

Materials Go/No-Go Decisions Made Within the Department of Energy Metal Hydride Center of Excellence (MHCoE)

In fulfillment of the end of Fiscal Year 2007 Project Milestone
on Materials Down-selection

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September/October 2007



Acknowledgements

The author wishes to acknowledge the contributions of all Principal Investigators within the Metal Hydride Center of Excellence (MHCoE) to the work summarized herein. Their names and affiliations are listed below. Especially significant contributions to this document were made by Dr. Ewa Ronnebro (SNL), Dr. John Vajo (HRL), Prof. Zak Fang (U. Utah), Dr. Robert Bowman Jr. (JPL), Prof. David Sholl (CMU) and Prof. Craig Jensen (U. Hawaii). The author thanks Dr. Ned Stetson (DOE), Dr. Sunita Satyapal (DOE), Dr. Carole Read (DOE) and Dr. Greg Olson for a critical review of this document and helpful suggestions.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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TABLE OF CONTENTS

Executive Summary	4
Introduction.....	5
Down-select Criteria	5
MHCoE Introduction	7
Figure 1: Organization of the MHCoE	8
Project A: Destabilized Hydrides.....	11
Project B: Complex Anionic Materials.....	13
Project C: Amide/Imide Hydrogen Storage.....	14
Project D: Alane (AlH_3).....	15
Summary:.....	15
References:.....	16
Table I: DOE Targets for On-board Hydrogen Storage Systems	17
Table II: List of materials investigated in Project A (Destabilized Hydrides)	18
Table III: List of materials investigated in Project B (Complex Anionic Materials)	21
Table IV: List of materials investigated in Project C (Amide/Imide Materials)	23
Table V: List of approaches used in Project D (Alane) to regenerate AlH_3 from Al.	25
Appendix I: Footnotes to Table I: DOE Targets for On-board Hydrogen Storage Systems	26
Appendix II: Selected Publications on Materials Investigated in the MHCoE	27

Executive Summary

This report presents a review of the materials which have been considered to date by the DOE Metal Hydride Center of Excellence (MHCoE), with an accounting given of those materials for which a “No-Go” decision was made (a decision not to pursue further) as well as for those materials which are considered to have promise, for which a “Go” decision was made (future work planned in FY 2008 and FY 2009).

While a variety of requirements must be met for a commercially viable hydrogen storage system, the MHCoE focused on 5 primary performance metrics on which Go/No-Go materials decisions were based: 1) the material’s hydrogen storage gravimetric density should be at least 5 weight percent with a clear potential for significantly higher, 2) the material should be at least 50% reversible, 3) the material should release its hydrogen for temperatures below 350 °C, 4) the material’s non-hydrogen volatilization products should not exceed 1000 ppm for a single thermal cycle and 5) the material should release hydrogen and reabsorb hydrogen in less than 24 hours. 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.

Over the course of the MHCoE work since the MHCoE inception in FY2005, 51 materials systems have been investigated in the 4 materials Projects in the Center. Of these 51 materials, 27 have satisfied the 5 performance metrics listed above (i.e. show promise as a viable hydrogen storage material) and are being studied further. For each MHCoE Project, a Table is provided that summarizes the current understanding and current status (Go, No-Go) for that material.

Among the materials being considered further, the incorporation of $\text{LiBH}_4/\text{MgH}_2$ into highly porous aerogels remains of interest due to the potential to improve the kinetic and thermodynamic properties of this material by nanoconfinement. This work is being pursued in Project A (Destabilized Hydrides). Borohydride materials ($\text{Ca}(\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2$, etc.) remain of great current interest in Project B (Complex Anionic Materials) because these materials have a high hydrogen gravimetric storage density. In Project C (Amide/Imide Materials) the $\text{Li}_3\text{AlH}_6/3\text{LiNH}_2$ and LiMgN systems are being pursued because they have reasonable theoretical hydrogen gravimetric capacities ($\sim 7 - 8$ wt %) and are reversible at temperatures between 250 °C and 300 °C. Aluminum hydride (AlH_3) continues to be of interest due to its high hydrogen capacity (10.1 wt. %) and favorable hydrogen release kinetics at low (100 °C) temperatures. Three research groups in the MHCoE will continue to investigate methods to rehydrogenate Al metal under moderate conditions. Note that the alane work in the MHCoE involves the hydrogenation/dehydrogenation of aluminum and not the hydrolysis reaction between aluminum and water.

The MHCoE continues to search for new materials systems to explore. Part of this search will involve combinatorial searches for new materials as well as catalytic systems. The MHCoE Theory Group will continue to use Density functional Theory (DFT) predictions of reaction thermodynamics to guide the experimental materials discovery efforts.

Introduction:

This document is in fulfillment of the Department of Energy's (DOE) metal hydride materials down-select milestone scheduled for the end of fiscal year (FY) 2007. This report presents a review of the materials which have been considered by the DOE Metal Hydride Center of Excellence (MHCoE), with an accounting given of those materials for which a "No-Go" decision was made (a decision not to pursue further) as well as for those materials which are considered to have promise, for which a "Go" decision was made (future work planned in FY 2008 and FY 2009).

A description of the technical challenges surrounding on-board vehicular hydrogen storage can be found at the DOE website [1]. The focus of the MHCoE is to find an on-board reversible material that satisfies the DOE hydrogen storage targets. A reversible material is one which can readily release hydrogen at a suitable temperature and pressure during operation of the vehicle, as well as re-absorb hydrogen on-board the vehicle at a hydrogen fueling station.

The DOE system targets for on-board hydrogen storage technologies are given in Table I. A full explanation of the formulation of these targets can be found at the DOE website [2]. An explanation of the footnotes (A-L) given in Table I can be found in Appendix I. The targets given in Table I for the system as a whole are quite aggressive, requiring a materials capability well beyond the state-of-the-art existing when the MHCoE began research activities in fiscal year (FY) 2005. As such, the targets demand innovative, even radical, approaches to developing new hydrogen storage materials.

