QUARTERLY PROGRESS REPORT

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/USML

Other Partners: MHCoE Partners

SNL Principal Investigators:
Tony McDaniel
Eric Majzoub
Ewa Ronnebro
Mark Allendorf
Robert Bastasz
Tim Boyle

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:

Subtask 2.1 – MHCoE Project B: Complex Anionic Materials

Subtask 2.1.1 – Metal Borohydrides

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.

Calcium borohydride

We are continuing our work on calcium borohydride which has potential to be absorbed/desorbed by a specific reaction route, resulting in theoretical 9.6wt% hydrogen. We are underway to characterize thermodynamics, kinetics and cycle life to understand how useful this material is for reversible on-board storage at more moderate temperatures and pressures.

By ball milling for a longer time before heat treating under high-hydrogen pressures, we were able to increase the yield of $Ca(BH_4)_2$ using the previously patented reaction route of reacting CaB_6 with CaH_2 and catalyst.

We prepared pure, crystalline $Ca(BH_4)_2$ as earlier described by heating up a sample of $Ca(BH_4)_2(THF)_2$ in vacuum. We submitted a manuscript to PRB in December 2007 which describes three different polymorphs of $Ca(BH_4)_2$ at different temperatures, as revealed by *in-situ* synchrotron data (ESRF). We are underway characterizing decomposition products in collaboration with our MHCoE partners and other collaborators: NMR & in-situ NMR (JPL/Caltech), in-situ XRD (GE) and neutron vibrational spectroscopy (NIST). Moreover, at Sandia, we are currently performing desorption/absorption experiments and in our first attempt, we observed desorption in vacuum starting at ~315C and thereafter partial absorption (re-hydrogenation) starting at ca 315C under 90bar H-pressure. We are currently reproducing this experiment and will perform XRD on desorbed and re-hydrided samples, as well as calculate weight percent hydrogen.

Investigation of thin film samples of Ca-B with dopants

In collaboration with Intematix, we are exploring thin films of Ca-B multilayers with catalysts in between to find the best catalyst for hydrogenation of these films. Four thin film samples were sent to us from Darshan Kundaliya. We performed Raman spectroscopy on the thin films as received and as heat treated under hydrogen pressures at the HP-station, i.e. 440C and 15000psig. The films as received did not show any peaks. The films after HP-treatment showed a peak at ca $2340cm^{-1}$, as can be seen in Figure 1, which indicates BH_4 as concluded by comparing with a Raman spectrum of $Ca(BH_4)_2$. The desolvated sample of $Ca(BH_4)_2$ shows a distinct number of peaks for the BH_4 group(s) between 2150 and 2436 cm^{-1}, with one of the main peaks at 2340. The samples from Intematix only have one peak around 2340. This could be BH_4, but the other strong peak in the $Ca(BH_4)_2$ spectrum does not show up. It is difficult to tell if there is any quantitative difference between the different catalysts added to the Ca-B multilayers.

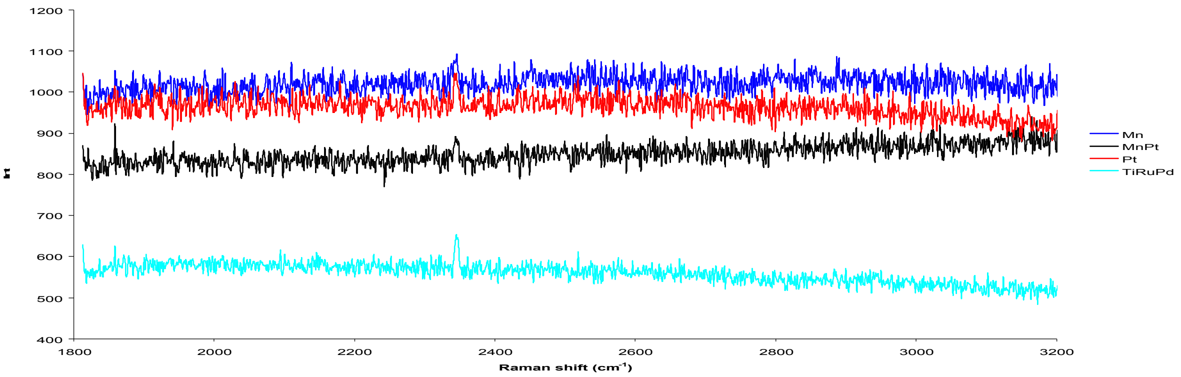


Figure 1. Raman spectra of four thin film samples from Intematix showing Ca-B multilayers with different catalysts: Mn (blue), MnPt (black), Pt (red) and TiRuPd (light blue).

Subtask 2.1.2 – New Hydrogen Storage Materials

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 gap between experimental results 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 pleased to report that our efforts in this area have been augmented by the recent hiring of Dr. Vitalie Stavila, who will bring considerable synthetic expertise to bear on our new materials synthesis activity.

We have decided to abandon our attempts in the ternary Si and Ge systems because these new materials phases only contained very small amounts of hydrogen, thus not worthwhile to pursue. Instead, we are focusing our new materials effort on new bialkali borohydrides and mixed alkali transition metal borohydrides.

Monte Carlo - DFT structure prediction for new materials searching:

A publication has been submitted to Physical Review Letters on the discovery of a low energy crystal structure for $Mg(BH_4)_2$, titled "First-principles prediction of a ground-state crystal structure of magnesium borohydride." The prototype electrostatic ground state (PEGS) search technique, using distance scaling method (DSM) Monte Carlo (MC) identified the lowest energy structure (I-4m2). First-principles calculations indicate the PEGS structure to be 5kJ/mol lower in total energy at 0K than the observed P61 structure, indicating a potential new ground state.

