SAND2009-3039P

QUARTERLY PROGRESS REPORT

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.

Project Title: Metal Hydride Center of Excellence (MHCoE)

Covering Period: January 1, 2009 through March 31, 2009

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Project Objective: The MHCoE is tasked with achieving the Grand Challenge of developing hydrogen storage materials that meet or exceed the FreedomCAR and Fuels Program targets for an on-board hydrogen storage system. This is a critical task for the DOE to be able to reach its goal of enabling an informed industry commercialization decision in 2015. MHCoE will meet this challenge through SNL's technical contributions, as well as guiding and supporting the university, industrial and national research laboratory partners within the MHCoE.

PROJECT STATUS:

Task 2: Sandia Research and Development within the MHCoE

Subtask 2.1 – New Complex Anionic Materials

Subtask 2.1.1 – Alkali and Alkaline- Earth Borohydrides

Principal Investigators: Vitalie Stavila, Eric Majzoub

Objective: To synthesize and explore reversibility of high-hydrogen content metal borohydrides guided by theory. There are currently no materials that meet the DOE hydrogen storage performance targets. In order to address this problem, we have undertaken the synthesis and testing of high-hydrogen content metal borohydrides (>9wt%) for use as reversible hydrogen storage materials. Computational modeling has assisted in directing these efforts. This is a collaborative effort within the MHCoE.

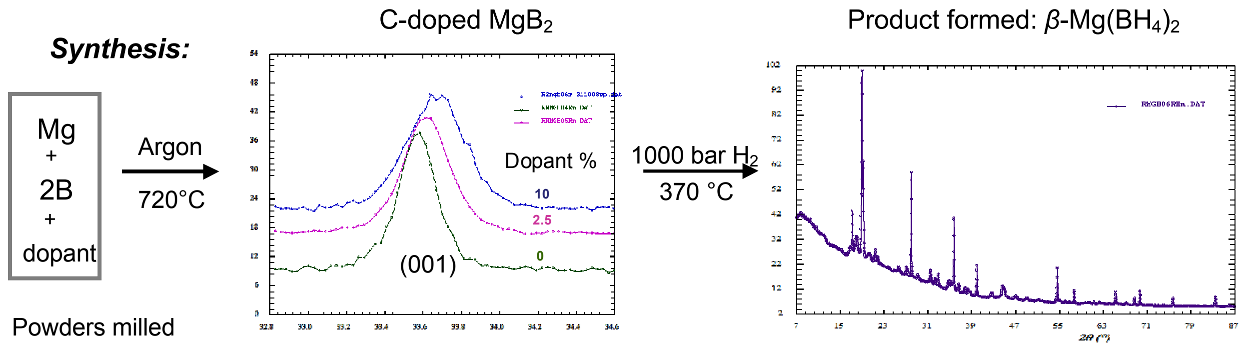
The bulk of the research conducted during this review period was concentrated on calcium and magnesium borohydride. We had previously reported that $Ca(BH_4)_2$ decomposes into CaH_2, CaB_6 and intermediate species with a broad ^{11}B MAS NMR peak comparable, as far as the chemical shift is concerned, to dodecahydro-*closo*-dodecaborate species. In order to compare the decomposition product with the reference material, we synthesized $CaB_{12}H_{12}$ and characterized it in collaboration with our NIST (XRD, NVS) and JPL/Caltech partners (^1H and ^{11}B NMR). Anhydrous $CaB_{12}H_{12}$ was obtained by dehydration/desolvation of $[Ca(H_2O)_7][B_{12}H_{12}]\cdot H_2O$ (Tiritiris, I. & Schleid, T. *Z. Anorg. Allg. Chem. 627*, **2001**, 1836-1845) and newly-synthesized $[Ca(H_2O)_5(MeCN)_2][B_{12}H_{12}]$, upon heating in vacuum up to 300 °C. $CaB_{12}H_{12}$ was characterized by elemental analysis, IR, ^1H and ^{11}B NMR, and neutron vibrational spectroscopy. We showed that $CaB_{12}H_{12}$ displays a remarkable thermal stability up to 420 °C. Attempts to hydrogenate/dehydrogenate mixtures of $CaB_{12}H_{12}$ and CaH_2 were made, however, no notable formations of calcium borohydride (during hydrogenation) or calcium boride (during dehydrogenation) occurred. A TPD study of ball-milled mixtures of $CaB_{12}H_{12}$ and CaH_2 revealed that less than 1% H_2 is released up to 400 °C. This lack of reactivity indicates that the formation of $[B_{12}H_{12}]^{2-}$ species is undesirable during the dehydrogenation/cycling of $Ca(BH_4)_2$. A paper describing the synthesis, structure and characterization of $CaB_{12}H_{12}$ is in progress.

Several theoretically predicted reactions involving $LiBH_4$, $Mg(BH_4)_2$ and $Ca(BH_4)_2$ (Ozolins, V., Majzoub, E. H. & Wolverton, C. *J. Amer. Chem. Soc. 131*, **2009**, 230-237) were explored experimentally. These borohydride systems are predicted to favor the $B_{12}H_{12}$ species formation. The calculations indicate that products with fewer anions or tightly bound bulk phase reduce the number of low frequency phonon branches which decreases ΔS from ~ 130 J/K·mol to ~ 100 J/K·mol H_2 for the reactions presented in the Table below.

Predicted Reactions	Theor. wt% H_2	ΔH^{300K} kJ/mol H_2	T_c (°C)	Exp. Data: wt% H_2 (350ºC, 4h)
$5Mg(BH_4)_2 + 2LiBH_4 \Rightarrow Li_2B_{12}H_{12} + 5MgH_2 + 13H_2$	8.4	24.4	-29	6.0
$5Mg(BH_4)_2 + Ca(BH_4)_2 \Rightarrow CaB_{12}H_{12} + 5MgH_2 + 13H_2$	7.7	25.7	-18	4.4
$5Ca(BH_4)_2 + 2LiBH_4 \Rightarrow Li_2B_{12}H_{12} + 5CaH_2 + 13H_2$	6.7	37.9	83	6.2

In this table, the critical temperature T_c is equivalent to T_{1bar}. Our kinetic experiments on ball-milled mixtures of borohydrides in the molar ratios required by the reactions presented in the Table above show a slight improvement in the kinetics of hydrogen release compared to the initial borohydrides. The desorption temperature was lowered by ~50 °C; however, a significant hydrogen capacity loss (>50%) was observed on the second cycle.