Down-select Criteria:

Although all of the DOE requirements indicated in Table I 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 viewed as the most challenging. One of these is system gravimetric density. As indicated in Table I, 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 are 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 is 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 are 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 learning has been gained by R&D directed at reducing the temperature of metal hydride materials below 350 °C.

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 I). Ideally, it is preferred that the hydrogen storage material liberates only hydrogen when heated and does not release volatile and reactive components such as NH₃, BH₃ or other gas-phase components. This requirement serves two purposes: preservation of fuel cell catalysts (which are poisoned by reactive impurities in the hydrogen gas stream); 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 fuel cell catalysts. 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 [2]. 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 weight percent (with potential for higher capacity to meet overall system targets), 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.

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.

This report on the materials down-select activities proceeds as follows. First a summary is given of the MHCoe, its organization and R&D activities. Then for each Project, a summary is given of the materials research as it relates to the down-selection process, with a Table listing the materials considered since the start of the MHCoe and the material's Go/No-Go status. As indicated above, Appendix I gives footnotes providing information on the DOE technical targets for hydrogen storage. Appendix II gives work published by the MHCoe on these materials, which can be consulted for more in-depth technical information.

MHCoe Introduction:

At the end of FY 2007, The DOE Metal Hydride Center of Excellence (MHCoe) consisted of eight universities: Caltech, Carnegie Mellon (CMU), Stanford, University of Hawaii (UH), University of Illinois-Urbana Champaign (UIUC), University of Nevada-Reno (UNR), University of Pittsburgh (PITT) and the University of Utah (UTAH).

There are also six National Laboratories/Federally Funded Research and Development Centers (FFRDCs) in the MHCoe: Brookhaven National Laboratory (BNL), The Jet Propulsion

Laboratory (JPL), National Institute of Standards and Technology (NIST), Oak Ridge National Laboratory (ORNL), Sandia National Laboratories (SNL), and Savannah River National Laboratory (SRNL).

The three industrial partners in the MHCoe are: GE Global Research, HRL Laboratories and Intematix. Two new partners were added at the end of FY2007. They are The University of New Brunswick, and United Technologies Research Center (UTRC). SNL is the lead laboratory, providing technical leadership and a structure to guide the overall technical program of the Center and to provide technical feedback to the DOE.

The purpose of the MHCoe is to develop hydrogen storage materials and engineering solutions that satisfy the DOE Hydrogen Program system requirements for automotive hydrogen storage. In an overall sense, the Center is a multidisciplinary and collaborative effort in three general 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 outlined by the Hydrogen, Fuel Cells and Infrastructure Technologies Program for 2010 and 2015 (Table I). The MHCoe focuses on “complex” metal hydrides, a review of which can be found in the recent literature [3]. The MHCoe organizational structure is given in Figure 1.

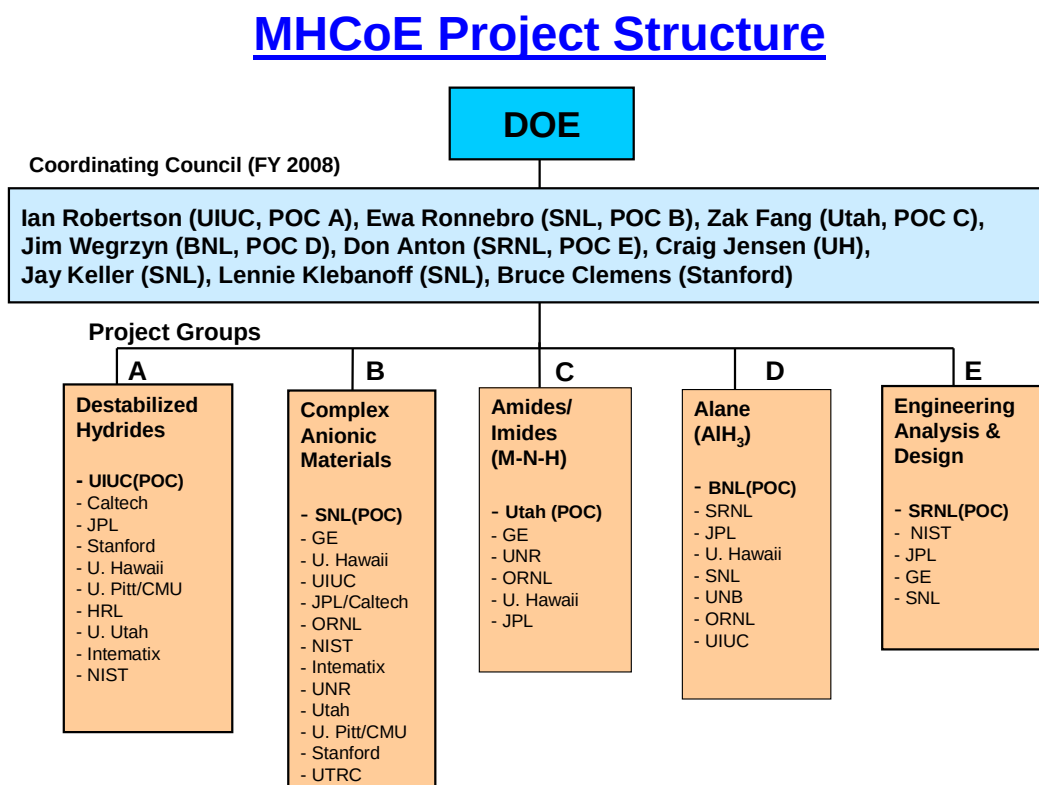


Figure 1: Organization of the MHCoe

The Coordinating Council is a technical review and advisory board for the MHCoE. Center-wide issues are discussed in the Coordinating Council, and the Council serves as a source of feedback for both the individual projects and for the DOE. As outlined in Figure 1, the technical work is currently divided into four materials projects A-D and an engineering project E. These project areas organize the MHCoE technical work along appropriate and flexible technical lines.