The PEGS method has also identified $NaK(BH_4)_2$ and $LiK(BH_4)_2$ compounds as potentially stable materials. First-principles T=0K calculations indicate decomposition into mono-cation borohydrides is weakly exothermic. The four highest symmetry crystal structures from the PEGS search for $NaK(BH_4)_2$ are, from lowest to highest symmetry, R3, R-3, P3m1, and R-3m. Remarkably, all generated structures are trigonal, belonging to the same fundamental lattice type. The total DFT energies, at T=0K, of the four structures are ordered monotonically with the crystal symmetry, with the highest symmetry R-3m having the lowest energy. The P3m1, R-3, and R3 structures have a T=0K total energy of 76, 80, and 110 meV per formula unit above the R-3m structure, respectively. Using the lowest energy R-3m structure for $NaK(BH_4)_2$, and ignoring the phonon contribution to the total free energy, we have calculated the energy for the decomposition reaction of $NaK(BH_4)_2$ into $NaBH_4$ and KBH_4 to be near -3kJ/mol formula unit at T=0K. This indicates that the decomposition will proceed spontaneously. However, zero point energy (ZPE) phonon contributions can be in the range of 5kJ/mol for these compounds due to low Z elements and resulting high vibration frequencies, and the potential for a stable compound could not be ruled out initially.

Samples of $NaK(BH_4)_2$ were prepared by mechanical milling of $NaBH_4$ and KBH_4 using a SPEX high energy ball mill. Raman spectra of prepared material indicated BH_4 anion vibrations. X-ray diffraction (XRD) peaks not belonging to $NaBH_4$ or KBH_4 from prepared materials indicated the existence of a new phase. Correlation of the peak positions with those of the predicted structures suggested a Rietveld refinement of the XRD data was necessary, and suggests that R3 may be the correct structure. Time resolved XRD also indicated that the material spontaneously decomposed into $NaBH_4$ and KBH_4 after approximately 14-24 hours. Interpretation of the data is ongoing, and a publication is in progress. The PEGS method has correctly predicted the existence of a metastable $NaK(BH_4)_2$ compound.

Exploration of new bialkali borohydrides

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

$NaK(BH_4)_2$

A new bialkali borohydride of $NaK(BH_4)_2$ has been predicted, as described above, to be almost stable by the Monte-Carlo technique (Eric Majzoub, SNL/UMSL) and was recently synthesized via a ball milling technique to introduce a potential candidate for a hydrogen storage material. The material was previously characterized using X-ray diffraction and Raman spectroscopic techniques. The proximity of the values of the Raman and XRD peaks of $NaK(BH_4)_2$ to peaks associated with KBH_4 indicates this new compound has crystalline features more similar to KBH_4 rather than $NaBH_4$.

From an experimental evaluation of the above proposed potential structures of $NaK(BH_4)_2$, it is clear that *R*3 give the best fit between the observed and calculated patterns, judging from the considerably lower R_B-value and better fit between observed and calculated diffraction patterns as compared to *R*-3 and *R*-3*m*. The plot from the Rietveld refinements is shown in Figure 2. The R_B values for *R*3, *R*-3 and *R*-3*m* respectively were: 26%, 44% and 40% refined to obtain the same unit cell parameters. The difference plots (not shown here) of *R*-3 and *R*-3*m* are very similar, and so are their respective R_B values. The cell parameters for $NaK(BH_4)_2$ were refined between $2\theta = 0.3\text{-}75°$ in space group *R*3 (Z = 3) to: $a = 4.615(2)$ and $c = 22.39(2)$ Å. R-values of $R_B = 25.6$ and $R_F = 21.4\%$ were obtained for the metal atom structure. It was to some extent possible to refine displacement factors and atom coordinates.

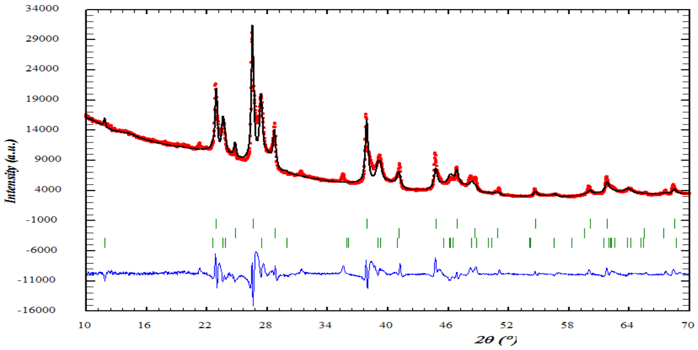


Figure 2. Difference plot from Rietveld refinements of from top to bottom: KBH_4, $NaBH_4$ and $NaK(BH_4)_2$. $NaK(BH_4)_2$ was refined in *R*3 with unit cell parameters $a = 4.615(2)$ and $c = 22.39(2)$ Å.

