SAND2009-0565P

QUARTERLY PROGRESS REPORT

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Project Title: Metal Hydride Center of Excellence (MHCoE)

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Primary POC: Lennie Klebanoff, (925) 294-3471, lekleba@sandia.gov

Subcontractors: Eric Majzoub, SNL/UMSL

Other Partners: MHCoE Partners

SNL Principal Investigators:
Eric Majzoub
Ewa Ronnebro
Mark Allendorf
Mutlu Kartin
Tim Boyle
Vitalie Stavila

DOE Managers: Ned Stetson, DOE Technology Development Manager
Rick Balthaser, DOE Field Project Officer

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: Ewa Ronnebro, 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.

Alkali earth borohydrides

We are continuing our work on calcium borohydride which has potential to be absorbed/desorbed by a specific reaction route, resulting in theoretical 9.6 wt% hydrogen.

It's crucial to fully understand the reaction mechanism to be able to improve H-storage reversibility. Eric Majzoub et al. and Duane Johnson et al. predicted two competing decomposition pathways resulting in formation of CaB_6 and $CaB_{12}H_{12}$ respectively. We are currently characterizing decomposition products. Teaming with JPL, Caltech and NIST, we are studying samples in desorbed and re-hydrided conditions, with and without additives. From XRD analysis we had been able to confirm that calcium borohydride indeed decomposes into CaB_6 and CaH_2 upon release of hydrogen, but also a small amount of $Ca(BH_4)_2$ remains. However, the MAS NMR also indicated another decomposition product. This peak is comparable to $B_{12}H_{12}$ species, which were identified as intermediate decomposition products of magnesium borohydride (Hwang et al., in press). In order to determine if this peak indeed belongs to $CaB_{12}H_{12}$, we independently synthesized this compound. It was recently successfully made by a solution based route, and we are finalizing the characterization by XRD and Rietveld refinements (SNL), NMR (Caltech), Raman, (UMSL), STMBMS (SNL) and Neutron vibrational spectra (NIST). Eric Majzoub predicted a crystal structure for $CaB_{12}H_{12}$, and in collaboration with NIST, we believe that we have a solution for the experimental crystal structure which is close to the theoretical prediction. In Fig. 1 we show the powder X-ray diffraction pattern collected at Sandia. We also attempted to form $Ca(BH_4)_2$ from a $CaB_{12}H_{12}$+CaH_2 mixture and observed its formation at 450°C and 15,000psig thus for the first time indicating reversibility of this reaction path. Please contact the PI for more information.

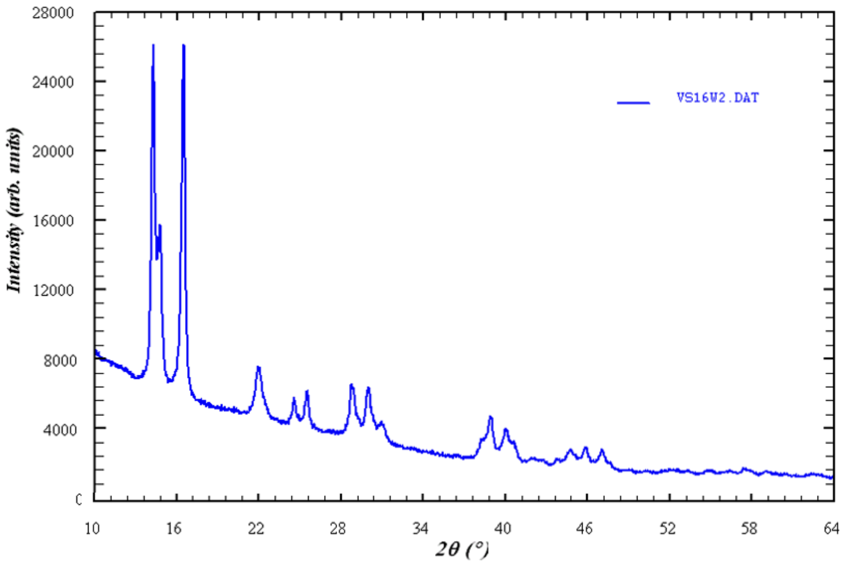

Fig. 1. Powder X-ray diffraction pattern of $CaB_{12}H_{12}$.