The objective of Project A (Destabilized Hydrides) is to develop strategies for reducing hydrogen storage thermal requirements and improve kinetics by destabilizing metal hydride systems. The technical approach is to alter the thermodynamics of the storage system by destabilizing the metal hydride through alloying, thereby reducing the energy needed to liberate hydrogen from the material and reducing the desorption temperature. The project aims to enhance kinetics by evaluating nanoengineering approaches towards minimizing the required hydrogen diffusion distance by decreasing particle size and creating nano-engineered scaffolds.

The objective of Project B (Complex Anionic Materials) is to predict and synthesize promising new anionic hydride materials. The technical approach involves using theory and chemical intuition to select promising target complex hydrides. Candidate materials are then synthesized by a variety of techniques, followed by extensive studies of structure and hydrogen sorption.

Project C (Amides/Imides Storage Materials) assesses the viability of amides and imides (materials containing -NH_2 and -NH moieties, respectively) for hydrogen storage. The technical approach is to reduce thermal requirements of these materials by alloying, elucidate the chemical pathways by which these materials absorb/desorb hydrogen, assess undesirable ammonia release, and determine the initial engineering issues (thermal expansion, cycling life) of these materials.

Project D (Alane) is organized to understand the sorption and regeneration properties of Alane (AlH_3) for hydrogen storage. The technical approach has been to synthesize the various structural forms of AlH_3 , and characterize the structure and hydrogen sorption properties of these forms. More recently, studies have investigated methods (chemical, electrochemical and physical) to rehydrogenate Al under moderate conditions. Note that the alane work in the MHCoE involves the hydrogenation/dehydrogenation of aluminum and not the hydrolysis reaction between aluminum and water.

Project E is the Engineering Analysis and Design project in the MHCoE, whose objective is to provide engineering analysis supporting the DOE system performance goals. The technical approach has been to develop engineering system-level storage models, use theory and modeling to provide target materials properties, perform thermal modeling of candidate hydride materials, and conduct expansion, heat transfer and stress measurements of promising materials. The analysis feeds back to the materials synthesis efforts, giving an engineering-based assessment of what the materials targets (for example weight percent) should be.

A review of the materials considered by the MHCoE from FY 2005 to the end of FY 2007 along with the “Go/No-Go” decisions made on these materials is given below on a Project-by-Project basis. For each project, a summary discussion is given, along with a detailed accounting of the materials listed in the accompanying Table. Published references for the materials are given in Appendix II. Materials results are listed for Projects A – C. Only one material (AlH_3) is of

consideration in Project D. For Project D, a brief review is given of the methods currently being pursued to hydrogenate aluminum, which is the main technical issue in Project D.

For Projects A – C, an example reaction is given for each material in the Tables provided. These reactions are only meant to indicate the anticipated reactions, between known compounds at the experimentally tested stoichiometry. In most cases, these were the "expected reactions", and as such do not necessarily convey the actual products observed in the experiments. In some cases, for example if the material performed poorly, a detailed characterization of the reaction products was not warranted.

Project A: Destabilized Hydrides

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 atmosphere. Formation of Mg_2Si during dehydrogenation was demonstrated experimentally. Unfortunately, rehydrogenation could not be achieved. 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.

The MHCoe has also investigated LiBH_4/MgX where X includes H, F, Cl, S, and Se, with $\text{LiX} + \text{MgB}_2$ being formed upon dehydrogenation. Full reversibility of ~10 wt% hydrogen was demonstrated for $\text{LiBH}_4/\text{MgH}_2$ (i.e., $\text{X} = \text{H}$) before the start of the MHCoe program. However, the kinetics were slow and consequently temperatures >350 °C were necessary. The compounds $\text{X} = \text{F}, \text{S}, \text{Se}$ were investigated beginning with the dehydrogenated phases $\text{LiX} + \text{MgB}_2$. For all cases, nearly complete hydrogenation to $\text{LiBH}_4 + \text{MgX}$ was demonstrated experimentally and the systems were partially reversible upon dehydrogenation. As a result of the better reversibility and higher hydrogen capacity for the $\text{LiBH}_4/\text{MgH}_2$ system, additional work was focused on improving the kinetics of this system.

To improve the kinetics of the $\text{LiBH}_4/\text{MgH}_2$ destabilized system, this system was incorporated into a nanoporous scaffold host. The idea is that the nanoscale dimensions of the scaffold will limit the sizes of the different phases, and therefore, reduce diffusion distances and increase interfacial contact, improving the overall hydrogen exchange rates. The scaffold introduces added weight but estimates and preliminary experiments indicate that this penalty can be reduced to acceptable levels. Using carbon aerogel scaffolds (in collaboration with Dr. Ted Bauman and co-workers at Lawrence Livermore National Laboratory (LLNL) and the DOE Hydrogen Sorption Center of Excellence), LiBH_4 has been incorporated successfully and has demonstrated increased reaction rates. In the current FY2008 project year, we are working on the incorporation of Mg with the ultimate goal being nanoconfinement of the complete destabilized material.

Table II provides a summary of the materials that have been investigated in Project A, with indication of the Go/No-Go status in the last column and by gray shading. A gray shading indicates a “No-Go” Status (not being considered further). No shading (i.e. clear) indicates a “Go” status (still being considered for future work). The last four reactions in Table II have been predicted by MHCoe theorists (Johnson/Sholl) to be of interest, and these will be examined in FY 2008.

For each system the Table includes the anticipated reaction, 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

($T_{1\text{ bar}}$), 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 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 $T_{1\text{ bar}}$, since a true equilibrium does not exist. A dash (-) is entered in the tables if no information on that quantity is available.

