversibility, high ΔH
$Ca(BH_4)_2 \cdot NH_3$	$Ca(BH_4)_2 \cdot NH_3 \rightarrow$ $[\text{Ca-B-N}] + 11/2H_2$	SNL	12.78 wt. %	-	-	-	Only desorbed NH_3
$LiCa(BH_4)_3 \cdot NH_3$	$LiCa(BH_4)_3 \cdot NH_3 \rightarrow$ $[\text{Ca-B-N}] + LiH + 7H_2$	SNL	13.93 wt.%	-	-	-	Large NH_3 release
$Na_2Zr(BH_4)_6$	$Na_2Zr(BH_4)_6 \rightarrow$ $[\text{Na-Zr-B}] + 12H_2$	UH	10.69 wt. %	-	-	100	Not reversible
$K_2Zr(BH_4)_6$	$K_2Zr(BH_4)_6 \rightarrow$ $[\text{K-Zr-B}] + 12H_2$	UH	9.36 wt. %	-	-	-	Not reversible
$Li_2Zr(BH_4)_6$	$Li_2Zr(BH_4)_6 \rightarrow$ $[\text{Li-Zr-B}] + 12H_2$	UH	12.46 wt. %	-	-	-	Not reversible
$Ca(BH_4)(AlH_4)$	$Ca(BH_4)(AlH_4) \rightarrow$ $[\text{Ca-B-Al}] + 4H_2$	UMSL, SNL	11.9 wt. %	-	-	-	Not reversible
$Ti(BH_4)_3$	$Ti(BH_4)_3 \rightarrow [\text{Ti-B}] + 6H_2$	ORNL, GE, SNL	13.1 wt. %	-	-	-	Not reversible
Mg-Ti-H	$Mg_7TiH_{16} \rightarrow$ $7Mg + Ti + 8H_2$	Utah, SNL	~7.0 wt. %	-	-	~300	Too high desorption temperature
A-Si-H (A=Li, Na, Ca)	$A_2SiH_x \rightarrow 2AH + Si + xH_2$	SNL, Utah, HRL, NIST	5-9 wt. %	-	-	370	Insufficient hydrogen capacity
Na-Ge-H	$A_2GeH_x \rightarrow$ $2AH + Ge + (x/2-1)H_2$	SNL, NIST	~5.0 wt. %	-	-	-	Too high desorption temperature
A-B-Ni-H (A=Li,Na,Mg,Ca)	$ABNiH_x \rightarrow$ $AH + BH + Ni + xH_2$	SNL	~ 4-6 wt. %	-	-	-	Not reversible, low capacity
Mg-Mn-H	$MgMnH_9 \rightarrow$ $MgH_2 + Mn + 7/2H_2$	SNL	~ 5-6 wt. %	-	-	-	Not reversible, low capacity