In an attempt to improve reversibility of calcium- and magnesium borohydrides, we are exploring a new route to synthesize modified compounds, and during this quarter we've obtained indications that this approach may be successful. We plan to file a technical advance in the next quarter, if appropriate. Please contact the PI for more information.

Subtask 2.1.2 – Discovery and Characterization of New Materials
Principal Investigators: Ewa Ronnebro, Eric Majzoub

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

Novel, light-weight, high-capacity metal hydrides have been determined to be potential candidates for on-board materials that will shrink the growing gap between experimental result and the desired goals. For our project, the discovery process involves preparation methods in the solid state; mainly ball milling and the high-pressure sintering technique (P <140MPa, T <773K). By utilizing different ball milling approaches in collaboration with our MHCoE partners, we are able to control the size of the particles which is crucial for creating diffusion paths for hydrogen. The high-pressure vessel that enables six sample holders has been proven to be an effective tool for discovering/screening for new hydrides in different ternary systems.

We are currently focusing our new materials effort on new bialkali borohydrides and mixed alkali transition metal borohydrides, as well as other borohydride related compounds.

Exploration of new borohydride materials

Objective: We are exploring borohydrides to find new high-capacity hydrogen storage materials by solid-state reactions predicted by the above described PEGS method.

We attempted to thermodynamically improve borohydride materials by changing the cation matrix and previously reported two new bialkali borohydrides, i.e. $NaK(BH_4)_2$ (8.8 wt%) and $LiK(BH_4)_2$ (10.6 wt%). The former is too unstable, and the later is too stable; thus, neither is suitable for reversible hydrogen storage applications. The synthesis and characterization of $NaK(BH_4)_2$ is described in our paper, recently in press, in the Journal of Alloys and Compounds. $LiK(BH_4)_2$ was synthesized by ball milling and characterized by XRD, Raman, NMR and NVS in collaboration with JPL, Caltech and NIST, and a paper is in progress. Because the bialkali borohydrides are not very promising for reversibility, we are undertaking synthesis of new 'borohydride alanate' materials, predicted by PEGS, such as $Li_2(BH_4)(AlH_4)$ (15wt%), $Na_2(BH_4)(AlH_4)$ (11wt%), $Mg(BH_4)(AlH_4)$ (11wt%) and $Ca(BH_4)(AlH_4)$ (9wt%) as well as mixed cation materials. Earlier, we found indications of $Ca(BH_4)(AlH_4)$ formation from a solid-state synthesis route, and this experiment is currently being reproduced. Samples will be sent to our MHCoE partners, i.e. Caltech and NIST, for thorough characterization.

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.

Our aim in exploring the nitrogen containing-borohydride systems is to lower the hydrogen desorption and absorption temperatures of metal borohydrides, specifically $Ca(BH_4)_2$ and $Mg(BH_4)_2$. In the first quarter we explored $Ca(BH_4)_2$-NH_3 and mixed-heterometallic $M'M''(BH_4)_x \cdot yNH_z$ systems (where M' and M''= Li, Na, Ca and/or Mg; x, y= 1, 2, 3, 4 and z= 1, 2, 3) by wet-chemistry and solid-state syntheses routes.

Soloveichik *et al.* (*Inorg. Chem.* **2008**, *47*, 4290-4298) have recently demonstrated that magnesium borohydride ammonia complex, $Mg(BH_4)_2(NH_3)_2$, exhibits improved hydrogen desorption properties compared to pure $Mg(BH_4)_2$, decreasing the dehydrogenation temperature by about 100 °C. We isolated $Mg(BH_4)_2(NH_3)_2$ and performed an RGA analysis of the product at various temperatures. The obtained results confirm that the major gaseous product of the reaction is hydrogen. We isolated three calcium-containing materials, $Ca(BH_4)_2$-NH_3, $LiCa(BH_4)_3$-NH_3, and $MgCa(BH_4)_4$-NH_3 by reaction of THF solutions of the corresponding borohydrides with excess ammonia. The compounds can be easily isolated and display increased stability compared to the initial borohydrides; however, we found that significant amount of ammonia was released upon heating. This indicates that the metal-ammonia bond in these complexes is more labile compared to $Mg(BH_4)_2(NH_3)_2$. In the case of $Ca(BH_4)_2$-NH_3 the ammonia release is quantitative and pure β-$Ca(BH_4)_2$ was recovered after heating the adduct in vacuum at 195 °C for 2 hours. We will attempt to overcome this difficulty by replacing Ca(II) with first row transition metal ions. In the next quarter the main efforts will be directed towards light transition metal borohydride ammonia complexes, *e.g.* $Ti(BH_4)_3(NH_3)_2$ and related materials.