However, the calculated peaks at $2\theta = 11.83°$ and $22.56°$ cannot be observed in the X-ray pattern. Thus, a new attempt was made to refine the structure in a unit cell with half the *c*-axis, similar to a suggestion from TREOR. The procedures were the same as described above. This resulted in considerably lower R-values (%) for all the three space groups: *R*3; $R_B = 15.4$ and $R_F = 12.6$, *R*-3; $R_B = 11.0$ and $R_F = 9.49$, *R*-3*m*; $R_B = 13.4$ and $R_F = 10.1$. In average, this gives: $R_B = 11\text{-}15\%$ and $R_F = 9.5\text{-}12.5\%$ which is acceptable for a pattern of amorphous character and without hydrogen atoms completing the true structure. It was possible to refine atom coordinates, but the displacement factors were not stable and had to be locked. The sample contains 33% of $NaK(BH_4)_2$, 56% of KBH_4 and 10% of $NaBH_4$.

The difference plots are identical, so it was not possible to distinguish between the three rhombohedral structures, since the metal atom structures are very close to each other. Figure 3 shows one of the plots from the Rietveld refinements. Neutron diffraction data would bring clarity in the true structure, but since the sample is metastable it would be difficult to collect data. It's important to note that the bonding distances become unreasonable short in the smaller unit cell, and thus it is more likely that the larger unit cell better describes the crystal structure.

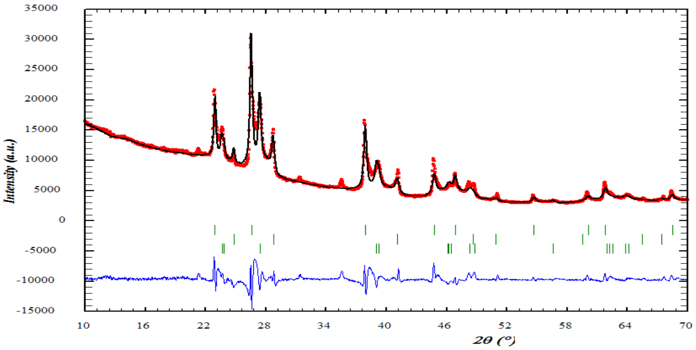


Figure 3. Difference plot from Rietveld refinements of from top to bottom: KBH_4, $NaBH_4$ and $NaK(BH_4)_2$. The plots of *R*3, *R*-3 and *R*-3*m* are similar, so here only one of them is shown. The unit cells were refined to *a* = 4.612(2) and *c* = 11.193(8) Å.

$LiK(BH_4)_2$

We also successfully prepared $LiK(BH_4)_2$ by ball milling $LiBH_4$ and KBH_4 in a similar way to preparing $NaK(BH_4)_2$. Powder X-ray diffraction and Raman spectroscopy (Figure 4 a) confirmed formation of a stable phase which has also been reported by Prof. Edwards group at U. Oxford, UK (Poster by Nickels et al at ISHE, Richmond, VA, Nov-07). We also collected Neutron Vibrational Spectra in collaboration with Terry Udovic (NIST) and NMR in collaboration with Bob Bowman (JPL)/Son-jong (Caltech). Figure 4b) shows TGA and DSC curves. DSC shows endothermic phase transitions at 100 and 110C and one major exothermic transition at 450C and a minor at 430C, the latter associated with a minor weight loss, according to the TGA curve. It doesn't seem like there is a major hydrogen loss within 500C, so this is not a promising material for reversible H-storage. We are currently summarizing the results for publication.

a) b)

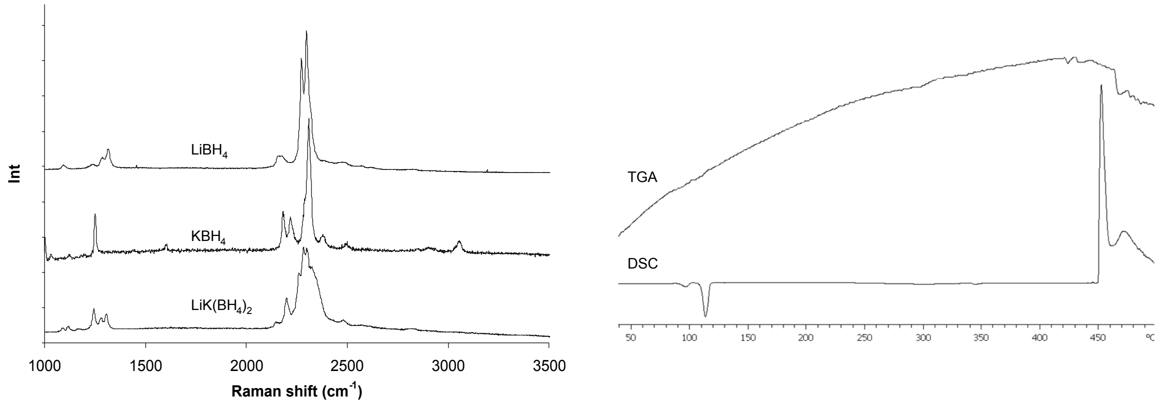


Figure 4. a) Raman Spectroscopy of $LiBH_4$, KBH_4 and $LiK(BH_4)_2$ and b) TGA and DSC curves of $LiK(BH_4)_2$.

$LiNa(BH_4)_2$

We are underway trying to prepare $LiNa(BH_4)_2$ by ball milling followed by heat treatment under high-hydrogen pressures. Ball milling $LiBH_4$ and $NaBH_4$ (with catalyst) does not result in a stable product. Thus, in a similar way to the reaction route for preparing $Ca(BH_4)_2$, we heat treated the ball milled sample at the HP-station. So far, we have not observed any reaction, but will try ball milling longer time.