The 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 Tables include 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.

Project B: Complex Anionic Materials

The partners in Project B, Complex Anionic Materials, are focusing 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 weight percent 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 weight percent.

A promising class of materials is the metal borohydrides with potential for more up to ~16 weight percent capacity. New synthesis routes to prepare $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ were established and these materials have been thoroughly characterized. The desorption temperature is 350-400°C, but can be lowered upon adding dopants. Work is currently on-going with respect to re-hydriding borohydrides of magnesium and calcium. Other $\text{Mg}(\text{BH}_4)_2$ related materials were also prepared and characterized, for example $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$, which is being analyzed for decomposition products and $\text{Mg}(\text{BH}_4)(\text{AlH}_4)$, whose synthesis yield is being optimized.

Alkali transition metal borohydrides of more than 10 weight percent capacity are also under consideration. The $\text{A}_x\text{Zn}(\text{BH}_4)_y$ and $\text{A}_x\text{Mn}(\text{BH}_4)_y$ materials ($\text{A} = \text{Li}, \text{Na}, \text{K}$) release hydrogen below ~150°C, but have not yet been shown to be reversible. The Zn-containing borohydrides are no longer under consideration due to very high material decomposition via release of diborane, B_2H_6 . Current possibilities are being investigated to re-hydride the Mn-containing borohydrides and other borohydrides, under higher pressures. In addition, the Center is currently preparing $\text{Al}(\text{BH}_4)_3$ and $\text{LiM}(\text{BH}_4)_4$ ($\text{M} = \text{Al}$ or Ti) in the liquid state and investigating their properties. Recently, guided by theory, a bialkali borohydride ($\text{AB}(\text{BH}_4)_2$) was predicted to be stable and was recently prepared in the solid state. Work on this material is ongoing.

Novel, light-weight, high-capacity metal hydrides are being synthesized that consist of a matrix of cations (such as Li, Na, K, Mg, Ca) that stabilizes the anionic complex (which may consist of a d-element (such as Sc, Ti, V) or a p-element (such as B, Al, Si)) that bonds to hydrogen and thus forms a ternary or higher metal hydride. A-Si-H ($\text{A} = \text{Li}, \text{Na}, \text{Ca}$) and A-Ge-H-systems ($\text{A} = \text{Li}, \text{Na}, \text{Ca}$) have been explored. The Na-Ge-H system showed a material with significant amount of hydrogen. This material is currently being characterized. New complex metal hydrides in the ternary and quaternary Ni, Fe and Mn systems with Li, Na or Ca in the cation matrix are also being screened. Another material of interest is $\text{Mg}_7\text{TiH}_{16}$ (~7wt% hydrogen) which in the literature has so far only has been made at GPa pressures or by thin film techniques. Attempts to prepare this material under more moderate conditions and with a high-energy milling technique are currently underway.

The materials considered by Project B are summarized in Table III, with their Go/No-Go status indicated in the last column and by gray shading.

Project C: Amide/Imide Hydrogen Storage

The focus of the MHCoe Project C is 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. [4] on the potential of using Li_3N as a hydrogen storage material. The original published reaction involving amide is indicated in the first row of Table IV. This reaction was considered by Project C, but was not pursued due to its poor dehydrogenation kinetics.

To improve the hydrogen storage properties of LiNH_2 , extensive studies were conducted on the $\text{LiNH}_2/\text{MgH}_2$ reaction. The use of MgH_2 improved the kinetic properties and significantly lowered the desorption temperature from 250°C to $\sim 200^\circ\text{C}$. However, this system was given a No-Go status in FY 2006 because a credible path could not be found for increasing the accessible hydrogen capacity beyond 5 weight percent. To achieve higher hydrogen storage capacity requires further dehydrogenation from lithium magnesium imide ($\text{Li}_2\text{Mg}(\text{NH})_2$), which is not possible for temperatures below $\sim 500^\circ\text{C}$.

On the basis of the result on LiNH_2 and published work on lithium alanate (LiAlH_4), studies were initiated of the reaction between lithium amide with lithium alanate. The $\text{LiNH}_2/\text{LiAlH}_4$ system was found to release considerable amounts of hydrogen (~ 8 weight percent) at temperatures of $\sim 300^\circ\text{C}$. However, this material system is not sufficiently reversible, so was given a No-Go status in FY 2006.

To continue to explore the opportunities of combining amide with alanate materials, SNL contracted with the National University of Singapore (NUS) to study the reaction between Li_3AlH_6 and LiNH_2 (in 1:2 and 1:3 ratios). Results show that the (1:2) reaction was not sufficiently reversible, so work on this material was discontinued. MHCoe work continues on the (1:3) reaction between Li_3AlH_6 and LiNH_2 , as well as reaction with magnesium amide $\text{Mg}(\text{NH}_2)_2$ (Rows 6 and 7 in Table IV, respectively). These two reactions demonstrated full (~ 7 and 6% respectively) reversibility at temperatures $\sim 300^\circ\text{C}$. Current work is focusing on the mechanisms of the reversible reactions and characterization of their thermodynamic and kinetic properties.

In FY 2007, MHCoe theory predicted that LiMgN could be an interesting material. Initial experiments suggested that LiMgN can reversibly store up to 8% of hydrogen by weight. This is an encouraging result. Experiments are in progress for elucidating both the hydrogenation and dehydrogenation reaction pathways.

The materials considered by Project C are summarized in Table IV, with their Go/No-Go status indicated in the last column and by gray shading.

Project D: Alane (AlH_3)

Work conducted in the MHCoE by BNL has demonstrated that the properties of AlH_3 make it a strong candidate for a hydrogen storage material. It has a high hydrogen gravimetric density (10.1 wt. %), and good dehydrogenation kinetics at a relatively low temperature (100°C). A significant challenge for this material is to find an efficient and low-cost means to regenerate AlH_3 from the Al-containing spent material.