$LiNH_2$, $LiBH_4$ and destabilization of these compounds through reactive binary mixtures such as $LiNH_2$-MgH_2, $LiBH_4$-MgH_2 and $LiBH_4$-$LiNH_2$ have been extensively studied with regard to their potential hydrogen storage properties. Yang and co-workers (*Angew. Chem. Int. Ed.* **2008**, *47*, 882-887) have recently reported a new ternary mixture of $LiBH_4$-$2LiNH_2$-MgH_2 complex possessing partial reversibility, improved (de)sorptions, lower-temperature kinetics and ammonia release, compared to their individual compounds and their binary mixtures. There is a great potential for novel materials discovery of binary and/or ternary mixed amide/imide-borohydride compounds. This quarter we focused on the synthesis and characterization of mixed $Ca(BH_4)_2$-amide/imide systems. We explored various molar ratios of the binaries and ternaries of $Ca(BH_4)_2$-$M'NH_2$-CaH_2 systems (where M' = Li and Na). PXRD data revealed that the ball-milling of these binary and ternary precursors resulted in the formation of a series of related M'-B-N-H (M'= Li, Na and/or Ca) phases. In addition to PXRD, we performed FTIR, Raman, STMBMS, TGA/DSC and RGA analyses on selected phases. TGA/DSC and RGA analyses showed that the significant amount of ammonia, starting <100 ºC, was released upon heating. STMBMS data of the ternary composition, $Ca(BH_4)_2$-$LiNH_2$-CaH_2 was collected and its detailed data process/analysis is in progress. Next quarter, we plan to continue the investigation of $Ca(BH_4)_2$-$M'(NH_2)$-$M''H_2$ (where M' and M''= Ca, Mg) systems by wet-chemistry and solid-state syntheses routes.

Subtask 2.1.4 – Additive Screening to Improve New Materials Properties

Principal Investigators: Eric Mzajoub, Mutlu Kartin

Objective: To coordinate center-wide additive screening activities for selected hydrogen storage systems. The purpose of this activity is to efficiently utilize and to maximize the throughput of the 20 kinetics/PCT instruments in the center by performing a large number of additive screening studies for materials of interest, as well as to better understand the role of additives to promote kinetics and lowered temperatures of hydrogen desorption and absorption.

This quarter, we distributed data input spreadsheets to MHCoE partners to assemble an “additive screening candidate systems” list. The catalyst screening subteam hosted a telecon on Dec 02, 2009, prior to the face-to-face meeting at Caltech. The subteam identified four candidate materials for additive screening:

1. $Li_2Zr(BH_4)_6$, submitted by U. Hawaii, that decomposes at about 50 °C with low or no diborane release,
2. LiMgN, submitted by U. Utah, a reversible (7 wt% H_2) material,
3. MgH_2-TiH_2 system, submitted by U. Utah, and
4. $LiBH_4$-MgH_2, a material first investigated by HRL.

Merits of each of the compound materials were discussed at the face-to-face meeting, and their relative priority is being assigned.

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).

A high-level computation of the heat of formation of $N(CH_3)_3$ was completed, allowing accurate corrections for N-C bonds to be made. This will improve the accuracy of the heats of formation computed for alane-amine complexes. We also completed the computation AlH_3-ether complexation energies late this quarter and will forward the results to the alane group early next quarter. We are postponing the writing of a journal article until next quarter, by which time we expect to resolve a few outstanding issues concerning the accuracy of the calculations.