System	Anticipated Reaction	Partners Involved	Theoretical Hydrogen Capacity	ΔH (kJ/mol-H_2)	T_{1bar} (°C)	T_K (°C)	Reasons for Discontinuing Work
$LiSc(BH_4)_4$	$LiSc(BH_4)_4 \rightarrow$ [LiScB] + H_2 OR $10LiSc(BH_4)_4 \rightarrow 4LiBH_4 + 10ScH_2 + 3Li_2B_{12}H_{12} + 4H_2$	JPL, Caltech, UH	14.6 wt. % OR 8.0 wt. %	24 (dft)	-	175	Some reversibility seen. Good model system, but downselected due to high cost of Sc
$NaSc(BH_4)_4$	$NaSc(BH_4)_4 \rightarrow$ [NaScB] + H_2	JPL, Caltech, UH	12.8 wt. %	-	-	175	Some reversibility seen. Good model system, but downselected due to high cost of Sc
$LiBH_4/Ca(AlH_4)_2$	$LiBH_4/Ca(AlH_4)_2 \rightarrow$ [Li-Ca-B-Al] + $6H_2$	JPL, Caltech, NIST	6-7 wt. %	-	-	400	$Ca(AlH_4)_2$ seems to Induce some reversibility in $LiBH_4$, but the desorption T is too high
$Mg(B_3H_8)_2$	$Mg(B_3H_8)_2 \rightarrow$ $MgB_2 + 4B + 8H_2$	OSU	15.3 wt. %	-	-	-	Material is too unstable
$Li_2B_{12}H_{12}/2CaH_2$	$Li_2B_{12}H_{12}/2CaH_2 \rightarrow$ $2CaB_6 + 2LiH + 7H_2$	SNL	6.7 wt. %	51.1 (dft)	123	550	Too high desorption temperature
$CaB_{12}H_{12}/CaH_2$	$CaB_{12}H_{12}/CaH_2 \rightarrow$ $CaB_6 + 6B + 6H_2$	SNL	6.3 wt. %	38.6 (dft)	86	500	Not reversible
$Li_2B_{12}H_{12}/6MgH_2$	$Li_2B_{12}H_{12}/6MgH_2 \rightarrow$ $6MgB_2 + 2LiH + 11H_2$	SNL	7.7 wt. %	60.1 (dft)	215	300	Desorption from MgH_2 before destabilization rxn
$Mg(NH_3)_6B_{10}H_{10}$	$Mg(NH_3)_6B_{10}H_{10} \rightarrow$ [Mg-N-B] + $14H_2$	OSU	11.5 wt. %	-	-	-	Large NH_3 release rather than H_2
$Mg(NH_3)_6B_{12}H_{12}$	$Mg(NH_3)_6B_{12}H_{12} \rightarrow$ [Mg-N-B] + $15H_2$	OSU	11.3 wt. %	-	-	-	Large NH_3 release rather than H_2 release
$Li(NH_3)_6B_{12}H_{12}$	$Li(NH_3)_6B_{12}H_{12} \rightarrow$ [Li-N-B] + $15H_2$	OSU	12 wt. %	-	-	-	Large NH_3 release instead of H_2
$Li_3AlH_6/2LiBH_4$	$Li_3AlH_6/2LiBH_4 \rightarrow$ [Li -N-B] + $7H_2$	Utah	14.5 wt. %	-	-	-	Too high desorption temperature
$NaBP_2H_8$	$NaBP_2H_8 \rightarrow$ [Na-P-B] + $4H_2$	SNL	7.7 wt. %	-	-	165	Not reversible
$Mg(H_2O)_6B_{12}H_{12} \cdot 6H_2O$	$Mg(H_2O)_6B_{12}H_{12} \cdot 6H_2O \rightarrow$ [Mg-N-B-O] + xH_2	OSU	6.5 wt. %	-	-	-	Too high quantities of H_2O release with H_2
$Mg(H_2O)_6B_{10}H_{10} \cdot 4H_2O$	$Mg(H_2O)_6B_{10}H_{10} \cdot 4H_2O \rightarrow$ [Mg-N-B-O] + $13H_2$	OSU	9.4 wt. %	-	--	-	Too low hydrogen wt. % in observed material

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System	Anticipated Reaction	Partners Involved	Theoretical Hydrogen Capacity	ΔH (kJ/mol-H$_2$)	T_{1bar} (°C)	T_K (°C)	Reasons for Discontinuing Work
Li$_2$B$_{12}$H$_{12}$·7NH$_3$	Li$_2$B$_{12}$H$_{12}$·7NH$_3$ → [Li-B-N] + xH$_2$	OSU	12.1 wt. %	-	-	-	Too high NH$_3$ release
NH$_4$B$_3$H$_8$	NH$_4$B$_3$H$_8$ → [B-N] + 6H$_2$	OSU	20.6 wt. %	-	-	-	Without hydrolysis material yields too much B$_2$H$_6$
NH$_2$B$_2$H$_5$	NH$_2$B$_2$H$_5$ →[B-N] +7/2H$_2$	OSU	16.5 wt. %	-	-	-	Poor stability, unsuitable for H$_2$ storage
Mg(AlH$_4$)(BH$_4$)	Mg(AlH$_4$)(BH$_4$) → [Mg-B-Al] + 4H$_2$	OSU	11.5 wt. %	-	-	-	Could not be synthesized
6LiBH$_4$/CaH$_2$	6LiBH$_4$/CaH$_2$ → 6LiH + CaB$_6$ + 10H$_2$	Caltech/JPL	11.7 wt. %	46.3	154	-	Not sufficiently reversible
TiH$_2$ + 2LiBH$_4$	TiH$_2$ + 2LiBH$_4$ → 2LiH + TiB$_2$ + 4H$_2$	Caltech	8.6 wt. %	22 (dft)	-	-	No coupling, H$_2$ release from LiBH$_4$ only
Project C							
Li$_3$N	Li$_3$N+2H$_2$→ LiNH$_2$+2LiH	UNR	11.5 wt. %	-80.5	250	300 - 400	The plateau pressure is too low and the dehydrogenation kinetics are too slow
Li$_2$Mg(NH)$_2$	2LiNH$_2$+MgH$_2$→ Li$_2$Mg(NH)$_2$+2H$_2$	SNL, NUS	5.5 wt. %	-38.9	72 (from exp. Van't Hoff Plot)	~250	No longer considered because the reversible storage capacity is too low
LiAlH$_4$/LiNH$_2$	LiAlH$_4$+LiNH$_2$→ Li$_2$NH+Al+2.5H$_2$	Utah	8.1 wt. %	26.8	-	200 - 300	No longer considered because the reaction is not sufficiently reversible
LiAlH$_4$/LiNH$_2$	LiAlH$_4$+2LiNH$_2$ → Li$_3$AlN$_2$+4H$_2$	SNL (NUS)	9.5 wt. %	-25.8	-	300 - 450	No longer considered because the temperature for complete dehydrogenation is too high, and the reaction is not reversible
Li$_3$AlH$_6$/LiNH$_2$ (1:2)	Li$_3$AlH$_6$+2LiNH$_2$→ 2Li$_2$NH+LiAl+4H$_2$	SNL (NUS)	8 wt. %	40.5	-	~300	No longer considered because the reaction is not sufficiently reversible
Li$_3$AlH$_6$/LiNH$_2$ (1:3)	Li$_3$AlH$_6$+3LiNH$_2$→ 3Li$_2$NH+Al+4.5H$_2$	Utah, SNL (NUS), JPL, HRL, UNR	7.3 wt. %	38.4	250 (exp)	200 - 300	Observed properties inferior to other amide systems