In collaboration with the U. Hawaii, we have recently demonstrated that it is possible to prepare $Mg(BH_4)_2$ from its end-decomposition product MgB_2 according to $MgB_2 + 4H_2 \rightarrow Mg(BH_4)_2$ (E. Rönnebro, C. Jensen, G. Severa, "*Direct Synthesis of Magnesium Borohyride*", U.S. Patent Application filed 2008). Doping $Mg(BH_4)_2$ with the appropriate material is one potential way to tailor the compound's thermodynamics and kinetics for the ultimate goal of reversibility at lower temperatures. This solid-state synthesis of $Mg(BH_4)_2$ provides a way to effectively dope the borohydride by first doping the precursor, MgB_2. The synthesis and corresponding data for the fabrication and hydrogenation of carbon-doped MgB_2 was accomplished and is diagramed in the Scheme below. This work is in progress.



Powders milled and pressed into pellets

XRD confirmation of C-doped MgB_2 from (001) peak shift

XRD of 10% C-doped MgB_2 after hydrogenation showing formation of β-$Mg(BH_4)_2$

We have completed our work on $Ca(BH_4)_2$ polymorph crystal structures, and the paper is now in print (E. H. Majzoub, E. Rönnebro, *J. Phys. Chem. C*, *113*, **2009**, 3352–3358). However, the compound $Ca(BH_4)_2$ has been down-selected (will not be pursued further) due to poor kinetics. An extensive investigation of catalysts and dopants has not shown greatly improved sorption properties (*for results see Subtask 2.1.4*).

Subtask 2.1.2 – Discovery and Characterization of New Materials

Principal Investigators: Mutlu Kartin, Eric Majzoub

Objective: To discover new light-weight, high-capacity complex metal hydrides for reversible on-board hydrogen storage guided by theory.

New materials discovery has focused on the synthesis of main group compounds containing borohydrides. Specifically, we have begun the synthesis of $M[PH_2(BH_3)_2]$ (M = Na or Li) and related species. Noteworthy, is the decomposition of the lithium salt $Li(PH_2BH_3)$ (ca. 10% H_2 by weight), which looses hydrogen slowly at 85 °C. A related sodium salt $Na[PH_2(BH_3)_2]$, which has ca. 9.0% H_2 by weight is also of interest. This class of materials was first reported in 1967 but little subsequent work has been published. The synthesis is challenging and begins from $PH_3{\bullet}BH_3$ or PI_3H—neither is currently commercially available . However, alternative routes from the action of $LiBH_4$ on PCl_3 or PI_3 are being attempted. As of April 2009, all starting materials have been acquired and equipment has been set up to perform these reactions properly. Preliminary attempts at reducing PCl_3 with $NaBH_4$ have yielded a product showing NMR data consistent with $Na[PH_2(BH_3)_2]$—the desired product. Full characterization is underway.

Work has also been done investigating solution routes to access mixed metal alanates/borates. For example, we have synthesized $CaLi(BH_4)_m(AlH_4)_n{\bullet}THF$ and begun structural characterization. Other mixed metal hydride systems are being explored but solution routes to access them are limited due to poor starting material solubility. Solvent-free $Ca(BH_4)(AlH_4)$ was isolated using a solid-state ball-milling approach. Raman spectroscopy indicates presence of both BH_4 and AlH_4 anions in the product. Initial studies show no reversibility at 200 °C and 65 bar H_2 pressure.

In collaboration with UTRC, we are exploring alkali-transition-metal borohdydrides such as $Li_nTi(BH_4)_m$, and $Na_nTi(BH_4)_m$. These mixed-metal borohydrides have the potential to be less stable than pure alkali-metal borohydrides, and may also exhibit better kinetics due to the presence of transition metals, which may help to catalyze hydrogen sorption reactions. Literature results for the structure of $Hf(BH_4)_4$ form the starting point for the theoretical calculations on the potential structure and stability of $Ti(BH_4)_n$. Experimental synthesis results indicate that the stable structure is $Ti(BH_4)_3$. However, a theoretical study of the stability of Ti^{3+} and Ti^{4+} hypothetical structures may illuminate the $Ti-BH_4$ coordination and bonding environment and help to understand the electronic structure of the alkali-Ti structures we are investigating. A search for structures for several mixed-metal compounds is currently underway using the method of potential electrostatic ground states (PEGS). Initial results for $NaTi(BH_4)_4$, indicate several structures in symmetries above P1. The bulk crystal structures of these compounds will also serve as starting points for cluster geometries for cluster/surface interaction calculations currently underway at UTRC.

Subtask 2.1.3 – Synthesis of Ammine Borohydrides, and Mixed Amide/Borohydride Materials

Principal Investigators: Vitalie Stavila, Mutlu Kartin

Objective: Assessment and discovery of novel ammine-borohydride and mixed amide/imide-borohydride materials for on-board hydrogen storage applications.

In this quarter we finalized the investigation of the three calcium-containing borohydride-ammonia systems we initiated in the previous quarter, $Ca(BH_4)_2$-NH_3, $LiCa(BH_4)_3$-NH_3 and $MgCa(BH_4)_4$-NH_3. We found that all three compounds suffer from ammonia release. The Ca and LiCa materials release all ammonia upon heating as proved by TGA (Figure 1), IR and XRD. IR spectroscopy revealed the presence of N-H stretches after heating the as prepared $MgCa(BH_4)_4$-NH_3 for 4 hours in vacuum at 120 °C. Preliminary STMBMS data indicate that ammonia and hydrogen are the major gaseous species upon heating. Further experiments to quantify the relative amounts of ammonia and hydrogen released are currently underway.

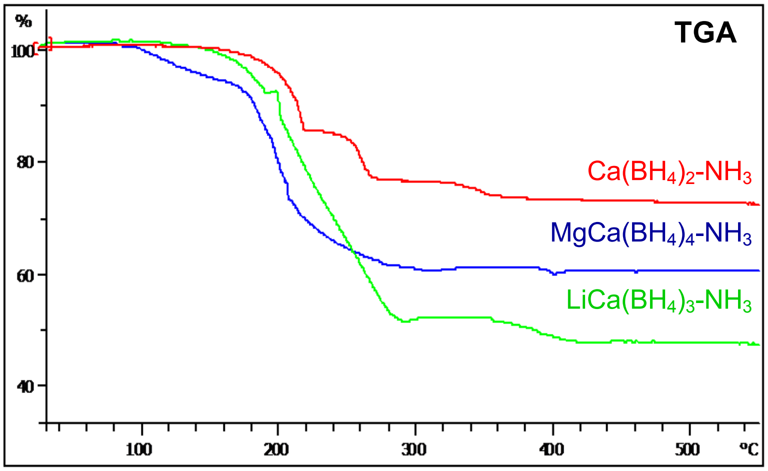


Figure 1. TGA results for $Ca(BH_4)_2$-NH_3, $LiCa(BH_4)_3$-NH_3 and $MgCa(BH_4)_4$-NH_3 materials.