This quarter we have initiated the use of Quantum-chemistry modeling to predict the thermochemistry of alanates complexes in solution with ethers.. We are using the Polarizable Continuum Solvation Model (PCM) of Tomasi et al. Our approach is to compute the relative energies of isolated metal ions, in particular Li^+, Na^+, or Mg^{+2}, in various ether-type solvents. We will also compare these energies with the energies for the corresponding contact ions with AlH_4^- to predict whether or not stable complexes will form in solution. The solvation of $LiAlH_4$ by ether-type solvents was previously investigated (Bikiel et al., *Inorg. Chem.* 44 (2005), 5286) and forms the basis for our approach. In that case, the alanate is found to dissociate to form a separated ion pair in THF, but in diethylether (Et_2O) a contact ion is formed. This results in a significant decrease in the solvation energy in Et_2O vs. THF. It is thought by Graetz et al. (*J. Amer. Chem. Soc.* ASAP 2008) that this is the reason for the much higher efficiency of rehydrogenation of LiH + Al in THF than Et_2O. Our preliminary calculations are consistent with this result (Fig. 2, right), which predict that the solvation of Li^+ is 54 kJ mol^{-1} more favorable in THF than in Et_2O. The optimized Li-O bond distance in $Li(THF)_4^+$ is 2.343 Å (Fig. 2, left), with large interatomic distances (3.88 Å), while Et_2O (not shown) there is considerably more steric crowding, which may contributed to the less favorable solvation. Calculations of the solvation energies of Na^+ and Mg^{+2} ions were completed this quarter and we will analyze and report these results in next quarter's report. These preliminary results were discussed with Project D researchers at the MHCOE face-to-face meeting in December 2008. Next quarter we expect to be able to offer some guidance with respect to the selection of an optimal ether solvent for the regeneration of other alanates.

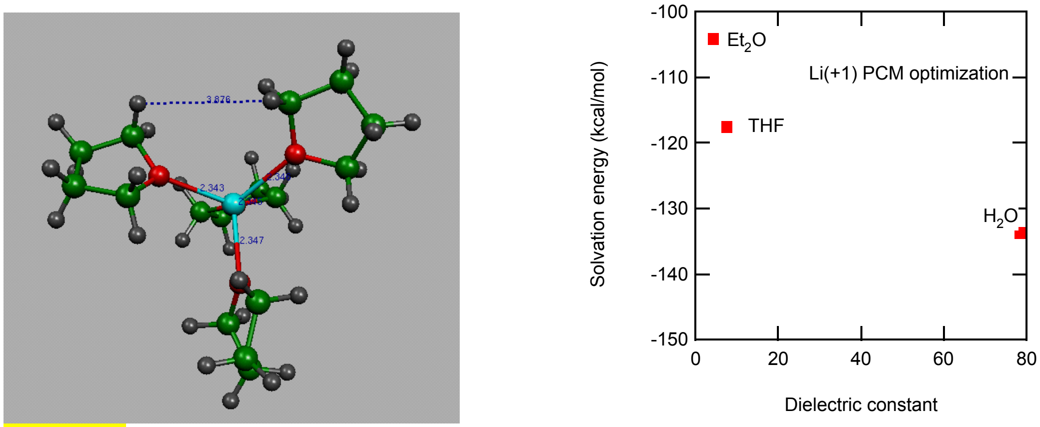

Figure 2. Density functional theory predictions (B3LYP/6-31G(d,p)) of the solvation of the lithium ion. Left: optimized geometry for $Li(THF)^+$. Right: solvation energies for Li^+ for diethylether, THF, and water, using the PCM model and optimizing the energy at the B3LYP/6-31G(d,p) level of theory.

Subtask 2.2.2 – Materials Kinetics and Nanoscale Theory.