Alkali and alkali earth transition metal borohydrides

In collaboration with U. Hawaii (Craig Jensen and Godwin Severa), we have undertaken high-pressure experiments at our HP-station to prepare a series of high-capacity alkali and alkali earth transition metal borohydrides. The synthesis routes involved mixing of transition borides of Sc, Mn and Zr with alkaline metal hydrides and/or borides by hand milling for about 10 minutes in glove box followed by mechanical milling in a SPEX mill 8000 instrument for 30 minutes. Last quarter, two high pressure experiments were done on the Sc samples at 400ºC and 15000 psig for about 24 hours. Initial TG/DSC studies showed that hydrogen is released in a broad interval between 300-400ºC upon phase transitions which has to be investigated further. NMR and FTIR analysis is underway at U. Hawaii to confirm reaction products. A 'technical advance' is currently in preparation as a collaborative effort between U. Hawaii and Sandia.

Caltech (Ahn and coworkers) provided us with a powder sample of ball milled mixture of ScB_2+2LiH+2%$TiCl_3$ for treatment at SNL's HP-station. A first attempt was made in December at 460C, 13000psig and 48hours, resulting in white scattered dots on the surface of the black pellet, which may indicate that a chemical reaction occurred, but the yield is too low to be able to identify the product by XRD. We will perform a second HP-test at higher temperatures.

Subtask 2.2 – Exploratory Routes to Materials Discovery

The objective of this subtask is to use an array of micro-hotplates integrated into a high pressure vessel as a means to rapidly synthesize and characterize large libraries of complex metal hydride materials processed at extremely high hydrogen pressure and high temperature. This effort is focused on applying combinatorial methods to discover new light-weight, high-capacity metal hydride compositions that will meet the FreedomCAR and Fuels performance targets for on-board storage.

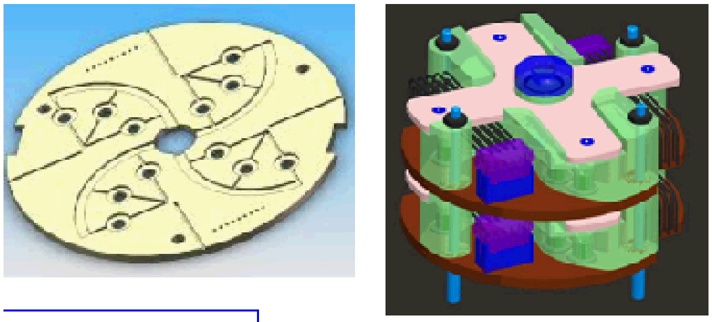
This section reports on progress made during the first quarter of FY08 (Oct-Dec 2007), and will focus primarily on efforts to achieve two major project milestones. These are: (1) design and fabrication of instrumentation to scale up the High Throughput Screening (HiTS) capability, (2) development of a viable process workflow for sample preparation

Scale-up of HiTS Capability

We are pleased to report the recent hiring of Dr. Mutlu Karten, who will be working with the PI McDaniel on new materials discovery using HiTS.

Work in the first quarter of FY08 focused on finalizing the designs for scale up of the HiTS apparatus to a 24 sample per reactor system. We were successful in extending our design limits from a planned 15 sample, 3 detector configuration on a single board to stacking two 12 sample, 4 detector boards into a smaller vessel. Four principle improvements were realized by these modifications: (1) the inner diameter of the pressure vessel was reduced by 40% which provides for a much lighter high pressure vessel while still maintaining the required safety margins, (2) the sample capacity per reactor increased by 60% thereby increasing throughput on the material synthesized per an attempt, (3) the number of TCD detectors increased from 3 to 8 allowing for a greater number of simultaneous desorption experiments per cycle which also increases throughput, and (4) the PC boards and fixture will fit inside either the low pressure Par reactor or the high pressure vessel meaning that samples may be easily swapped between the two systems.

A schematic of the new PC board is illustrated in Figure 5 along with a detailed model of the fixture used to stack the boards in the pressure vessel. The top view of the board shows 4 separate flow channels with 3 sample wells and one TCD detector on each channel oriented to maintain optimal flow symmetry. Another important modification not pictured is a stainless steel plate which will be bonded to the PC board in order to seal the flow channels, thereby removing the likelihood of gases leaking from the channel or possible occlusion of a channel by the extrusion of a flat gasket (known to be problematic with the 4 sample, low pressure prototype). A separate fixture was designed in order to stack two PC boards, one atop the other, into a fairly compact arrangement that provides for a common gas manifold and routing of electrical wires. This design fits within a 2.5 inch ID vessel and is a mere 1.6 inches tall. The design is sufficiently flexible to stack more boards if desired, however, the practical limit of two (holding 24 hotplates) was determined by the number of programmable power supplies required to control the system and difficulties of finding pressure-rated, high density electrical feedthroughs.



PCB top view
flow channels

internal flow paths, hotplates, and circuitry mounted on Cu-clad PTFE board

Figure 5: Top view of the 16 hotplate PC board (12 samples and 4 thermal conductivity detectors), and the compact fixture used to stack two boards within a single pressure vessel.

Designs were also finalized for the low and high pressure vessels that accommodate the PC boards that comprise the array of micro-hotplates. The internal features of both pressure vessels are identical so that the 24 sample array can be swapped between pressure stations if desired. All parts for the PC boards, stacking fixture, and low pressure vessel are in fabrication with delivery expected by middle second quarter FY08. The high pressure vessel will be fabricated shortly thereafter.