AlH_3 will continue to be investigated (a “Go” Decision). Table V gives a summary of the three lines of investigation for Al regeneration that are being pursued within Project D of the MHCoE. The first investigation, adduct stabilization, searches for a chemical agent that can complex with and stabilize the Al- H_3 moiety, thereby facilitating the hydrogenation of aluminum. The second project investigates if aluminum hydrogenation can be facilitated in a supercritical fluid environment. The third line of study, electrochemical regeneration, examines the conditions for which AlH_3 can be regenerated from Al via electrochemical reduction of protons at aluminum surfaces in solution.

Summary:

As fulfillment for the FY 2007 milestone for down-selecting materials within the MHCoE, this report documents the materials that have been investigated in the MHCoE since its inception, and gives the “Go” and “No-Go” decisions made for each of these materials. Over the course of the MHCoE work since FY2005, 51 materials systems have been investigated in the 4 materials projects (A-D) in the Center. Of these 51 materials, 27 have satisfied the 5 performance metrics described earlier (i.e. show promise as a viable hydrogen storage material) and are being studied further. The report began with a summary of the DOE system targets for hydrogen storage, as well as the materials performance metrics adopted within the MHCoE upon which the Go, No-Go decisions were based. A review was given of the materials examined in Projects A, B and C, with a tabulation of the Go/No-Go assignments. In Project D, there are three viable approaches to aluminum rehydrogenation (to form AlH_3), which all remain of current research interest. The MHCoE continues to search for new materials systems to explore. Part of this search will involve combinatorial materials searches for new materials as well as catalytic systems. The MHCoE Theory group will continue to use Density functional Theory (DFT) predictions of reaction thermodynamics to guide the experimental materials discovery efforts.

References:

1. http://www1.eere.energy.gov/hydrogenandfuelcells/storage/current_technology.html
2. http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/freedomcar_targets_explanations.pdf - 354.3KB
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Table I: DOE Targets for On-board Hydrogen Storage Systems

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 H₂^l	Scc/h -- -- (g/h)/kg H ₂ stored	Meets or exceeds applicable standards		
		1	0.1	0.05

Table II: List of materials investigated in Project A (Destabilized Hydrides) including those that were considered and discontinued, and those that are still under investigation. A gray shading indicates the material is no longer being considered (No-Go Decision). No shading (i.e. clear) indicates the material is being investigated further (Go Decision).

System	Anticipated Reaction	Partners Involved	Theoretical hydrogen capacity	ΔH (kJ/mol- H_2)	T_{1bar} ($^{\circ}C$)	T_K ($^{\circ}C$)	Status
MgH ₂ /Si	$2MgH_2 + Si \rightarrow Mg_2Si + 2H_2$	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	$MgSiN_2 + 2H_2 \rightarrow Mg(NH_2)_2 + Si$	HRL	4.7 wt%	-	-	-	No longer considered because no hydrogenation was observed (system not reversible)
Li ₂ SiN ₂	$Li_2SiN_2 + 2H_2 \rightarrow 2LiNH_2 + Si$	HRL	5.4 wt%	-	-	-	No longer considered because of difficulty synthesizing Li ₂ SiN ₂
LiF/MgB ₂	$2LiF + MgB_2 + 4H_2 \rightarrow LiBH_4 + MgF_2$	HRL	7.6 wt%	45 (db)	150 (db)	~300	No longer considered because the reaction is not sufficiently reversible.
LiCl/MgB ₂	$2LiCl + MgB_2 + 4H_2 \rightarrow 2LiBH_4 + MgCl_2$	HRL	5.8 wt%	29 (db)	-10 (db)	-	No longer considered because no hydrogenation was observed
Li ₂ S/MgB ₂	$2Li_2S + MgB_2 + 4H_2 \rightarrow 2LiBH_4 + MgS$	HRL	8.0 wt%	47 (db)	170 (db)	~300	No longer considered because the reaction is not sufficiently reversible.
Li ₂ Se/MgB ₂	$2Li_2Se + MgB_2 + 4H_2 \rightarrow 2LiBH_4 + MgSe$	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	$Li_2CO_3 + MgB_2 + 4H_2 \rightarrow 2LiBH_4 + MgCO_3$	HRL	6.3 wt%	42 (db)	110 (db)	-	No longer considered because the CO ₃ anion decomposes.
LiBH ₄ /Mg ₂ Cu	$4LiBH_4 + Mg_2Cu \rightarrow 4LiH + 2MgB_2 + Cu + 6H_2$	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	$4LiH + B_4C \rightarrow 4LiBH_4 + C$	HRL	12.0 wt%	55 (db)	290 (db)	-	No longer considered because no hydrogenation was observed
LiBH ₄ /Si	$3LiBH_4 + Si \rightarrow 3LiH + B_3Si + 4.5H_2$	HRL	9.5 wt%	-	-	-	No longer considered because no B ₃ Si was observed

Table II Continued...

System	Anticipated Reaction	Partners Involved	Theoretical hydrogen capacity	ΔH (kJ/mol-H_2)	T_{1bar} (°C)	T_K (°C)	Status
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)	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 ₄ Si ₂ H 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 ₄ Ge ₂ H 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	Continuing. A combinatorial catalyst search in thin-film and bulk form to improve reaction
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)	-	-	Continuing. Focusing on incorporating Mg into aerogel, and increasing reaction rate and aerogel loading.
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)	-	Theory predicts excellent thermodynamics, but has kinetics & reversibility issues, looking into possible catalysts, etc.
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. Experimental investigation to be conducted in FY 2008
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. To be studied experimentally

Table II Continued...