This quarter we started the exploration of the $Ti(BH_4)_3$-NH_3 system. The synthesis of the initial material, $Ti(BH_4)_3$ turned out to be challenging. Our initial attempts to synthesize $Ti(BH_4)_3$ using a published procedure (Hoekstra, H. R. & Katz, J. J., *J. Amer. Chem. Soc. 71*, **1949**, 2488-2492) by reacting $TiCl_4$ and excess $LiBH_4$ yielded only traces of the desired material. We are currently exploring an alternative route to prepare larger amounts of pure $Ti(BH_4)_3$ and react it *in situ* with ammonia gas or liquid. The new procedure avoids the use of titanium(IV) halides as starting materials.

We investigated several binary and ternary compositions in the $Ca(BH_4)_2$-$M'NH_2$-CaH_2 $Mg(BH_4)_2$-$M'NH_2$-MgH_2 systems (where M' = Li and Na). We obtained XRD evidence that new phases are formed during the ball-milling process at room temperature. The XRD results show striking differences between the patterns observed when various borohydrides or amides are employed (Figure 2). We are currently finalizing the spectroscopic and diffraction characterization of the resulting materials and initiated the assessment of their hydrogen storage properties.

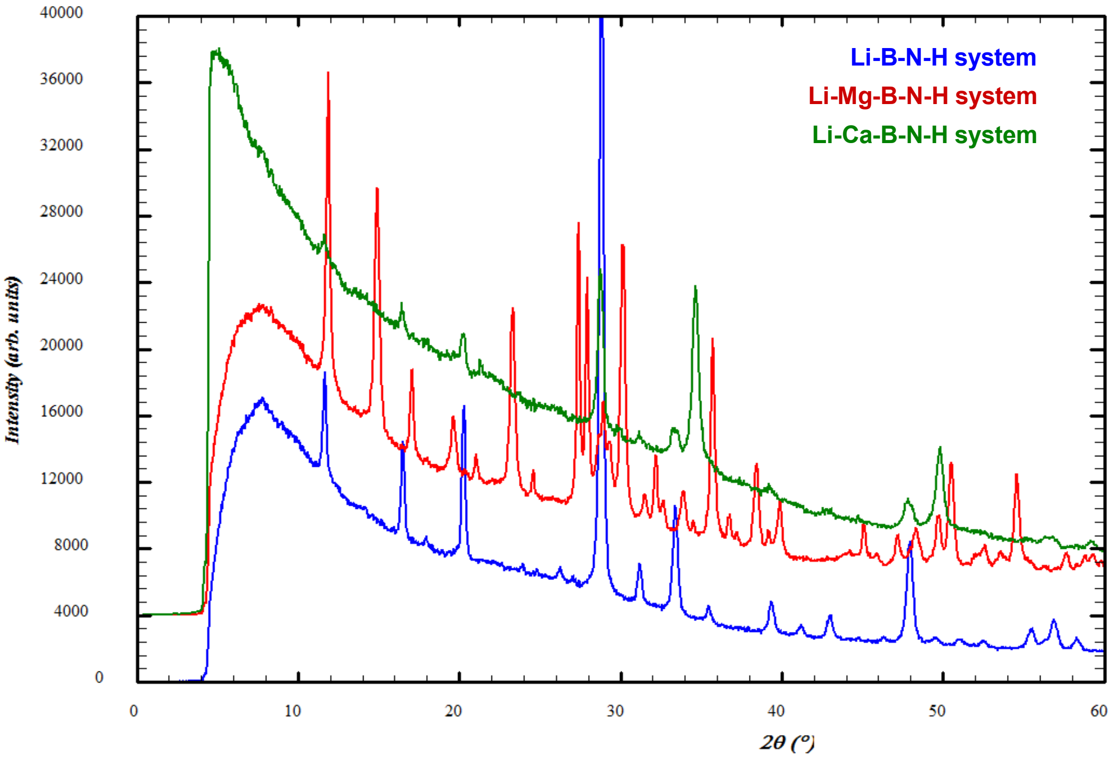


Figure 2. Powder XRD patterns of selected Ca(Mg)$(BH_4)_2$-M'NH_2 phases.

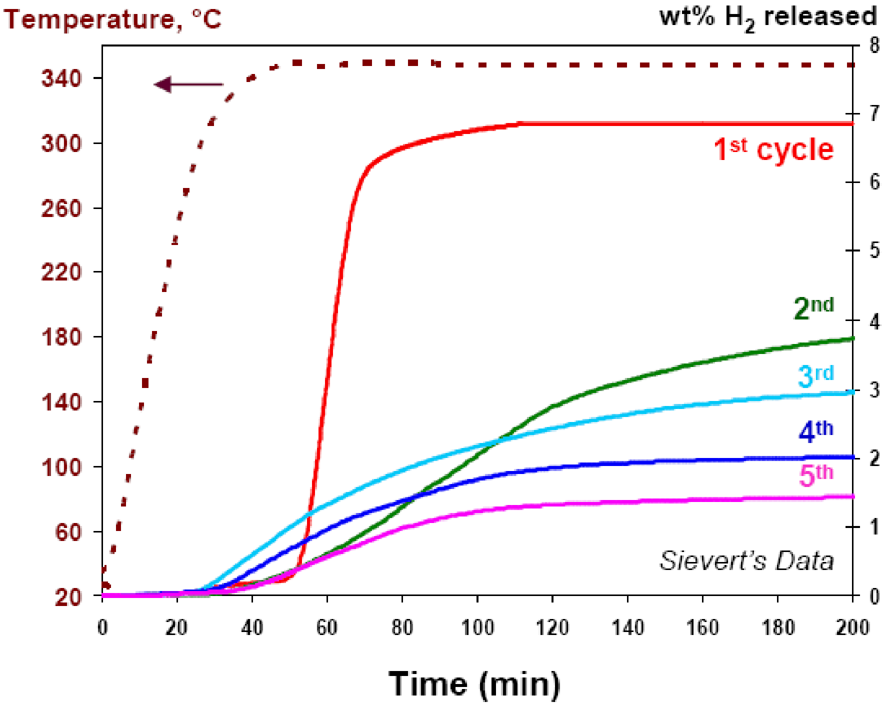


Figure 4. Cycle-life of $Ca(BH_4)_2$ ball-milled with 4wt% $PdCl_2$.