Principal Investigator: Mark Allendorf

In addition to the ongoing work on nanoscaffolds by the UTRC-lead team (progress in which is routinely updated during TG conference calls), the UIUC group continued their calculations of the energies of $(MgH_2)_n$ clusters. This quarter the UIUC geometries and energies for six cluster sizes were sent to Dr. Jeff Grossman at U.C. Berkeley (UCB), whose group is collaborating with Mark Allendorf on the related Tuneable Thermodynamics project. Preliminary results from UCB agree with respect to the trend predicted by UIUC, but the dehydrogenation energies are more positive by ~ 25 kJ mol^{-1}. Computations are underway to verify this shift. In addition, UCB finds that results using DFT are highly sensitive to the functional that is used. Ultimately, we expect both the trend and the absolute values of the dehydrogenation energies to be determined accurately by the quantum Monte Carlo calculations currently underway in the Tuneable Thermo project.

Gas-phase equilibrium modeling. Sandia (Mark Allendorf) continued 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: $LiNH_2$, $LiNH_2$ + LiH, and $LiBH_4$ + C. The Georgia Tech group provided condensed-phase thermodynamic data from their DFT calculations. Some illustrative results are presented in Figure 3 for the latter two systems:

In the case of $LiNH_2$, the nominal reactions in the absence of LiH are:

$$2LiNH_2 \leftrightarrow Li_2NH + NH_3 \qquad (1)$$

$$2LiNH_2 \leftrightarrow Li_2NH + 0.5N_2 + 1.5H_2 \qquad (2)$$

However, when LiH is added, a new channel is possible:

$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$ (3)

The results show that the NH_3 concentration is ~ 30 ppm for $LiNH_2$ alone, but that addition of LiH reduces NH_3 by nearly two orders of magnitude (~ 0.5 ppm) at temperatures desired for on-board regeneration with a fuel cell power train (~ 375 K).

In contrast, $LiBH_4$ destabilized by adding carbon does not produce fuel cell poisons like NH_3. However, the formation of gas-phase hydrocarbons is possible. The nominal reaction is:

$LiBH_4 + C \leftrightarrow LiBC + \mathbf{2H_2}$ (4)

Also possible are these reactions:

- $LiBH_4 + 2C \leftrightarrow LiBC + \mathbf{CH_4}$ (5)
- $LiBH_4 + 0.75C \leftrightarrow LiH + B + \mathbf{0.75CH_4}$ (6)

In this case, reactions (5) and (6) are thermodynamically favorable and redirect the hydrogen to form methane (small amounts of other hydrocarbons are also formed). Hydrogen does not become the thermodynamically favored gas-phase product until temperatures exceed 800 K. Of course, there may be a kinetic barrier that prevents methane formation. If we simulate this situation by removing the gas-phase hydrocarbons from the species list in the calculation, we find that hydride reaction with graphite does not become significant (> 50% reaction) until temperatures $\geq$ 500 K. Since LiBC must form to make either H_2 or CH_4, it does not seem out of the question that significant amounts of hydrocarbon byproduct could be formed when $LiBH_4$ reacts with graphite. The products LiBC + H_2 are, in essence, metastable in the presence of a kinetic barrier to forming CH_4.

The University of Pittsburgh team is in the process of augmenting their code to allow prediction of gas-phase species other than H_2.