System	Anticipated Reaction	Partners Involved	Theoretical hydrogen capacity	ΔH (kJ/mol-H_2)	T_{1bar} ($^{\circ}C$)	T_K ($^{\circ}C$)	Status
C/LiNH ₂	$2 \text{ LiNH}_2 + \text{C} \rightarrow \text{Li}_2\text{CN}_2 + 2 \text{ H}_2$	U. Pitt/CMU	7.0 wt%	31 (dft)	-100 (dft)	-	Theory predicts excellent thermodynamics and hydrogen storage capacity. Experimental investigation to be conducted in FY 2008
LiH/Mg(NH ₂)/VN	$28 \text{ LiH} + 9 \text{ Mg(NH}_2)_2 + 4 \text{ VN} \rightarrow 4 \text{ Li}_7\text{N}_4\text{V} + 3 \text{ Mg}_3\text{N}_2 + 32 \text{ H}_2$	U. Pitt/CMU	6.5 wt%	47.5 (dft)	-	-	Theory predicts excellent thermodynamics and hydrogen storage capacity. Experimental investigation to be conducted in FY 2008

Table III: List of materials investigated in Project B (Complex Anionic Materials) including those that were considered and discontinued, and those that are still under investigation. A gray shading indicates the material is no longer being considered (No-Go Decision). No shading (i.e. clear) indicates the material is being investigated further (Go Decision).

<i>Compound</i>	<i>Anticipated Reaction</i>	<i>Partner Involved</i>	<i>Theoretical hydrogen capacity</i>	<i>ΔH (kJ/mol-H_2)</i>	<i>T_{1bar} ($^{\circ}C$)</i>	<i>T_K ($^{\circ}C$)</i>	<i>Status</i>
Ti-NaAlH ₄	NaAlH ₄ $\rightarrow$ 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 ₂ LiAlH ₆	K ₂ LiAlH ₆ $\rightarrow$ 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 _x Zn(BH ₄) _x A=Li, Na,K	A _x Zn(BH ₄) ₂ $\rightarrow$ [A _x -Zn-B] + 2xH ₂	UH	~11 wt%	-	-	100- 150	Desorbs H ₂ below 150C. No longer considered because of significant release of B ₂ H ₆ upon decomposition.
NaK(BH ₄) ₂	NaK(BH ₄) ₂ $\rightarrow$ [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) ₂	Mg(BH ₄) ₂ $\rightarrow$ MgH ₂ + 2B + 3H ₂	GE, SNL, Utah ORNL, JPL, Caltech, UNR, PITT	14.8 wt%	47 (exp)	-	230	Full reversibility not yet shown, but will attempt to re-hydrate at higher pressures at SNL. Found intermediate phase. Tohoku Univ. recharged it to 6 wt. % at 700 bar.
Mg(BH ₄) ₂ (NH ₃) ₂	Mg(BH ₄) ₂ (NH ₃) $\rightarrow$ [Mg-B-N] + 11/2 H ₂	GE	16.0 wt.%	-	-	100	Decomposition mechanism study.
Mg(BH ₄)(AlH ₄)	Mg(BH ₄)(AlH ₄) $\rightarrow$ [Mg-B-Al] + 4H ₂	GE	11.4 wt.%	-	-	120	Continuing on synthesis trials to make single phase material

Table III Continued....

Compound	Anticipated Reaction	Partner Involved	Theoretical hydrogen capacity	ΔH (kJ/mol-H_2)	T_{1bar} ($^{\circ}C$)	T_K ($^{\circ}C$)	Status
$Al(BH_4)_3$	$Al(BH_4)_3 \rightarrow Al + 3B + 6H_2$	ORNL	16.8 wt%	-	-	-	Continuing study of decomposition products
$LiM(BH_4)_4$ (M=Ti or Al)	$LiM(BH_4)_4$ (M=Ti or Al) $\rightarrow$ Li + M + 4B + 8H ₂	ORNL	14-17 wt%	-	-	-	Preparation and study of decomposition products will be undertaken
$A_xMn(BH_4)_x$ A=Li, Na, K	$A_xMn(BH_4)_x \rightarrow [A_x-Mn-B] + 2xH_2$	UH, SNL	~12.0 wt%	-	-	100 (A=Na)	Continuing. Desorbs H ₂ below 150°C. Focusing on reversibility.
$LiK(BH_4)_2$	$LiK(BH_4)_2 \rightarrow [Li-K-B] + 4 H_2$		10.6 wt%	-	-	-	Continuing characterization
$Ca(BH_4)_2$	$3Ca(BH_4)_2 \rightarrow CaB_6 + 2CaH_2 + 10H_2$	SNL, UNR, UMSL	9.6wt%	41.4 (dft)	350		Continuing characterization, looking for catalysts
$Ca(BH_4)(AlH_4)$		UMSL, SNL	11.9 wt%	-	-	-	Continuing characterization
$Ti(BH_4)_3$	$Ti(BH_4)_3 \rightarrow [Ti-B] + 6 H_2$	ORNL, GE	13.1 wt%	-	-	-	Initiating study
Mg-Ti-H	$Mg_7TiH_{16} \rightarrow 7Mg + Ti + 8H_2$	Utah, SNL	~7.0 wt%	-	-	~300	Continuing. Focusing on different reaction routes and additives.
A-Si-H (A=Li, Na, Ca)	$A_2SiH_x \rightarrow 2AH + Si + xH_2$	SNL, Utah, HRL, NIST	5-9 wt%	-	-	-	Continuing synthesis effort. Theory predicted existence of ternary Si-hydrides.
Na-Ge-H	$A_2GeH_x \rightarrow 2AH + Ge + (x/2 - 1)H_2$	SNL, NIST	~5.0 wt%	-	-	-	Continuing characterizing of new material.
A-B-Ni-H (A=Li, Na, Mg, Ca)	$ABNiH_x \rightarrow AH + BH + Ni + xH_2$	SNL	~ 4-6 wt%	-	-	-	Effort on-going
Mg-Mn-H	$MgMnH_9 \rightarrow MgH_2 + Mn + 7/2H_2$	SNL	~ 5-6 wt%	-	-	-	Continuing optimizing reaction conditions
$Li_mSc_n(BH_4)_{m+n}$		JPL, Caltech UH	9-14 wt%	-	-	-	BM synthesis, NMR characterization, & desorption studies looking for reversibility
$LiBH_4/Ca(AlH_4)_2$		JPL, Caltech NIST	6-7 wt%	-	-	-	BM synthesis, NMR & NVS characterization, & desorption studies at moderate temperature showing some reversibility

Table IV: List of materials investigated in Project C (Amide/Imide Materials) including those that were considered and discontinued, and those that are still under investigation. A gray shading indicates the material is no longer being considered (No-Go Decision). No shading (i.e. clear) indicates the material is being investigated further (Go Decision).