Although both experimental and theoretical data indicate that $Ca(BH_4)_2$ has favorable thermodynamics of hydrogen release, high kinetics barriers to dehydrogenation and rehydrogenation preclude its utility as a viable hydrogen storage material. As a result, we made a decision to discontinue our efforts on calcium borohydride and will focus on other materials.

Subtask 2.1.4 – Additive Screening to Improve New Materials Properties

Principal Investigators: Eric Mzajoub, Mutlu Kartin

The coordinated additive screening group has begun experiments on two systems. (1) MgH_2-8%TiH_2 mixture, and (2) Li-Mg-N. Thermodynamic data on system 1 indicates a decrease in the enthalpy from pure MgH_2 by about 8kJ/mol H_2 and an equilibrium pressure of about 2 bar at 290C. HRL is performing more accurate measurements to determine the equilibrium pressure change from bulk MgH_2. Sandia is performing XRD analysis of samples to determine if any Ti substitution occurs in Mg and MgH_2 through mechanical milling of materials, and after absorption/desorption cycles. The Li-Mg-N system is being screened for catalysts at Sandia where Dr. Weifang Luo will extend the work previously performed on Li-amide/MgH_2.

Subtask 2.2 – Cross-Cutting Theory

Efforts in the Cross-cutting Theory subtask are primarily focused on three areas at this time: 1) thermodynamics and kinetics of borohydride decomposition; 2) nanoscale effects; and 3) gas-phase equilibrium modeling. In addition, Mark Allendorf is performing quantum-chemistry modeling to obtain thermodynamic data for aluminum complexes in support of Project D. Progress in each area is briefly discussed below. Full details of efforts lead by other partners are provided in the quarterly reports of the non-Sandia institutions involved in these efforts (U. Pitt, UIUC, Georgia Tech, NIST, UMSL, and UTRC).

Subtask 2.2.1 – Alane and alanate complexes

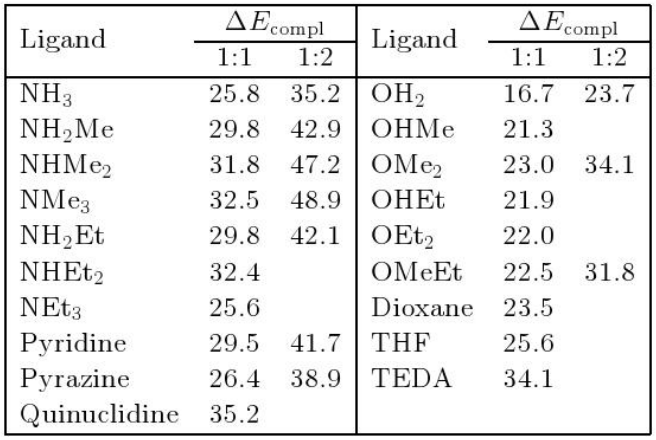
To help identify the best electron donor for stabilizing AlH_3 in solution, we determined complexation energies, i.e., reaction energies for the reaction $AlH_3{:}(L)_n \rightarrow AlH_3 + nL$, n=1,2, for a wide range of alane complexes with amines and ethers. Our computational approach entails using a number of high-level correlated electronic structure methods, employing the most sophisticated and accurate methods for the smaller complexes, and using less computationally demanding methods for the larger complexes for which the highest-level methods are prohibitively expensive.

For the smaller complexes, we computed complexation energies with the G3(MP2) method, which is very accurate but too computationally intensive for the largest complexes. Using these results, combined with energies determined with the high-level CCSD(T) method, we are currently finalizing the parameterization of the BAC-MP2 method, which is a reasonably accurate method applicable to large molecules, Once this parameterization is complete, we will use the BAC-MP2 method to determine complexation energies for all of the complexes of interest here.

Table 1 summarizes the complexation energies computed with the G3(MP2) method. The energies for the 1:1 alane complexes with amines are found to range from about 25 to 35 kcal/mol, and for the 1:1 ether complexes, the energies lie in the 16--34 kcal/mol range. The energy of the second Al:N or Al:O bond is significantly weaker than for the first, and total complexation energies for the 1:2 complexes are only about 40% higher than for the 1:1 complexes. The complexation energy tends to increase with the substitution level on the amine (primary < secondary < tertiary), and a similar trend is observed for ether complexes. Steric effects, however, reduce the stability of some tertiary amine complexes (e.g., AlH_3NEt_3).

Table 1 includes results for a range of ethers, which we are reporting for the first time, having resolved several issues concerning the performance of the various quantum-chemistry methods we applied to these systems. The trends for ethers are similar to, but less pronounced than, those exhibited by the amine complexes. In general, the ether complexation energies are weaker by ~ 8 – 10 kcal/mol than the corresponding amine energies. In addition, steric effects are far smaller because there are only two R groups that can be bound to the oxygen, as opposed to three for the amines. From these calculations it appears that an alane complex with any of the ethers would be thermodynamically favorable relative to TEDA, the amine originally used by BNL and that was found to bind too tightly to AlH_3 to allow regeneration of the hydride. Water of course is too reactive with the hydride but dioxane and THF may be good choices, since these should provide sufficient driving force to form the complex while still allowing it to be thermally decomposed at reasonable temperatures.

This quarter we continued our modeling to predict the thermochemistry of alanates complexes in solution with ethers to identify the most favorable solvent for use in regenerating these compounds. Currently, we are optimizing geometries for complexes in solution of the form M^+L_4, in which M is Li, Na, or K and L is an ether, such as THF or Et_2O. These optimizations are time-consuming due to the large number of atoms involved, so we do not expect them to be complete until next quarter. Once these are finished we will be able to compute complexation energies in solution, using the Polarizable Continuum Solvation Model, as described in last quarter's report. We will perform these for a range of oxygen-containing solvents to provide qualitative guidance for experimental efforts at BNL in Project D.