System	Anticipated Reaction	Partners Involved	Theoretical Hydrogen Capacity	ΔH (kJ/mol-H_2)	T_{1bar} (°C)	T_K (°C)	Reasons for Discontinuing Work
$Li_3AlH_6/Mg(NH_2)_2$	$2Li_3AlH_6+3Mg(NH_2)_2 \rightarrow$ $3Li_2Mg(NH)_2+2Al+9H_2$	Utah, JPL, GE	6.5 wt. %	21.4	-	200 - 300	Desorption T too high, Kinetics too slow, complex reactions
$Ca(NH_2)_2$	$Ca(NH_2)_2 \rightarrow$	SRNL	5.6 wt. %	-	-	-	Downselected, as material releases only NH_3
$Mg(NH_2)_2$	$Mg(NH_2)_2 \rightarrow$	SRNL	7.2 wt. %	-	-	-	Downselected, as material only releases NH_3
$Ca(NH_2)_2/LiBH_4$	$Ca(NH_2)_2/LiBH_4 \rightarrow$ [Ca-N-Li-B] + $4H_2$	SRNL	8.6 wt. %	-	-	-	Some reaction took place, leading to 2 wt. % reversibility. Downselected due to poor weight capacity
$Mg(NH_2)_2/LiBH_4$	$Mg(NH_2)_2 + 2LiBH_4 \rightarrow$ $MgH_2 + 2LiH + 2BN + 4H_2$	SRNL	8.1 wt. %	21 (dft)	-	-	Precursors did not react, no new materials observed under process conditions
$Ca(NH_2)_2/LiNH_2$	$Ca(NH_2)_2/LiNH_2 \rightarrow$ [Ca-N-Li] + $3H_2$	SRNL	6.4 wt. %	-	-	-	Precursors did not react, no new materials observed under process conditions
$Mg(NH_2)_2/LiNH_2$	$Mg(NH_2)_2/LNH_2 \rightarrow$ [Mg-N-Li] + $3H_2$	SRNL	7.6 wt. %	-	-	-	Precursors did not react, no new materials observed under process conditions
$2LiNH_2/Ca(BH_4)_2$	$2LiNH_2/Ca(BH_4)_2 \rightarrow$ [Li-N-Ca-B] + $6H_2$	SRNL	11.5 wt. %	-	-	280	Not reversible, too high desorption T
$4LiNH_2/Ca(BH_4)_2$	$4LiNH_2/Ca(BH_4)_2 \rightarrow$ [Li-N-Ca-B] + $8H_2$	SRNL	10.7 wt. %	-	-	280	Not reversible, too high desorption T
$Mg(BH_4)_2 + LiNH_2$	$Mg(BH_4)_2 + LiNH_2 \rightarrow$ [Mg-B-Li-N] + $5H_2$	SRNL	11.8 wt. %	-	-	225	No new material formed
$3Mg(BH_4)_2 + LiNH_2$	$3Mg(BH_4)_2 + LiNH_2 \rightarrow$ [Mg-B-Li] + $13H_2$	SRNL	13.3 wt. %	-	-	215	Not reversible
$Mg(BH_4)_2 + 3LiNH_2$	$Mg(BH_4)_2 + 3LiNH_2 \rightarrow$ [Mg-B-Li] + $7H_2$	SRNL	10.2 wt. %	-	-	300	Excessive NH_3 release

Appendix II:
Publications and Patents from the MHCoE

The publications from the MHCoE are listed below, organized according to Project, and also those developed in the Theory Group (TG). Also listed are Patents from the MHCoE.