System	Anticipated Reaction	Partner Involved	Theoretical hydrogen capacity	ΔH (kJ/mol- H_2)	T_{1bar} ($^{\circ}C$)	T_K ($^{\circ}C$)	Status
Li_3N	$Li_3N + 2H_2 \rightarrow LiNH_2 + 2LiH$	NUS	11.5 wt%	-80.5	250	300 -400	Not considered. The plateau pressure is too low and the dehydrogenation kinetics is too slow.
$Li_2Mg(NH)_2$	$2LiNH_2 + MgH_2 \rightarrow Li_2Mg(NH)_2 + 2H_2$	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.
$LiAlH_4/LiNH_2$	$LiAlH_4 + LiNH_2 \rightarrow Li_2NH + Al + 2.5H_2$	Utah	8.1 wt%	26.8	N/A	200 - 300	No longer considered because the reaction is not sufficiently reversible.
$LiAlH_4/LiNH_2$	$LiAlH_4 + 2LiNH_2 \rightarrow Li_3AlN_2 + 4H_2$	SNL (NUS)	9.5 wt%	-25.8	N/A	300 - 450	No longer considered because the temperature for complete dehydrogenation is too high, and the reaction is not reversible.
$Li_3AlH_6/LiNH_2$ (1:2)	$Li_3AlH_6 + 2LiNH_2 \rightarrow 2Li_2NH + LiAl + 4H_2$	SNL (NUS)	8 wt%	40.5	N/A	~300	No longer considered because the reaction is not sufficiently reversible.
$Li_3AlH_6/LiNH_2$ (1:3)	$Li_3AlH_6 + 3LiNH_2 \rightarrow 3Li_2NH + Al + 4.5H_2$	Utah, SNL (NUS), JPL, HRL, UNR	7.3 wt%	38.4	250 (exp)	200 - 300	Continuing. Focusing on the reaction mechanisms and improving the dehydrogenation and rehydrogenation kinetics.

Table IV Continued...

System	Anticipated Reaction	Partner Involved	Theoretical hydrogen capacity	ΔH (kJ/mol-H_2)	T_{1bar} ($^{\circ}C$)	T_K ($^{\circ}C$)	Status
Li ₃ AlH ₆ /Mg(NH ₂) ₂	2Li ₃ AlH ₆ +3Mg(NH ₂) ₂ → 3Li ₂ Mg(NH) ₂ +2Al+9H ₂	Utah, JPL, GE	6.5 wt%	21.4	TBD	200 - 300	Temporarily on-hold until work on Li ₃ AlH ₆ /3LiNH ₂ is complete.
LiMgN	LiNH ₂ +MgH ₂ → LiMgN+2H ₂ ↔LiH+ 0.5MgH ₂ +0.5Mg(NH ₂) ₂	Utah, PITT/CMU, JPL	8.2 wt%	32 step 1 51 step 2	TBD	220 - 270	Continuing. Focusing on reaction mechanisms and determination of the plateau pressure and kinetic properties.

Table V: List of approaches in Project D (Alane) to regenerate AlH_3 from Al .

<i>Al Regeneration</i>	<i>Partner</i>	<i>Status</i>
Adduct Stabilization of AlH_3	BNL	Initial results demonstrate approach, improvements in progress
Supercritical fluid regeneration of AlH_3	UH, UNB	Project just funded, initial experiments underway
Electrochemical regeneration of AlH_3	SRNL	Initial results demonstrate approach, improvements in progress

Appendix I: Footnotes to Table I: DOE Targets for On-board Hydrogen Storage Systems

- a. Generally, the ‘full mass (including hydrogen) is used, for systems that gain weight, the highest mass during discharge is used.
- b. 2003 US\$; total cost includes any component replacement if needed over 15 years or 150,000 mile life.
- c. 2001 US\$; includes off-board costs such as liquefaction, compression, regeneration, etc.; 2015 target based on H₂ production cost of \$2 to \$3/gasoline gallon equivalent untaxed, independent of production pathway.
- d. Stated ambient temperature plus full solar load. No allowable performance degradation from -20°C to 40°C. Allowable degradation outside this limit is TBD.
- e. Equivalent to 100,000; 200,000; and 300,000 miles respectively (current gasoline tank spec).
- f. All targets must be achieved at end-of-life.
- g. In the near term, the forecourt should be capable of delivering 10,000 psi compressed hydrogen, liquid hydrogen, or chilled hydrogen (77 K) at 5,000 psi. In the long term, it is anticipated that delivery pressures will be reduced to between 50 and 150 atm for solid state storage systems, based on today’s knowledge of sodium alanates.
- h. Flow must initiate within 25% of target time.
- i. At operating temperature.
- j. The storage system will not provide any purification, but will receive incoming hydrogen at the purity levels required for the fuel cell. For fuel cell systems, purity meets SAE J2719, Information Report on the Development of a Hydrogen Quality Guideline in Fuel Cell Vehicles. Examples include: total non-particulates, 100 ppm; H₂O, 5 ppm; total hydrocarbons (C₁ basis), 2 ppm; O₂, 5 ppm; He, N₂, Ar combined, 100 ppm; CO₂, 1 ppm; CO, 0.2 ppm; total S, 0.004 ppm; formaldehyde (HCHO), 0.01 ppm; formic acid (HCOOH), 0.2 ppm; NH₃, 0.1 ppm; total halogenates, 0.05 ppm; maximum particle size, <10µg/L H₂. These are subject to change. See Appendix F of DOE Multiyear Research, Development and Demonstration Plan (www.eere.energy.gov/hydrogenandfuelcells/mypp/) to be updated as fuel purity analyses progress. Note that some storage technologies may produce contaminants for which effects are unknown; these will be addressed as more information becomes available.
- k. Total hydrogen lost into the environment as H₂; relates to hydrogen accumulation in enclosed spaces. Storage system must comply with CSA/NGV2 standards for vehicular tanks. This includes any coating or enclosure that incorporates the envelope of the storage system.
- l. Total hydrogen lost from the storage system, including leaked or vented hydrogen; relates to loss