Ligand	ΔE_{compl} 1:1	ΔE_{compl} 1:2	Ligand	ΔE_{compl} 1:1	ΔE_{compl} 1:2
NH_3	25.8	35.2	OH_2	16.7	23.7
NH_2Me	29.8	42.9	OHMe	21.3	
$NHMe_2$	31.8	47.2	OMe_2	23.0	34.1
NMe_3	32.5	48.9	OHEt	21.9	
NH_2Et	29.8	42.1	OEt_2	22.0	
$NHEt_2$	32.4		OMeEt	22.5	31.8
NEt_3	25.6		Dioxane	23.5	
Pyridine	29.5	41.7	THF	25.6	
Pyrazine	26.4	38.9	TEDA	34.1	
Quinuclidine	35.2				

Table 1. Complexation energies (kcal/mol) for 1:1 and 1:2 alane complexes with amines and ethers, computed using the G3(MP2) method.

Subtask 2.2.2 – Materials Kinetics and Nanoscale Theory.

Principal Investigator: Mark Allendorf; collaboration with D. Sholl (Georgia Tech) and K. Johnson (Univ. Pitt.)

Gas-phase equilibrium modeling. Sandia (Mark Allendorf) incorporated a large number of gas-phase B_nH_m species into our thermodynamic database so that we can treat phase equilibria for boron-containing hydrides. We also completed phase equilibrium calculations using the FactSage code to model the complex gas phase resulting from the decomposition of various metal hydrides. Calculations were performed for the following hydride systems:

$LiNH_2 + LiH$
$LiBH_4 + C$
$LiBH_4 + MgH_2$

In addition, we also completed calculations for the following two destabilized reactions, but analysis of the results is not yet complete:

$2LiNH_2 + C \rightarrow Li_2CN_2 + 2H_2$
$BN + 4Mg(BH_4)_2 \rightarrow 3MgH_2 + MgB_9N + 13H_2$

The Georgia Tech group is providing condensed-phase thermodynamic data from their DFT calculations. Phonon calculations are underway for MgB_2C_2 to enable us to compute equilibra for the reaction $2C + Mg(BH_4)_2 \rightarrow MgB_2C_2 + 4H_2$; these are expected to complete next quarter. From these combined results we will complete an analysis of the following general categories of hydride systems: 1) hydride + carbon; 2) nitrogen-containing hydrides; 3) boron-containing hydrides. Our objective is to assess the overall importance of non-hydrogen gas-phase species in these systems, as well as identify conditions under which mixed condensed-phase products may form. This will provide guidance to the hydrogen storage community that until now has not been available, although some experimental results suggest that formation of products such as NH_3 and CH_4 can occur. A draft of a journal article is also being prepared at this time.

Subtask 2.3 – Catalyzed Nano-Framework Stabilized High Density Reversible Hydrogen Storage Systems

Subtask 2.3.1 – Incorporation of Hydride Material into the Catalyzed NanoFramework Structure by Solid-State Synthesis Routes

Principal Investigators: Mutlu Kartin, Joseph Cordaro

Preliminary experiments were performed in order to test the compatibility of metal hydrides (typically strong reducing agents) with various nanoporous materials. Samples were prepared by high-energy ball milling $Ca(BH_4)_2$ with nanoporous frameworks. After ball milling the hybrid material was analyzed via TGA-MS and X-ray diffraction. For all materials a decrease in the H_2 gravimetric capacity was observed compared to pure $Ca(BH_4)_2$. When ball-milled samples were discharged and recharged with H_2 no formation of $Ca(BH_4)_2$ was observed in SiO_2 or Al_2O_3. Only trace amounts of $Ca(BH_4)_2$ were reformed in YSZ. These results, in addition to powder X-ray diffraction data suggest that these inorganic porous metal oxide frameworks are reduced by the metal hydride. On the other hand, $Ca(BH_4)_2$ mixed with the carbon aerogel (polyimide derived) showed more $Ca(BH_4)_2$ after a H_2 discharged and charge cycle compared to the YSZ sample. Reduction of the carbon-based nanoporous framework is not anticipated. In all cases, once $Ca(BH_4)_2$ had been mixed with the nanoporous material, powder X-ray analysis revealed little to no peaks for the original metal hydride. A better analytical tool to characterize incorporation of metal hydrides into porous materials is needed.

Bulk incorporation of $Ca(BH_4)_2$ into the polyimide derived carbon aerogels was explored via melting under high H_2 pressure and temperature. Control experiments were done in order to assess the stability of both the carbon aerogel and $Ca(BH_4)_2$ under these conditions (560 °C and 10,000 psi H_2). BET measurements of the carbon aerogel as received from UTRC gave a surface area of approximately 400 m^2/g. This material was then subjected to 10,000 psi of H_2 at 560 °C for 18h. The measured BET surface area came in at 700 m^2/g, indicating that the porous structure had not collapsed. Why the surface area of the carbon aerogel treated at 560 °C and

10,000 psi H_2 is higher than the untreated aerogel is unknown but duplicate experiments are needed. Furthermore, the mechanical properties of the material have not been investigated. Similarly, $Ca(BH_4)_2$ was heated to 560 °C under 10,000 psi of H_2 for 18h. The originally powder material appeared to have sintered forming a larger bulk phase. Preliminary powder X-ray diffraction showed α-phase $Ca(BH_4)_2$ with some numerous other unidentified signals. More experiments and analyses are required to quantify this transformation.

Previously, it was reported that when a sample of $Ca(BH_4)_2$ and carbon aerogel was heated to 560 °C under 10,000 psi of H_2 it appeared that $Ca(BH_4)_2$ wetted the surface of the aerogel. No cross-sectioning of the composite material was done to determine whether the material filled the pores. The change in mass for the carbon aerogel was low, suggesting only minimal incorporation of $Ca(BH_4)_2$ within the pores. BET measurements showed a significant decrease in pore volume after the heating step with $Ca(BH_4)_2$ from 400 to 2 m^2/g. The pore volume decreased from 2.5 to 0.02 cm^3/g. It is unclear how such a large reduction in pore size could be achieved with only a small wt% increase attributed to $Ca(BH_4)_2$ infiltration.
Using Sandia's STMBMS instrument, desorption experiments on carbon aerogels infiltrated with $Ca(BH_4)_2$ via melting were performed. Samples were analyzed by heating from room temperature up to 1000 °C at 5 °C/min. The results are summarized below:

1. The evolution of H_2 below 300 °C is near zero in the $Ca(BH_4)_2$ in the carbon aerogel, whereas it is a significant signal in both the uncatalyzed and Ti-catalyzed $Ca(BH_4)$ samples.