Project A

1. Anant Kulkarni, Lin-Lin Wang, Duane D. Johnson, David Sholl, and Karl Johnson, "First-Principles Characterization of Amorphous Phases of $MB_{12}H_{12}$, M=Mg, Ca," *J. of Phys. Chem. C,* **114**, 14601-14605 (2010).

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Project B

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Appendix III:
MHCoE Lessons Learned Summary

Background

A lessons-learned session was held on November 5, 2009 at the final face-to-face meeting of the MHCoE at the University of Utah. The session was attended by 50 participants from the Metal Hydride Center of Excellence including university, national laboratory, industry and government representatives. The session was lead by a trained facilitation professional provided by DOE, and a follow-up survey was then conducted via email to capture any additional feedback. All information was gathered and reported by an independent third party to avoid any conflict of interest.

Purpose

The goal of the lessons-learned session and follow-up report was to review the five year period in which the center was in operation and discuss accomplishments, review the challenges and successes, and record the lessons that were learned. The information captured and the recommendations recorded will be useful for forming and running future centers and projects, and is one of the requirements requested in the Center's Final Report. To do this, members of the Metal Hydride Center of Excellence were asked to provide feedback on the Center's management and operating processes, collaboration and communication mechanisms (both formal and informal), and technical approach and techniques. The raw feedback is captured below in bulletized statements.

1. Metal Hydride Center of Excellence Successes

Participants were asked to provide input on what they viewed as the biggest successes of the Center. They were asked to consider events that occurred during the entire five year lifetime of the center and to be specific, but also general enough that these lessons could be used by future Centers. Specific technology successes were not gathered as they were deemed as not being useful in the creation of future centers and/or projects.

The response that received the most consensus from the participants was that the center concept provided an efficient way for technical collaboration that otherwise would not have occurred. The statement that more technical progress was made in the Center than would have in independent projects was the overarching theme of the Center Successes Session.

Benefits of working and collaborating with other researchers

- The center enabled an infusion of new people and ideas and brought in diverse perspectives.

- There was more freedom to conduct research in specific areas than in independent projects.

- There were clear divisions of responsibilities.

- Having a Center increases the knowledge base and gives researchers access to qualified people.

- Collaboration

  - The Center concept provides an efficient way for technical collaboration and fosters collaboration that would not have occurred otherwise.

  - Collaborations and sharing of the workload with other partners was a big plus of the Center.

  - The face to face meetings discussions aided in collaborations.

  - It was easy to collaborate because exchange of samples could occur without the worry of money exchanges.

- Shared Learnings

  - The exchange of ideas gave researchers access to new ideas and different views early on in the experimentation process.

  - The Center provided access to many, various and specialized experts.

  - Persons with complementary capabilities and expertise were able to work together.

  - The Center provided a good opportunity for critical peer reviews.

Increase in knowledge beyond that gained in independent projects

- Technical Knowledge

  - Advances in science beyond what would have occurred in an independent project.

  - There were advances and technical progress in all projects.

  - Researchers were able to develop an understanding of all projects, including those they did not personally work on.

  - There were discoveries of new phenomena and compounds.

  - There were more publications than would have been produced from independent projects.

- Inclusion of Theory Projects

  - The Metal Hydride Center of Excellence should be used as a model for how to utilize a theory group effectively.

  - The theory group was very proactive and used tutorials effectively.

  - The theory group was able to get-up and going quickly and served as a huge attribute to the Center.

  - The theory and experiment interplay was very valuable.

- The theory development was very useful and the projects were used to help guide research.

- Non-Technical Knowledge

  - Having the projects in the form of a Center eliminated duplication of efforts.

  - Safety plans and learnings were shared within the Center.

  - Having the Center enabled continuity of funding.

Access to specialized facilities and instrumentation

- Researchers within the Center had access to special facilities and expertise that they otherwise would not have had.

- The Center structure gave researchers access to shared capabilities and instrumentation.