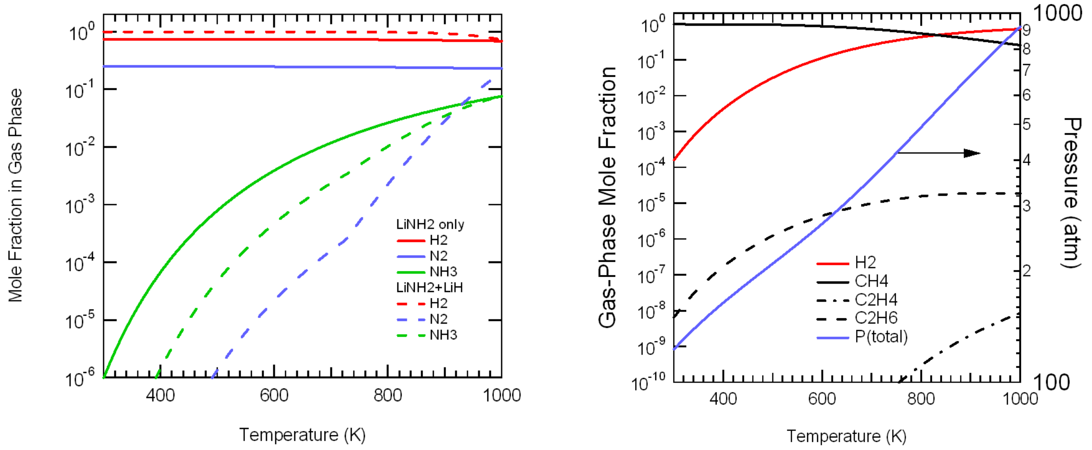

Figure 3. Gas-phase composition at equilibrium as a function of temperature for left: $LiNH_2$ (+ LiH) and right: $LiBH_4$ + C.

Thermodynamics and kinetics of borohydride decomposition. The group at Univ. Illinois/Urbana-Champagne (D. Johnson; UIUC) completed DFT calculations to predict the structure of $CaB_{12}H_{12}$. Details are included in their report, but in brief, they found a distorted wurtzite ground-state structure, but there are at least four other structures within 2 kJ mol^{-1} of each other. The presence of multiple crystalline phases on the nano- or microscale in the material could destroy the Bragg criterion, leading to x-ray diffraction spectra that would appear to correspond to an amorphous material. One of these structures (distorted wurtzite hcp C2/m) is similar to the structure predicted by E. Majzoub (U. Missouri, St. Louis) using his PEGS method. However, Majzoub found another structure (C2/c) that is > 40 kJ mol^{-1} lower in energy. We hoped to discuss this at the Face-to-Face meeting at Caltech in December 2008, but D. Johnson was unable to attend because his flight was canceled due to weather conditions. The Theory Group will instead discuss this at its next conference call on Jan. 26, 2009.

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 Investigator: Ewa Ronnebro

Objective: To incorporate a high-capacity hydrogen storage material (HSM), such as a metal borohydride, into the catalyzed nanoframework structure (CFS) by solid-state synthesis routes.

Discussion: We will prepare high-capacity hydride materials previously developed through the MHCoE. These materials will include but are not limited to $Ca(BH_4)_2$. We have recently shown that it is feasible to partially re-hydride $Ca(BH_4)_2$ from the decomposition products CaB_6 and CaH_2. These previously developed materials will be incorporated, *in-situ* or *ex-situ*, into a tailored nano-structured framework, provided by UTRC. Though our initial trials will be on incorporation of $Ca(BH_4)_2$, we will extend our approach to include other borohydride and amide materials, especially promising ones from Project B and C, as well as suggested materials from the MHCoE Theory Group.

We will utilize our existing sintering technique under high-hydrogen pressures, potentially in combination with high-energy milling, for synthesizing complex metal hydrides and/or metal borohydrides. These hydride materials will be either formed *in-situ* in the CFS, or *ex-situ*, *i.e.* prepared in advance and then incorporated into the CFS. For rapid evaluation to monitor how the synthesis effort is progressing, we will utilize XRD, STMBMS, TGA and DSC techniques for characterization. After successfully incorporating the metal hydride in the NFS, the team will investigate the thermodynamics, kinetics and cycle life led by UTRC.

One of the most promising high-capacity hydrogen storage materials is $Ca(BH_4)_2$ which is partially reversible ~5wt% at 620 K and 100 bar. Although it releases hydrogen rapidly up to 7wt%, re-hydrogenation process is very slow. Thus, in order to improve kinetics, we will, in FY09, incorporate $Ca(BH_4)_2$ in a NFS and test its hydrogen storage performance. We have initiated our first attempts to incorporate $Ca(BH_4)_2$ into a small-pore-sized carbon aerogel, which is obtained from HRL, by melt processing under hydrogen pressure to avoid decomposition. We have recently reproduced the procedure, comparing a C-aerogel with and without calcium borohydride powder. Characterization is currently on-going, including TGA, DSC and XRD. We will also utilize Sandia's unique tool STMBMS (Simultaneous thermo-gravimetric modulated-beam mass spectrometer) to investigate what species comes off during heating of a C-aerogel as is, and with infiltrated metal hydride. If this approach turns out to be successful, we will continue this solid-state synthesis route to incorporate doped-$Ca(BH_4)_2$ into carbon-aerogels, as well, and other possible NFS, which are determined to be promising by the UTRC modeling effort, before moving on to the other potential hydride materials. The hydrogen storage performance will be investigated according to above.