2. The rates of release of hydrogen in the main hydrogen evolution region (320 to 340°C) are similar for the catalyzed aerogel $Ca(BH_4)_2$ samples and more abrupt for the uncatalyzed $Ca(BH_4)_2$ sample.

3. The second main H_2 evolution peak occurs between 400 and 500 °C in the uncatalyzed and catalyzed $Ca(BH_4)_2$ samples. In the $Ca(BH_4)_2$ aerogel sample the hydrogen continues to evolve over a much higher temperature range (400 to 580 °C) suggesting that incorporated CaH_2 is stabilized relative to free CaH_2.

The inability to achieve high sample loadings plus the ambiguous results of BET measurement have led Sandia National Laboratories to down-select (not pursue further) solid-state methods for incorporating $Ca(BH_4)_2$ into the carbon aerogel samples. Furthermore, due to the lack of a kinetic effect on the release of hydrogen from hybrid materials prepared via melt-incorporation new experiments have been suspended.

Subtask 2.3.2 – Incorporation of Hydride Materials into the Catalyzed Nano-Framework Structure by a Metathesis Wet-Chemical Route

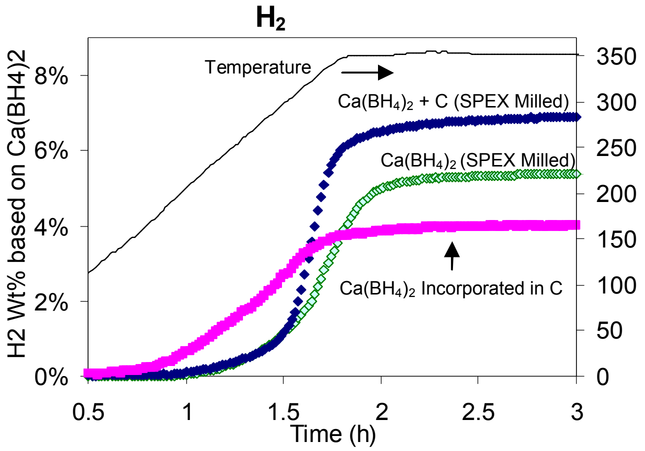
Principal Investigators: Tim Boyle

Solution deposition of $Ca(BH_4)_2(solv)_x$. Continued efforts on the modification of $Ca(BH_4)_2(THF)_2$ with alternative Lewis basic solvents has been u investigated including py, NH_3, DME, Et_2O. If products crystallize they were characterized by single crystal X-ray diffraction and if not they were characterized by beryllium dome X-ray diffraction and FTIR spectroscopy. Since dip-coating loading studies of the THF adduct on two different substrates yttria stabilized zirconia (YSZ) and carbon aerogel (CA) were inconclusive on the capabilities of these substrates, the efforts switched to incipient wetness loading of $Ca(BH_4)_2(THF)_2$ in a THF solution onto both substrates. Initial results are listed below in table 1.

TABLE 1

Substrate	Substrate Porosity	Molarity	BeD-XRD Phase	Weight Change	Calc'd Loading
YSZ -1	0.72 mL/g	0.16g/cc	St. Mat	0.09g	4 %
YSZ -2	0.72	Conc.	St. Mat	0.10g	10 %
CA	3.67	0.21	St. Mat	0.10g	14 %

FIGURE 1



- Incorporation of Ca(BH4)2 in C aerogel lowered H2 desorption temperation,
- Desorption capacity needs to be optimized

The incipient wetness approach yielded higher loadings of the CA; however, calculations based on the pore volume of the aerogel indicated that the even higher loadings were possible Therefore, efforts focused on super-saturating the CA with a very concentrated solution of $Ca(BH_4)_2(THF)_2$ in THF (2.5 g in 3mL) on 0.345 g CA. After the CA was soaked in the solution, it was dried under vacuum at 100 °C for 2 h to remove the solvent. The results from this coated aerogel suggest that the amount of $Ca(BH_4)_2$ incorporated is 50%, but the desorption capacity is low and improvements are needed to compete with the previous milled samples (figure 1).

In order to confirm the amount of $Ca(BH_4)_2$ incorporated, additional samples were made for weight determination of the CA, before and after incorporation,. The sample was prepared by using 0.76 g carbon aerogel, used 3.5g $Ca(BH_4)$THF in 4.5 mL THF. The sample was heated to 100 °C under vacuum for 2 h and final weight of aerogel and incorporated borohydride, 1.3 g, suggesting a 0.54 g weight gain. This sample was shipped to UTRC for testing and results are pending. Once this baseline is established, coating of CA and YSZ will be done and tested for loading. In addition to using the THF adduct, the other synthesized $Ca(BH_4)_2(Solv)_x$ will be used to coat the aerogels of interest.

PLANS FOR NEXT QUARTER

Task 2: Sandia Research and Development within the MHCoE

Subtask 2.1 – New Complex Anionic Materials

Subtask 2.1.1 – Alkali and Alkaline- Earth Borohydrides

Principal Investigators: Vitalie Stavila, Eric Majzoub

In collaboration with our colleagues at NIST and JPL/Caltech, we plan to finalize our assessment of hydrogen storage properties of several $B_{12}H_{12}$ compounds, including $Li_2B_{12}H_{12}$, $Na_2B_{12}H_{12}$, $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$. We will attempt to hydrogenate the ball-milled mixtures of these compounds with various metal hydrides using our high-pressure station. After successfully accomplishing the carbon doping in MgB_2, we will attempt to achieve doping on the metal part with various transition metals. In addition, we plan to investigate the effect of transition metal borohydrides on the hydrogen sorption properties of alkali and alkali-earth metal borohydrides.

Subtask 2.1.2 – Discovery and Characterization of New Materials

Principal Investigators: Mutlu Kartin, Eric Majzoub

We will continue our search of high-capacity reversible borohydride/alanate materials. We will complete the synthesis and characterization of $M[PH_2(BH_3)_2]$ (M = Na or Li) and asses their hydrogen sorption properties. In collaboration with UTRC, we will continue our theoretical and experimental efforts on $LiTi(BH_4)_4$, $NaTi(BH_4)_4$ and other titanium-containing borohydride materials. We will study the thermal decomposition of these compounds and determine the reversibility of hydrogen evolution.