- Researchers were able to stay abreast with the state-of-the-art equipment and techniques.

- There was good use of Center-wide facilities and equipment.

2. Improvements for Future Centers

Participants were again asked to provide input, but in this case they were asked to think of the Center's biggest shortcomings. These shortcomings were viewed as ways to improve future center's technical progress by eliminating or reducing disconnects and roadblocks. Provided here is a listing of some comments focusing on the Center's shortcomings.

In this session, improving communication was listed as the biggest improvement that could be made for improving future center success. This included internal communication, meetings and external communication. Increasing the amount of the technical discussion and communication of project progress were listed as priorities, as well as improving the effectiveness of face-to-face and virtual meetings.

Communication could have been improved within the Center

- Internal Communication

  - There needed to be better communication between project participants.

  - There was not enough internal communication on the progress of projects.

  - Increasing technical discussions would have improved the project prioritization process.

  - More high level direction and discussion were needed when making decisions.

  - Interactive website needed less stringent administrative controls and should not be run through National Labs.

- There should have been a common location to find, place and store information easily, such as quarterly reports.

- Internal Meetings

  - There should have been twice as much face-to-face contact between members and meeting time should have been better utilized.

  - Face-to-face meetings should have been finalized earlier (times and locations).

  - More frequent small group meetings were necessary.

  - The Center should have better utilized virtual meetings.

  - Meetings should have had more technical discussions and less bureaucracy.

- External Communication

  - The Center should have better communicated progress to others.

  - The Center should have considered implementing a Center sponsored conference to communication findings.

  - There should have been better communication and information exchange with other Centers of Excellence and BES.

Theory / experimentation

- Faster screening of materials was needed so that down selections could occur faster and less fundamental studies required.

- There should have been a more structured approach in having theory predications followed up by experimentation.

Focus of research

- More focus and better understanding of mechanistic studies is needed without the complaint of being too fundamental.

- Earlier focus on materials that worked was needed.

- There needs to be a better understanding of kinetics.

- More structured approach is needed for testing new materials (ΔH).

- Analysis with stronger consideration of application operating conditions is necessary (example: desorption against pressure versus vacuum).

Individual project reporting requirements

- There was more paperwork than what seemed necessary.

- There needed to be more time spent in the lab and less time spent on reporting.

- Reporting requirements should be consolidated or streamlined in future Centers.

- Impact of DOE Targets on Research

- The research did not find a material that satisfied all of the targets.

- The preset goal of meeting the targets may have not been the best way to start the center.

- The five year time frame of the Center is not realistic for finding a material that meets the targets.

- The DOE targets needed to be more realistic, as they led research down the hardest path possible.

- Targets and goals should be more flexible.

- Center's focus on DOE Targets

- There needed to be a better focus within the Center on the DOE targets.

- The Center needed to better embrace the DOE targets and customer requirements.

3. Unexpected Surprises or Outcomes in the Center

In the last part of the initial brainstorming session, participants were asked to think of surprises or unexpected outcomes or events that occurred during their participation in the Center. The listings below include positive results that were above and beyond what participants expected and results or events that did not meet participants' expectations for the Center.

Positive outcomes that were not expected

- There were new materials discovered, this is a great achievement.

- The theory group proved to be more useful than expected on focusing activities and efforts.

- The Center's progress was greater than the sum of accomplishments of individual projects.

Unwanted outcomes that were not expected

- There was a lack of rapid screening capabilities, which were needed for the Center.

- A catalysis effort was not achieved because of IP concerns and issues.

- It was difficult for small companies to be involved because of IP, a problematic issue.

- There are still some materials and properties that are not well understood.

4. Center Structure and Organization

In the next brainstorming session participants were asked to consider how the Center structure or approach could be differed to increase the rate of progress. As part of this exercise, participants

were to consider the size, structure, and management of the Center. A common theme was that the five year lifetime of the Center was too short. With that being the case, a large portion of this time was spent specifically addressing how a future R&D Center could reduce ramp-up time and therefore increase the efficiency of the Center.

Facilitating a faster ramp-up of a Center of Excellence

- Communication
  - The establishment of a robust and intuitive web-based communication system at the start of a Center would help the exchange of information.
  - Having a good game plan and communication with Center members is essential.
- Establish a team atmosphere
  - There should be more face-to-face activities in the beginning of the Center to help establish a team atmosphere.
  - Team building activities and exercises as part of group activities.
- Identify challenges and scope early
  - Indentify the key challenges that the center must meet upfront and then re-evaluate periodically.
  - Design work scope around project concepts in the very beginning of the Center.
  - IP needs to be clarified and addressed early.
  - Engineering goals should be identified early and compared to current progress.
  - Implement "theory group tutorials" and establish periodic interaction with PIs.