Sample Preparation Process Workflow

The other major activity executed in the first quarter of FY08 was the development of a viable and affordable sample preparation workflow. Given budgetary constraints, we could not consider an automated or robot-driven powder dispensing station to support the HiTS activity, such a solution typically costs $200K and in all actuality is not necessary for the successful implementation of our combinatorial approach. Instead, a manual workflow was devised and is depicted in Figure 6. Precursor powders are pre-processed by milling and sieving to achieve a fairly narrow particle size distribution. They are then placed into a series of “many-to-many” gravity fed dispensing units supplied by Symyx, which will efficiently generate our variable sample compositions according to the experimental design. The mixtures are then mixer milled using a multi-sample adapter plate that can process 20, 2 mL samples simultaneously. After milling, small pellets of sample are pressed and then distributed into the hotplate wells. Preparing samples and loading the reactor could take 4 to 6 hours, which is well proportioned to the time spent “on-line” running experiments. It is anticipated that an operator will spend 16 or more hours running through a course of synthesis and characterization experiments, meaning that manual sample preparation will not create a bottleneck in the HiTS process. The Symyx gravity feed system will reduce the likelihood of operator error when dispensing powders and also minimize sample-to-sample variability. With the exception of the contract to Symyx, all equipment orders have been processed and delivery is expected middle of second quarter FY08. The entire sample preparation work flow will located within a dedicated dry box.

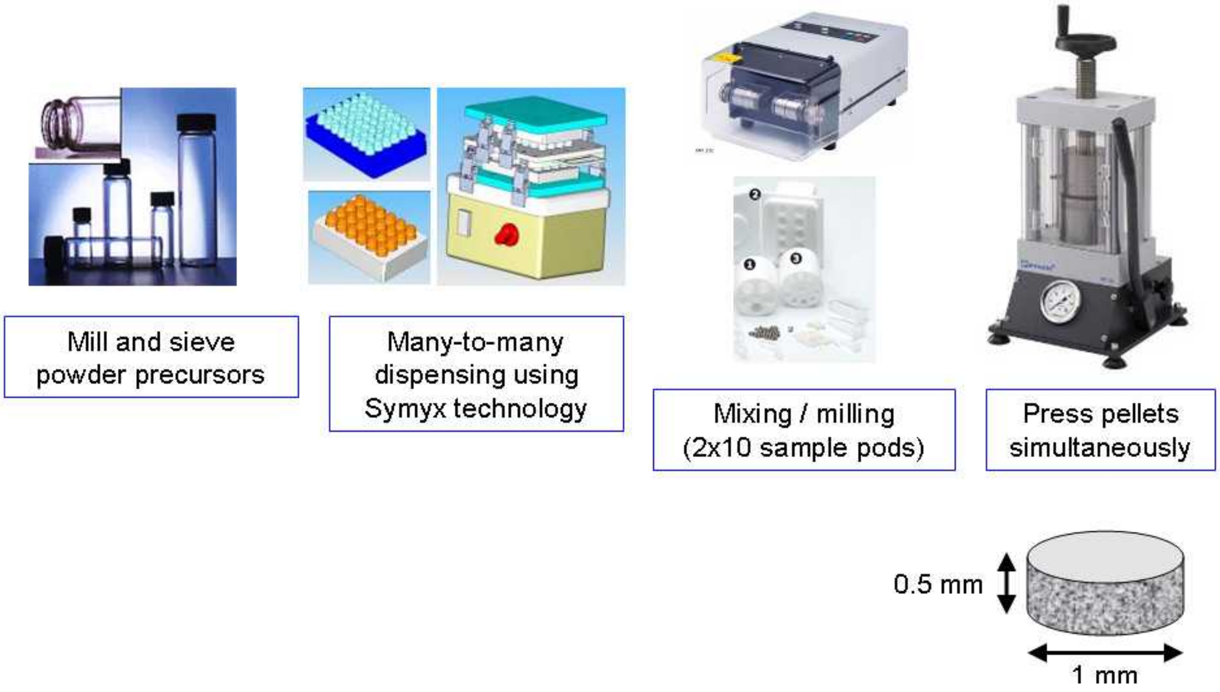


Figure 6: Depiction of process workflow for preparing powder samples.

Subtask 2.3 – MHCoE Project E: Engineering Analysis and Design
Effort on hold.

Subtask 2.4 – Cross-cutting Theory and Contamination Studies

2.4.1 – Cross-cutting Theory

Efforts in the Cross-cutting Theory subtask are primarily focused on four areas at this time: 1) reactions of H_2O and O_2 on MH surfaces; 2) nanoscale effects; 3) complex hydride discovery; and 4) quantum-chemistry modeling of aluminum complexes. Progress in each is briefly discussed below. Full details are provided in the quarterly reports of the non-Sandia institutions involved in these efforts (U. Pitt, UIUC, Georgia Tech, NIST, UMSL, and UTRC).