During the previous quarter (Q4 FY08), we performed solid-state experiments to incorporate $Ca(BH_4)_2$ by melting under high-hydrogen pressures and this was continued during this quarter. Calcium borohydride was obtained by desolvating Aldrich $Ca(BH_4)_2$ at ca 150°C for a few hours, resulting in a mixture of alfa and beta polymorphs. Carbon aerogel was obtained from HRL (John Vajo) in the form of ca5x3mm sized cubes. The C-aerogel cubes were covered with calcium borohydride powder and placed in a commercial autoclave for further treatment at our high-pressure station. The sample was heated to 560°C under 10,000psig hydrogen pressure during 24hours. After treatment the sample appeared to have melted and covered the surfaces of the C-aerogel. Moreover, the C-aerogel had crumbled which may indicate that a reaction, rather than incorporation, has taken place. During this quarter, we also tried incorporation into functionalized C-aerogels and an oxide material provided by UTRC. It was observed that if the C-aerogel is in the form of a powder, instead of in a cube, no indication of incorporation was visible after heat treatment under high-hydrogen pressures. The oxide material is in the form of a powder and was mixed with calcium borohydride followed by heat treatment at the above conditions. Thereafter, the sample was analyzed by XRD, but no peaks from $Ca(BH_4)_2$ were observed which we currently cannot explain. In order to rule out if incorporation occurred in any of the nanoframeworks, we will send samples for analysis, i.e. BET and TG-MS, to UTRC.

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 $Ca(BH_4)_2(solv)_x$

The modification of $Ca(BH_4)_2(THF)_2$ with alternative Lewis basic solvents has been further investigated. In particular, weaker Lewis bases such as ethers and alcohols have been reacted with $Ca(BH_4)_2(THF)_2$ and efforts are underway to fully characterize them. Initial loading studies, therefore, focused on the THF adduct. Two substrates were chosen to determine loading capacity: yttria stabilized zirconia (YSZ) and carbon aerogel (CA). For initial testing $Ca(BH_4)_2(THF)_2$ was dissolved in THF to form a ~0.3 M solution. The CA were modified by this solution through (a) rapid dip coating, (b) saturated soaking for 48 h. and (c) heated in solution. The samples were removed and allowed to dry under circumjacent atmospheres (argon) in a glovebox. Beryllium dome (BeD) XRD and weight variations were used to determine if $Ca(BH_4)_2(THF)_2$ was incorporated into the substrate. The BeD-XRD data was collected and found to yield little insight into the inclusion of $Ca(BH_4)_2(THF)_2$. This is most likely due to the fact that PXRD is a surface technique which lends little insight into the porosity of the material. Weight data implied the CA was gaining weight, while the YSZ was difficult to interpret since both the powder and the YSZ are white.

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 %

The method for loading was then changed from the previously used dip-coatings to one based on incipient wetness wherein the amount of solution added is directly related to the porosity of the final material. Table 1 shows the data associated with the results. Based on the pore volume in the CA a solution of $Ca(BH_4)_2(THF)_2$ in THF was added to the CA. Upon addition, the entire solution was absorbed by the aerogel leaving a dry wafer. This suggests that that the precursor was completely incorporated into the pores. This was done for 2 YSZ and 1 CA substrate (see Table 1), which were sent to UTRC for initial testing. One YSZ was saturated and the other the incipient wetness, based on the porosity, was attempted. Table 1 lists the calculated values and observed phases. Baseline determination of the inclusion and properties of the THF adduct are being determined using GC-MS, SEM, BET, and TGA/DTA. Once established the alternative samples (*vide infra*) will be treated and tested in a similar manner. Current work with the crystallographically characterized py adduct is underway using larger batch sizes to allow for full characterization.