Subtask 2.1.3 – Synthesis of Ammine Borohydrides, and Mixed Amide/Borohydride Materials

Principal Investigators: Vitalie Stavila, Mutlu Kartin

In the next quarter, we will continue our efforts on the $Ti(BH_4)_3$-NH_3 system. We also plan to extend our efforts on mixed alkali-transition metal systems, such as $LiTi(BH_4)_4$-NH_3 and $NaTi(BH_4)_4$-NH_3. We also plan to investigate in detail the hydrogen storage properties of the new phases formed in the $Ca(BH_4)_2$-$M'NH_2$-CaH_2 and $Mg(BH_4)_2$-$M'NH_2$-MgH_2 systems.

Subtask 2.1.4 – Additive Screening to Improve New Materials Properties

Principal Investigators: Eric Majzoub, Mutlu Kartin

Next quarter, we plan to collect data input spreadsheets from MHCoE partners to assemble an "additive screening candidate systems" list. This will allow people who are already running some additive screening to capture what they are actively working on, as well as allow partners to submit their candidate materials for study by the additive screening group. We also anticipate building an archival additive screening spreadsheet on the systems that have been already been performed in the center.

Subtask 2.2 – Cross-Cutting Theory

Subtask 2.2.1 – Al- Adduct Binding Calculations

Principal Investigators: Mark Allendorf

Resolve outstanding issues concerning accuracy of BAC predictions of AlH_3 complexes with amines and ethers; begin journal manuscript.

Complete geometry optimizations required to compute solvation energies for alanate contact ions and compare with cations (Li^+, Na^+, and Mg^{2+}) solvated by ethers. Forward and discuss results with Project D investigators.

Subtask 2.2.2 – Materials Kinetics and Nanoscale Theory

Principal Investigators: Mark Allendorf

Complete phase equilibrium calculations for remaining systems required for analysis of gas-phase composition in representative hydride classes. Thermodynamic data for MgB_2C_2 are required from the Georgia Tech group to complete this work.

Subtask 2.3 – Catalyzed Nano-Framework Stabilized High Density Reversible Hydrogen Storage Systems

Subtask 2.3.1 Incorporation of Hydride Material into the Catalyzed NanoFramework Structure by Solid-State Synthesis Routes

Principal Investigators: Mutlu Kartin, Joseph Cordaro

Future collaborations with UTRC will focus on incorporating metal hydrides into porous materials via solution routes. We also plan to investigate stabilization of metal hydrides by incorporating them into porous nano-frameworks. Additionally, we will explore alternative nanoframeworks derived from organic polymer foams and aerogels.

Subtask 2.3.2 – Incorporation of Hydride Materials into the Catalyzed Nano-Framework Structure by a Metathesis Wet-Chemical Route

Principal Investigators: Tim Boyle

Refer to work reported under the Project Status section of this report for continued work plans on this subtask 2.3.2.

PATENTS:

- "Direct synthesis of calcium borohydride", E.C.E. Rönnebro and E.H. Majzoub, U.S. Patent Application Serial Number 60/901,248 originally filed 02/12/2007.
- "Direct synthesis of magnesium borohydride", E.C.E. Rönnebro, C. M. Jensen and G. Severa, U.S. Patent Application, 2008.

PUBLICATIONS/PRESENTATIONS:

- E. Majzoub and E. Rönnebro, "Calcium borohydride crystal structure candidates from electrostatic ground state prototypes: Theory and Experiment", Accepted in J. Phys. Chem. C.

- Y. Filinchuk, E. Rönnebro, D. Chandra, "Crystal Structures and Phase Transformations in $Ca(BH_4)_2$", Acta Materialia 57 (2009) 732–738.

- L. Seballos, J. Zhang, E. Rönnebro, J.L. Herberg, E.H. Majzoub, "Metastability and crystal structure of $NaK(BH_4)_2$", J. Alloys Compd., in press (2008).

- Ewa Rönnebro, "Energy Storage by Formation of Chemical Bonding Between Metals and Hydrogen or Lithium", Invited seminar, Savannah River National Laboratory, Aiken, South Carolina, September 17, 2008.

- Ewa Rönnebro, "Discovery and Development of New Metal Borohydrides", Invited presentation, Discussion Moderator "Mg-based compounds" session, IEA HIA Task 22 Experts workshop, Rome, Italy, 6-10 October, 2008.

- Ewa Rönnebro, Chair Hydrogen Storage session at AVS, 55th International Symposium and Exhibition, Boston, Massachusetts, October 19-24, 2008.

- Ewa Rönnebro, "Current Challenges and Needs in Metal Hydride Research", Invited Lecture, NCMC-14, A DOE-EERE/NIST Joint Workshop on Combinatorial Materials Science for Applications in Energy, NIST, Maryland, November 5-7, 2008.

- Ewa Rönnebro, “High-hydrogen Pressure Technique for Solid State Synthesis of New Hydrogen Storage Materials”, Invited Lecture, Metallurgy Division Seminar Series, NIST, MD, November 7, 2008.

COLLABORATIONS:

- For subtasks 2.1.1 and 2.1.2, collaborators include MHCoE Project B partners. The characterization team for Alkali BH and new materials discovery includes Caltech, JPL, NIST, UH, UNR, UMSL, PITT, Georgia Tech, UIUC and Rice University (Prof. Kenton H. Whitmire). A student from UC Santa Cruz, CA, Rebecca Newhouse, continues work on synthesis and characterization of metal borohydrides.
- For subtasks 2.1.3 and 2.1.4, collaborators include UMSL, Ohio State University, Utah, Caltech/JPL, and NIST.
- For subtasks 2.2.1 and 2.2.2, collaborators include PITT, Georgia Tech, and UIUC.
- Subtasks 2.3.1 and 2.3.2 are conducted in collaboration with UTRC, Caltech and HRL. The collaboration with Dr. Jeff Grossman at UCB on the Tunable Thermodynamics Project may also impact our work within the MHCoE.