Reactions on MH surfaces. We continued our calculations on the properties of LiH, NaH and KH surfaces this quarter. We have computed the dissociation pathways and energetics of water on each of these surfaces and have examined the coverage dependence of the energy and structure of atomic and molecular oxygen. In addition, we are in the process of developing microkinetic models for H_2O dissociation on the surface of LiH. Calculations to predict the dissociation of O_2 on LiH and NaH are complete, but we are continuing to search for the reaction pathway for O_2 dissociation on KH. Calculations to date using the Nudged Elastic Band method have not been successful (the results are nonsensical). We also performed a molecular dynamics calculation at 600 K in VASP, running the simulation to 3.75 ps and the oxygen still does not dissociate there either, although the dissociated state is known from our calculated thermodynamics to be lower in energy than the undissociated state. Instead, the initial relaxation results in the formation of an OO-H bond with the O_2 in a "hole" on the KH surface where the H atom used to be. It appears that there is a substantial barrier to dissociation on this surface which so far we have been unable to surmount. We are currently discussing how to approach this problem, which we would like to solve before submitting a manuscript discussing the results.

Nanoscale effects. Work in this area is proceeding on two fronts: 1) influence of oxide nanoframeworks on hydride stability, hydride dehydrogenation intermediates and product formation (at UTRC) and 2) influence of surface energy on the stability of metal and metal-hydride clusters.

In the first area, UTRC conducted first-stage atomic modeling of to predict the influence of oxide nanoframeworks on hydride stability, hydride dehydrogenation intermediates, and product formation to prepare for simulating nanoframework modification of frameworks with dopants, surface functionalization and hydrogen-activation catalysts. Interfacial interactions of oxide nanoframework slabs formed from alpha-Al_2O_3 (0001), gamma-Boehmite (010), ZrO_2 P121/c1 (111), and SiO_2 quartz P3121 (001) surfaces with $LiBH_4$ and $Mg(BH_4)_2$*$2NH_3$ hydride clusters were modeled (see the the UTRC quarterly report for details). Atomic and thermodynamic modeling of oxide framework reactions with $LiBH_4$ was also conducted to assess oxide stability against potential reduction and degradation mechanisms. The adsorption behavior of borane intermediates and elemental and binary hydride decomposition products was also simulated. Finally, preliminary molecular dynamics calculations of oxide supported-$LiBH_4$ decomposition behavior were conducted.

In the second area, the Pitt/Georgia Tech group computed surface energies for several metals and their corresponding metal hydrides using DFT, and used this information to compute the size effects on a transition temperature. This temperature compares the hydrogen desorption properties of the nanoparticle with those of bulk metal. They also calculated the zero point energy contributions to the surface energies and have performed Bader charge analysis for some of the metal hydrides. Transition metals, Na, and Mg are included in the calculations. Two interesting results are that first, quite small particles (nanoscale) are needed to cause a significant change in the transition temperature for most materials. Second, the transition temperature actually increases with decreasing size for most things except MgH_2 and NaH. These results are preliminary at this stage, however, and will be checked next quarter (see the Pitt/GeorgiaTech report for additional details).

To support the DFT calculations on metal hydride clusters described above, we are discussing with the Computational Nanosciences Group at U. C. Berkeley (Dr. Jeffrey Grossman) the possibility of conducting quantum Monte Carlo (QMC) calculations to predict the onset of nanoscale behavior in Mg and/or Al clusters. This collaboration is informal at this time (i.e., no financial support is being provided by the MHCOE) so these calculations will, of necessity, be on a relatively small scale. However, since QMC provides much more accurate energies in many cases than DFT, we hope that a limited study will provide both insight and motivation to pursue the investigation further and will seek support from DOE.

Complex hydride discovery. The TG continues to be fully engaged in materials discovery efforts. Some highlights of this quarter's work (again, details may be found in reports from individual institutions) are:
Majzoub (UMSL): The metastability of $NaK(BH_4)_2$ was predicted using PEGS search. The compound was subsequently synthesized and analyzed for structure and stability; metastability was confirmed. A similar search in the $LiK(BH_4)_2$ system is ongoing. PEGS searches for $Ca(BH_4)_2$ structures containing 2, 3, and 4 formula units is ongoing. A PEGS search for $LiSc(BH_4)_3$ structures was also initiated.
Sholl/Dai (U. Pitt): A paper presenting DFT calculations on the experimental low and high temperature structures of $Mg(BH_4)_2$ was submitted. The structures were relaxed and a higher symmetry low-temperature structure was found than identified in the experiments. Experimental structures have been compared with various hypothetical structures that are structurally much simpler, but have similar energies.
Kattner (NIST): Development of a thermodynamic description for Ca-B-H is now in progress. An evaluation of the literature for ternary M-B-H systems is also underway.
Johnson (UIUC): 1) In collaboration with experimentalists, the DFT-derived boron p-DOS was evaluated for EELS (electron energy loss spectroscopy) analysis of the calcium borohydride system. The results show that it should be possible to use the boron EELS edge to differentiate on the nanometer scale between boride and borohydride. 2) A new DFT-based approach was developed to quantitatively predict the enthalpy changes in phase transformations and hydrogen-storage reactions by including critical non-harmonic vibrational contribution. Excellent quantitative agreement with experiment is found for LiBH4 systems, including $LiBH_4$ destablized with MgH_2. A paper has been accepted by *Physical Review Letters* (to appear in 2008).

Quantum-chemistry modeling of aluminum complexes. The objective of this SNL (Allendorf) activity is to predict bond energies for aluminum Lewis acid-base complexes that may be used to stabilize AlH_3. We will be using the Bond Additivity Correction (BAC) method, which typically predicts bond energies for small molecules with an accuracy of ± 2 kcal/mol. This quarter we brought the codes on line and completed testing them (they were moved from one computer to another and had not been recently used). Preliminary calculations for a range of Al-N complexes were completed. Predicted bond energies compare well with limited data available from the literature. We also are planning to establish a collaboration with Prof. Sean McGrady (Univ. New Brunswick), who performed similar calculations, but using a different method.