The size of the center

- The Metal Hydride Center of Excellence is comprised of about 18 members and this is an optimal size, there should not be any more members.
- The Center may have been too large.
- Having a large center create challenges at the start-up of the Center.
- The larger the center the more difficult it is to coordinate schedules and it results in less one-on-one time with each partner.

Funding of the center and projects

- The 5 year total funding was at approximately $40 million.
- There needs to be more funding and it needs to be more fluid.
- To increase the involvement of project activities there needs to be more funding for each partner.
- The Center needed more funding for equipment.

The structure of the center

- Center Organization

  – Five years is insufficient time for a Center. The Center's efforts started to harmonize in the last few years.

  – The Center needs better organizational direction.

  – There should be earlier focus on materials that work.

  – More and higher level direction and discussion is needed for decision making.

  – The Center and each member need to have structured roles.

  – The Establishment of groups and group leaders was very beneficial.

- Projects Organization

  – A mechanism is needed to redefine member/partner roles.

  – More flexibility is needed within each project.

  – Partners should be involved in resource planning and funding allocation decisions.

  – Projects A-D were too large and insular which resulted in too much overlap.

- Downselects

  – Go/No-go decisions were not valuable to the Center, there needs to be a better way to stop projects.

  – The ability to stop or adjust projects would be a useful Center function.

  – Some materials were retired too early and others were not retired quickly enough.

- Center Membership and Inclusion

  – The Center should have more say on who can and cannot become a Center member.

  – There needs to be a way to eliminate unnecessary road blocks for Center membership.

  – Centers should absorb and/or embrace closely related activities.

  – Presently, existing projects have no way of joining the center, there needs to be a way for this to happen.

Center management

- Center management was always quick to respond to requests and assisted in fostering collaborations.

- The Center management made member participants want to achieve more and follow through with obligations.

- Communication from the coordinating council and Center management needs to be improved. Information was not distributed from the coordinating council in an effective manner.

Center/stakeholder communication

- There should be increased communication of customer requirements from the beginning of the Center.

- The Center should have a continuous interface with stakeholders.

- There needs to be better communication between DOE and the Center

Intellectual property issues

- Intellectual property management and lack of IP agreements were issues.

5. Technical Approach

The technical approach was the last section of the lessons-learned session. The goal of this section was to gather information on ways to change the technical approach of the Center to increase the rate of technical progress. The results were grouped into three categories: Technical Management which focused on how the Center could have been structured differently; Technical Method including how research should have been approached to increase the rate of progress; and Research Focus which listed research areas that should have been a higher priority.

Technical management

- R&D needs to have a defined flow or sequencing to facilitate a more systematic approach.

- Capabilities and abilities need to be identified and grouped appropriately.

- There needs to be more technical discussions at meetings

- A more structured Center-wide approach to R&D would have been beneficial.

- Technical challenges need to be defined so that they can be grouped for discussion and/or debate.

- There needs to be better results confirmation and a broad follow-up on results.

Technical method

- More brainstorming was needed during Center start-up phase.

- There should be a target and actually prioritize and reward according to targets

- Indentify progress based on goals and emphasize new findings.

- The Center did a good job of surveying the space and down selecting material classes.

- The Center used a wide breadth of techniques for material characterizations.

- There needs to be a viable rapid screening capability.

- Experimental screening studies were not implemented across the entire Center.

- There was too much reliance on familiar experimental methods which may have prevented thorough scientific measurements.

Research focus

- More projects focusing on material engineering would be a plus for future centers.

- The Center should have developed methods to reduce material oxidation.

- There should have been more allocation of resources towards priority materials (AlH_3, $LiMgN$, and $LiAlH_4$)

- There were not enough *in-situ* investigations performed.

- More kinetics studies were needed with a focus on general kinetic mechanisms and the rate limiting step.

- More mechanistic studies aimed at researching goals were needed.

- Many compounds identified met thermodynamic criteria, but there was not enough emphasis on thermodynamic testing.

- An earlier emphasis on characterizing non-hydrogen volatiles would have been beneficial.

Fundamental studies

- Allow some amount of fundamental studies that are not target driven.

- Integrate BES projects into the center.

- The center would have benefited from having the ability to direct fundament studies.

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