MILESTONE STATUS TABLE:

Task	Planned Completion	Actual Completion	Comments
Task 1 – Program Management			
Project Cost Report	15th of each month	Ongoing	
Coordinate MHCoE Partner meetings	Quarterly	Ongoing	Face-to-face meeting held Dec. 18 – 19, 2008
Organize MHCoE Coordinating Council meetings	Quarterly	Ongoing	UTRC Phase I to II review conducted Apr. 23, 2009
Technical Progress Report	Quarterly	Ongoing	
Storage Tech Team Review	02/09	2/09	
Annual DOE Hydrogen Program Merit Review	05/09		
Annual Program Technical Report	6/09		
2010 Annual Operating Plan	7/09		
Subtask 2.1: New Complex Anionic Materials			
Subtask 2.1.1: Alkali and Alkaline-earth Borohydrides			
Milestone: Complete PCT isotherms for $Ca(BH_4)_2$ to determine reaction enthalpy	10/1/08	4/15/09	Reaction enthalpy measured by DSC instead of PCT
Go/No-Go: Go if we are able to demonstrate micelle sizing in non-aqueous solvents using THF	11/30/08	3/1/09	No-Go Decision made on micelle technique
Go/No-go: Continue with transition metal atom substituted calcium boride if successful in hydrogenation of La-doped CaB_6.	12/31/08	Deferred	Doping of CaB_6 is currently on hold and the efforts shifted to focus on MgB_2.
Milestone: Lowering of $Ca(BH_4)_2$ desorption temperature	2/28/09	3/15/09	Efforts to significantly lower desorption T were not successful

Task	Planned Completion	Actual Completion	Comments
Go/No-Go on Ca(BH$_4$)$_2$: Characterize and improve Ca(BH$_4$)$_2$ kinetics properties (Teaming with JPL, Caltech, NIST)	3/31/09	3/15/09	No-Go Decision made on Ca(BH$_4$)$_2$
Go/No-go: Continue with mixed Ca $_{1-x}$Tm$_x$(BH$_4$)$_z$ materials if reversibility has been shown at improved P and T compared to calcium borohydride.	5/31/09		
Go/No-go on AkTm(BH$_4$)$_x$: Reversibility of alkali transition metal borohydrides (Teaming with U. Hawaii)	8/31/09		
Go/No-go: Develop other methods to address transition-metal (TM) and mixed TM-alkali borohydrides if the PEGS method does not produce experimentally observable structures.	9/30/09		
Milestone: Demonstrate synthesis of nanoparticles of complex borohydrides prepared through surfactant templating	11/30/09		
Subtask 2.1.2: Discovery and Characterization of New Materials			
Milestone: Complete STMBMS characterization of Ca(BH$_4$)$_2$	12/31/08	On-going	We designed a new experiment to better reveal the reaction mechanism
Milestone: Complete PEGS searches for mixed cation imides including Li$_2$CaN$_2$H$_2$, Li$_2$MgN$_2$H$_2$ and MgCaN$_2$H$_2$	2/28/09	ongoing	Work ongoing
Milestone: Discover new borohydride related materials (Teaming with MHCoE partners)	03/31/09	On-going	Characterization in progress

Task	**Planned Completion**	**Actual Completion**	**Comments**
Go/No-Go: Go if the PEGS method produces useful nanoparticle conformations which are stable when investigated with first-principles DFT theory	5/31/09		
Go/No-Go on AkTm(BH$_4$)$_x$: Reversibility of alkali-transition metal borohydrides (Teaming with U. Hawaii)	05/31/09		
Go/No-go: Develop other theoretical methods to address imide compounds if the PEGS method does not produce experimentally observable structures.	9/30/09		
Subtask 2.1.3 Synthesis of Ammine Borohydrides and Mixed Amide/Borohydride Materials			
Milestone: Synthesize Ca(BH$_4$)$_2$/NH$_3$ system	12/31/08	12/31/08	Completed
Milestone: Demonstrate reversibility in Ca(BH$_4$)$_2$/NH$_3$ system	5/31/09		
Milestone: Demonstrate mixed borohydride/amide compound searches using PEGS	7/31/09		
Go/No-go: Go/No-go decision on further work on Ca(BH$_4$)$_2$/NH$_3$ system	7/31/09		
2.1.4 Additive Screening to Improve New Materials Properties			
Milestone: Complete additive screening study of MHCoE borohydride	3/31/09	suspended	MHCoE did not identify a borohydride needing additive screening
Milestone: Complete additive screening study of MHCoE amide	7/31/09		
Milestone: Complete additive screening study of mixed amide/borohydride	9/30/09		

Task	Planned Completion	Actual Completion	Comments
Subtask 2.2 Cross-cutting Theory			
Subtask 2.2.1 - Al-Adduct Binding Calculations			
Go/No-Go: Model reactions of alane-amine surface interactions	12/31/08	10/23/08	BES program at BNL already doing this
Milestone: Complete calculations on alanate-amine complexes	05/31/09		
Milestone: Complete calculations on alanate-ether adducts	09/31/09		
Subtask 2.2.2 Materials Kinetics and Nanoscale Theory			
Milestone: Formulate theoretical approaches to understanding the factors limiting the rehyrogenation kinetics of $Ca(BH_4)_2$	5/31/09		
Milestone: Guide Theory Group on Kinetics Studies and Nanoscale Theoretical Effects	9/31/09		
Milestone: Complete initial theoretical studies of the factors limiting rehydrogenation kinetics of $Ca(BH_4)_2$	9/31/09		
Subtask 2.3 - Catalyzed Nano-Framework Stabilized Reversible Materials to Enable High Density Systems			
Subtask 2.3.1 - Incorporation of hydride material into the catalyzed nano-framework structure by solid-state synthesis routes			
Milestone: Incorporation of $Ca(BH_4)_2$ in NFS by solid-state process.	10/1/08	10/1/08	Level of incorporation in evaluation

Task	Planned Completion	Actual Completion	Comments
Go/No-Go: A Go decision means it is possible to incorporate the hydride material into the nano-structured framework via a solid-state route, meeting our target of 50% loading of a hydride material with a hydrogen storage capacity greater than 5% in the nano-structured framework.	05/31/09		
Milestone: Show improved kinetics of hydride material in a catalyzed nanoframework	9/30/09		
Subtask 2.3.2 - Incorporation of hydride materials into the catalyzed nano-framework structure by a metathesis wet-chemical route			
Go/No-Go: Go if successfully coating the substrate with metal hydride.	10/1/08	10/08	Go
Go/No-Go: A Go decision means it is possible to incorporate the hydride material into the nano-structured framework via a solution-based route, and meeting our target of 50% loading of a hydride material with a hydrogen storage capacity greater than 5% in the nano-structured framework.	05/31/09		