2.4.2 – Study of Surface Contamination and Catalysts on Hydrogen Storage
Effort on hold.

2.5.1 – Catalyzed Nano-Framework
Solutions of $Ca(BH_4)_2(solv)_x$ (Solv= THF, py, MeOH, and MeCN) were synthesized, purity verified by single crystal XRD when possible, and deposited onto fused silica substrates. Several methods to characterize these highly reactive species were undertaken with the beryllium dome (BeD) XRD proving the most fruitful. Initial data indicates successful deposition of the material. Further characterization awaiting new BeD-XRD (expected to arrive in late January) to determine if solution deposition is consistent with the bulk powder of these materials.

PLANS FOR NEXT QUARTER

Subtask 2.1 – MHCoE Project B: Complex Anionic Materials

Subtask 2.1.1 – Metal Borohydrides

We are currently underway attempting to show full reversibility of $Ca(BH_4)_2$ at lower H_2-pressures than 70MPa. We will prepare batches of desolvated $Ca(BH_4)_2$ in order to investigate decomposition products with XRD, NMR, *in-situ* NMR, Raman, *in-situ* Raman, neutron vibrational spectra and TGA/DSC in collaboration with our partners. Calcium borohydride will be fully characterized with respect to desorption and absorption and reversibility at pressures within 100bar and temperatures within 350C. We will also investigate desorption/absorption of a sample of calcium borohydride as destabilized by Cr, as was recently suggested by Seagel et al.

A postdoc (Leo Seballos) will begin preliminary work on surfactant directed synthesis of nanoparticle complex hydrides. The first step in this area is to determine the minimum size micelle that can be accurately produced and measured using the Brookhaven Instruments dynamic light scattering apparatus. Once micelles reproducibility is achieved, we will begin preparation of nanoparticle materials.

The PEGS method is currently being utilized to investigate the low energy structures for $Ca(BH_4)_2$ to address questions resulting from the experimental determination of the low and high temperature phases and polymorphs discussed in the sections above. In collaboration with JPL, we will also continue a PEGS search for $LiSc(BH_4)_4$ to complement ongoing structure and NMR studies.

Subtask 2.1.2 – New Hydrogen Storage Materials

We will continue our experimental efforts on screening for new borohydride materials. In collaboration with U. Utah we are investigating ternary Ti-systems and in collaboration with U. Geneva and Stockholm University we are investigating Mg-containing materials. We are planning on submitting an abstract to MH2008 on a new high-yield route to prepare Mg_2FeH_6 (work done in 2004 at SNL) and how dopants effect kinetics (work done at U. Geneva).

We will summarize our findings regarding the two new bialkali borohydrides that were predicted by the MC-method and prepared in the solid state in a paper to be published in the literature.

Subtask 2.2 – Exploratory Routes to Materials Discovery

Fabricate parts for the scaled-up HiTS system and execute a detailed materials discovery investigation of the Li-Na-K-BH_4 material compositional space.

Subtask 2.3 – MHCoE Project E: Engineering Analysis and Design

Effort on hold.

Subtask 2.4 – Cross-cutting Theory and Contamination Studies

2.4.1 – Cross-cutting Theory

The TG will continue its coordinated materials discovery efforts, in line with existing plans for individual research groups. In particular, however, we plan to provide theory support for the experimental effort to develop $Ca(BH_4)_2$. We will also complete the manuscript describing DFT calculations of reactions on MH surfaces and submit to a peer-reviewed journal. An approach to address cluster size effects will be developed, focusing on Mg and Al clusters. BAC-MP4 calculations of Al-N and Al-O clusters will be performed, and a plan for coordinating these efforts to produce a comprehensive study will be developed with Prof. McGrady.

2.4.2 – Study of Surface Contamination and Catalysts on Hydrogen Storage

Effort on hold.

2.5.1 – Catalyzed Nano-Framework

Throughout the next quarter, it will be determined if $Ca(BH_4)_2(solv)_x$ solutions can be deposited on substrates and maintain the same phase as the bulk powder. Once the BeD (beryllium dome apparatus) arrives XRD can be done to determine if this is route to deposition will work. Go No Go will be decide in early February.

PATENTS:

E. Rönnebro, E. Majzoub, “A New Synthesis Route of Calcium Borohydride and its use for Reversible Hydrogen Storage”, U.S. Patent Application Serial Number 60/901,248 filed 02/12/2007.

W. Luo, K. Stewart, Patent application # 11/487,527, Reactor for Removing Ammonia, filed July 13, 2006.

PUBLICATIONS/PRESENTATIONS:

E. Rönnebro et al, “Discovery and Development of New Metal Borohydrides”, Poster presentation at ISHE, Richmond, VA, November 12-15, 2007.

E. Rönnebro, E. Majzoub, "Hydrogen Storage in Calcium Borohydride: Catalysis and Reversibility", J. Physical Chemistry B Letters, published online 10/03/2007.

Y. Filinchuk, E. Rönnebro, D. Chandra, "Crystal Structures and Phase Transformations in $Ca(BH_4)_2$", manuscript submitted to PRB on 12/23/07.

"First-principles prediction of a ground-state crystal structure of magnesium borohydride," V. Ozolins, E.H. Majzoub, C. Wolverton, submitted PRL, Nov 2007.