Appendix II: Selected Publications on Materials Investigated in the MHCoE

MgH₂/Si:

B. Dai, D. S. Sholl, and J. K. Johnson, "First Principles Investigation of Adsorption and Dissociation of Hydrogen on Mg₂Si Surfaces", J. of Phys. Chem. C, **111(18)** 6910-6916 (2007).

MgX/LiBH₄:

J. J. Vajo, T.T. Salguero, A. F. Gross, S. L. Skeith and G. L. Olson, "Thermodynamic Destabilization and Reaction Kinetics in Light Metal Hydride Systems," J. of Alloys and Compounds, **446-447**, 409-414 (2007).

J.J. Vajo and G.C. Olson, "Hydrogen Storage in Destabilized Chemical Systems," Scripta Materiala **56**, 829-834 (2007).

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

LiH/Si & LiH/Ge:

H. Wu, M. R. Hartman, T. J. Udovic, J. J. Rush, W. Zhou, R. C. Bowman, Jr., and J. J. Vajo, "Crystal Structure of a Novel Class of Ternary Hydrides Li₄Tt₂D (Tt=Si and Ge)," Acta Crystallographica B **63**, 63 (2007).

Ca-Si-H:

H. Wu, W. Zhou, T. J. Udovic, and J. J. Rush, "Hydrogen Storage in a Novel Destabilized Hydride System, Ca₂SiH_x: Effects of Amorphization," Chemistry of Materials **19**, 329 (2007).

H. Wu, W. Zhou, T. J. Udovic, and J. J. Rush, "Structure and Hydrogenation Properties of the Ternary Alloys Ca_{2-x}Mg_xSi (0 ≤ x ≤ 1)," J. Alloys Compd. **446-447**, 101 (2007).

NaAlH₄:

J.L. Herberg, R.S. Maxwell, E.H. Majzoub, " ²⁷Al and ¹H MAS NMR and ²⁷Al Multiple Quantum Studies of Ti-doped NaAlH₄", J. Alloys and Comp. **417**, 39-44, (2006).

E.H. Majzoub, V. Ozolins, K.F. McCarty, "Lattice dynamics of NaAlH₄ from High-temperature Single-crystal Raman Scattering and Ab initio Calculations: Evidence of Highly Stable AlH⁻ Anions", Phys. Rev.B, **71**, 24118 (2005).

Ca (AlH₄)₂:

H. Kabbour, C.C. Ahn, S.-J. Hwang, R.C. Bowman Jr. and J. Graetz, "Direct Synthesis and NMR Characterization of Calcium Alanate," *J. Alloys and Compounds*, **446-447**, 264-266 (2007).

K₂LiAlH₆:

E. Rönnebro, E. Majzoub, "Crystal Structure, Raman Spectroscopy and Ab-initio Calculations of a New Bialkali Alanate K₂LiAlH₆", *J. Phys. Chem. B.*, **110**, 25686 – 25691 (2006).

Mg(BH₄)₂, Mg(BH₄)₂(NH₃)₂:

J.-H. Her, P.W. Stephens, Y. Gao, G.L. Soloveichik, J. Rijssenbeek, M. Andrus, and J.-C. Zhao, "Structure of Unsolvated Magnesium Borohydride Mg(BH₄)₂", *Acta Crystallographica B*, **B63**, 561-568 (2007).

G.L. Soloveichik, M. Andrus, and E.B. Lobkovsky, "Magnesium Borohydride Complexed by Tetramethylethylenediamine", *Inorganic Chemistry*, **46**, 3790-3791 (2007).

G.L. Soloveichik, "Metal Borohydrides as Hydrogen Storage Materials," *Materials Matters (Aldrich)*, **2** (2), 11-14 (2007).

S.-J. Hwang, R.C. Bowman, Jr., J.W. Reiter, J. Rijssenbeek, G.L. Soloveichik, J.-C. Zhao, H. Kabbour, and C.C. Ahn, "NMR Confirmation for Formation of B₁₂H₁₂ Complexes during Hydrogen Desorption from Metal Borohydrides", *Journal of Physical Chemistry C*. Submitted November 2007.

Ca(BH₄)₂

E. Rönnebro, E. Majzoub, "Calcium Borohydride for Hydrogen Storage: Catalysis and Reversibility", *J. Phys. Chem. B. (Letter)*; **111** 12045 – 12047 (2007).

LiBH₄/MgH₂, LiBH₄/ScH₂, C/ Mg(BH₄)₂, B/Mg(BH₄)₂, C/LiNH₂, LiH/Mg(NH₂)/VN, LiMgN:

S. V. Alapati, J. K. Johnson, and D. S. Sholl, "Using First Principles Calculations To Identify New Destabilized Metal Hydride Reactions for Reversible Hydrogen Storage", *Phys. Chem. Chem. Phys.* **9**, 1438-1452 (2007).

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