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: Ewa Ronnebro, Eric Majzoub

In order to be able to improve kinetics and lower the desorption temperature of $Ca(BH_4)_2$, we need to understand the reaction mechanism. When we have identified the decomposition products we can try to manipulate the reaction path to improve the performance of this material. We will undertake a desorption experiment with $Ca(BH_4)_2$, as THF free, utilizing the STMBMS and stopping the reaction at different temperatures and analyze the decomposition products with XRD (Sandia) and NMR (Caltech). Thereafter, samples as ball-milled and alternatively with an additive will be undergoing the same test. Moreover, we will aim at finishing our assessment of hydriding $CaB_{12}H_{12}$ under high H_2-pressures, as well as simulating re-hydrogenation of potential decomposition products, i.e. mixtures of CaB_6+CaH_2+$CaB_{12}H_{12}$ to better understand potential for reversibility.

Subtask 2.1.2 – Discovery and Characterization of New Materials

Principal Investigators: Ewa Ronnebro, Eric Majzoub

We will characterize $Ca(BH_4)(AlH_4)$ by XRD, NMR, Raman and NVS by teaming with our MHCoE partners in order to prove formation of this compound.

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

Principal Investigators: Vitalie Stavila, Mutlu Kartin

In the next quarter, our main focus will be on the synthesis and characterization of the transition metal borohydride ammonia complexes, $M(BH_4)_x(NH_3)_y$, where M = first raw transition metals. We will also investigate some promising magnesium-based mixed-metal borohydride ammonia materials. Our efforts on the exploration of $Ca(BH_4)_2$-$M'(NH_2)$-$M''H_2$ (M' and M''= Ca, Mg) systems by wet-chemistry and solid-state syntheses routes will continue. We will also attempt to synthesize calcium and magnesium amide/imides, in order to incorporate them into the mixed amide/imide borohydride materials.

Subtask 2.1.4 –Additive Screening to Improve New Materials Properties

Principal Investigators: Eric Mzajoub, Mutlu Kartin

U. Hawaii will perform NMR analysis on desorbed $Li_2Zr(BH_4)_6$ and send desorbed samples to SNL for XRD and additive screening analyses. LiMgN additive screening analyses will be performed at HRL using their six-sample holder system. MgH_2-TiH_2 additive screening analyses will be performed by U. Utah, HRL, Sandia and UMSL. HRL will compile their additive screening results of $LiBH_4$-MgH_2 for further consideration of this material.

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.

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

Incorporate gas-phase B_nH_m species into phase-equilibrium calculations and complete FactSage modeling of boron-containing hydride systems. Begin draft of journal article.

Discuss results of UIUC and UMSL calculations predicting the $Ca(B_{12}H_{12})_2$ structure and identify a pathway to establishing which is the correct ground-state structure.

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 Investigator: Ewa Ronnebro

The efforts on melt-incorporation of $Ca(BH_4)_2$ in different nanoframeworks will continue and samples will be sent for analysis to UTRC and other MHCoE partners. Though we have indications of partial incorporation, we need to complement SNL's XRD analysis with UTRC's BET and MS-TG analysis to learn how much is incorporated in each nanoframework. We are aiming at having enough results in February/March timeframe to be able to make a go/no-go decision on the solid-state approach.

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, and UNR. 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 Long 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	UH review conducted Nov. 17, 2008
Technical Progress Report	Quarterly	Ongoing	
Storage Tech Team Review	02/09		
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	Deferred	Sent sample for calorimetry at SRNL
Go/No-Go: Go if we are able to demonstrate micelle sizing in non-aqueous solvents using THF	11/30/08		
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		

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		
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 $Li_2CaN_2H_2$, $Li_2MgN_2H_2$ and $MgCaN_2H_2$	2/28/09		
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		
Milestone: Complete additive screening study of MHCoE amide	7/31/09		
Milestone: Complete additive screening study of mixed amide/borohydride	9/30/09		
Subtask 2.2 Cross-cutting Theory			

Task	**Planned Completion**	**Actual Completion**	**Comments**
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		