"Prototype electrostatic ground state approach to predicting crystal structures of ionic compounds: Application to hydrogen storage materials," E.H. Majzoub, V. Ozolins, submitted PRB, Oct 2007.

"Global optimization of complex hydride crystal structures," E.H. Majzoub, Invited talk Materials Science and Technology conference, Detroit, MI, September 2007.

"Prototype electrostatic ground state (PEGS) structure prediction for $NaK(BH_4)_2$," E.H. Majzoub, Materials Research Society Meeting, Boston, Nov 2007.

COLLABORATIONS: Describe any networks or collaborations fostered.

- Sandia is leading the team effort among the MHCoE partners of Project B-Complex Anionic Materials.
- Several collaborations is on-going within MHCoE to characterize calcium borohydride's decomposition products.
- We are working with U. Utah (Fang) on materials discovery using reactive milling in these systems: Mg-Ti-H and Li-Ti-H
- A student from U. Santa Cruz, CA, Rebecca Newhouse, has in December joined the group to work (50/50 UCSC/SNL) on synthesis and characterization of metal borohydrides.
- We will continue collaborating with Klaus Yvon and Radovan Cerny of U. Geneva, Switzerland, on new materials.
- We are collaborating with Prof. Craig Jensen (U. Hawaii) and colleagues on transition metal borohydrides.

MILESTONE STATUS TABLE:

FY 2008 Milestones/Deliverables	Planned Completion	Actual Completion	Comments
Subtask 2.1: MHCoE Project B: Complex Anionic Materials			
Subtask 2.1.1: Metal borohydrides			
Prepare higher yields of $Ca(BH_4)_2$ at lower pressures and temperatures	12/07	12/07	
Characterize hydrogen sorption properties and explore reversibility	05/08		On-going
Investigate structural features with XRD, synchrotron and/or neutron diffraction and Raman	12/07	12/07	Paper submitted to PRB
Explore reversibility of other metal borohydrides using high-pressures in collaboration with U. Hawaii	05/08		
Explore reversibility of $Mg(BH_4)_2$ using high-pressures in collaboration with GE	05/08		
Prepare mixed metal borohydrides guided by theory*	03/08*		On track
Subtask 2.1.2: New Hydrogen Storage Materials			
Synthesize new complex metal hydrides in the ternary Si/Ge-system	12/07		No-go on the Si- and Ge-systems. New hydrides had too low of a hydrogen content. New materials search shifted to focus on new borohydrides.
Investigate structural features with XRD, synchrotron and/or neutron diffraction and Raman	03/08		
Characterize hydrogen sorption properties of potential candidates*	05/08*		Delayed due to budget constraints
Discover new complex metal hydrides guided by theory	09/08		
Subtask 2.2 : Exploratory Routes to Materials Discovery			
Subtask 2.2.1: Micro-Hotplate Synthesis of New Materials			

FY 2008 Milestones/Deliverables	**Planned Completion**	**Actual Completion**	**Comments**
Refine and validate sample preparation procedures (powder delivery, pressed powders, vacuum deposition)	12/07	12/07	Developed viable process workflow and procured equipment
Incorporate second generation hotplate devices into the RTP platform	03/08		
Modify DRIFTS apparatus to incorporate micro-hotplate fixtures	03/08		
Evaluate second generation mask set and 3-D patterns to optimize hotplate durability and performance	09/08		
Synthesize and characterize candidate materials from the Li-Na-K-B-H system with the RTP platform	09/08		
Subtask 2.3 Engineering Modeling*			Delayed due to budget constraints
Develop fundamental kinetics mechanism	04/08*		Delayed due to budget constraints
Test Mechanisms against reaction data	08/08*		Delayed due to budget constraints
Integrate fundamental kinetic model into engineering tank design tool	09/08*		Delayed due to budget constraints
Subtask 2.4 Cross-cutting Theory and Fundamental Studies			
Identify focus area for nanoscale computation investigation	10/07	1/08	
Bring BAC codes on line	2/08	11/07	
Compute BDE for representative Al-N complexes	7/08		underway
Complete BAC quantum-chemistry investigation of alane compounds	9/08		
Identify focus area for nanoscale computation investigation	10/07	1/08	
Subtask 2.4.2 - Study of Surface Contamination and Catalysts on Hydrogen Storage Materials*			Delayed due to budget constraints

FY 2008 Milestones/Deliverables	**Planned Completion**	**Actual Completion**	**Comments**
Complete surface characterization of selected candidate storage material specimens	6/08*		Delayed due to budget constraints
Complete hydrogen adsorption/desorption study on a model storage material	9/08*		Delayed due to budget constraints
Subtask 2.5 - Catalyzed Nano-Framework Stabilized Reversible Materials to Enable High Density Systems			
Subtask 2.5.1 - Incorporation of hydride material into the catalyzed nano-framework structure by solid-state synthesis routes			
Determine promising chemistries of NSF and catalyst for solid state route in collaboration with UTRC	5/08		
Synthesize HSM for solid state route to use in *ex-situ* incorporation and initial evaluations of stabilization.	9/08		
Synthesize HSM within the NFS *in-situ* by solid state routes	12/08		
Subtask 2.5.2 - Incorporation of hydride materials into the catalyzed nano-framework structure by a metathesis wet-chemical route			
Determine promising compositions of NSF and catalyst for wet chemistry route in collaboration with UTRC.	02/08		BeD-XRD fabrication underway while facilitate ID of coatings

***Denotes activities that will be postponed in the event the project is not fully funded.**