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QUARTERLY PROGRESS REPORT

Project Title: Metal Hydride Center of Excellence (MHCoE)

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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

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. The next step is to characterize thermodynamics, kinetics and cycle life to understand how useful this material is for reversible on-board storage.

To compare the characterization of $Ca(BH_4)_2$ as prepared by high-pressure synthesis (samples which also contain CaB_6 and CaH_2), we made an attempt to prepare pure material. By heating up a sample of $Ca(BH_4)_2(THF)_2$ in vacuum we successfully prepared pure, crystalline $Ca(BH_4)_2$ according to XRD. We are underway characterizing this sample in collaboration with our MHCoE partners and other collaborators: NMR & in-situ NMR (JPL,LLNL), in-situ XRD (U. Nevada), synchrotron (ESRF, France), catalyst screening (Intematix). Moreover, at Sandia we will perform PCT-measurements.

Removal of solvent from $Ca(BH_4)_2 \cdot 2THF$ results in various mixtures of α and β-polymorphs of $Ca(BH_4)_2$. These mixtures were studied by *in-situ* synchrotron powder diffraction, see Figure 1.

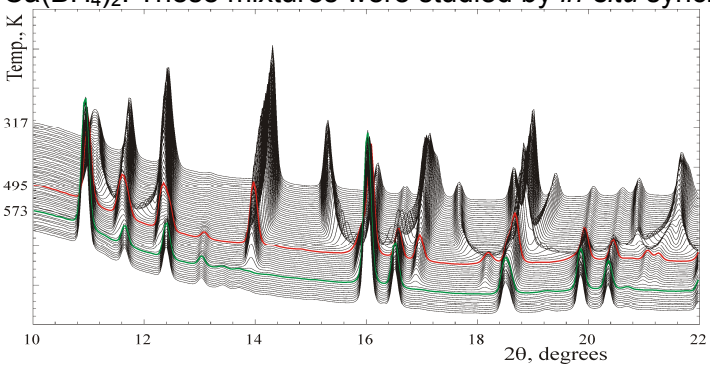

Figure 1. *In-situ* synchrotron powder diffraction data collected at 317-573K. Completion of the α-to-γ and γ-to-β transitions is highlighted in red and green, respectively.

The material α-$Ca(BH_4)_2$, crystallizes in the noncentrosymmetric *F*2*dd* space group, and contains an ordered BH_4^- anion. Upon increasing the temperature, the cell parameters *a* and *c* of the α-phase approach each other, and at 495K, the α-phase shows a second order transition into a tetragonal *I*-42*d* γ-phase, see structures in Figure 2. Moreover, the γ-phase converts into the β-phase at two different rates, and the conversion is completed at ~570K. The β-phase (space group $P4_2nm$) is 3.7-5.6% denser than the α and γ-phases, depending on the temperature. Structure is shown in Figure 3. The β phase remains stable during cooling to room temperature. It was observed that the β phase starts to slowly decompose at ~570K to unknown compounds yet to be identified. This conversion is completed at ~655K within 1 minute. These findings are supported by DSC and TGA data. The reaction mechanism has shown to be much more intriguing than anticipated and the stability of the different polymorphs will be important in the reversible reaction. We also performed *in-situ* synchrotron experiments in collaboration with GE (Zhao et al) at Brookhaven and this data is under evaluation.

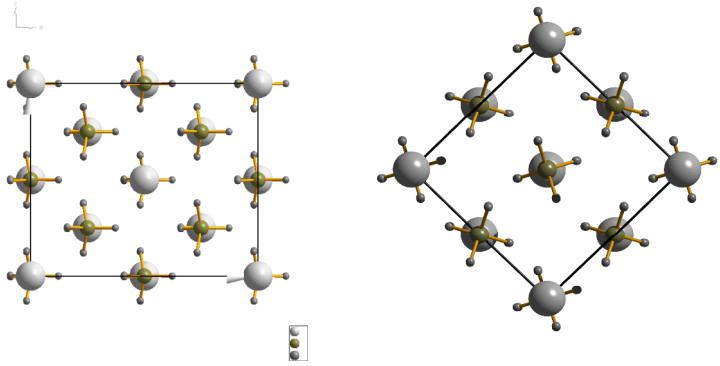

Figure 2. The α-polymorph (*F*2*dd*) (left) transforms into the γ-polymorph (I-42d) (right) at 160°C

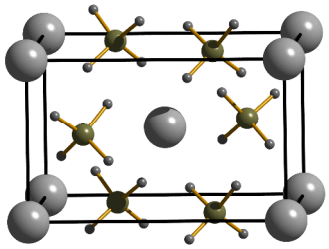

Figure 3. The β-polymorph (*P*4$_2$*nm*) does not transform into the γ-polymorph (I-42d) before decomposition. Instead, the γ-polymorph transforms into the β-polymorph.

Exploration of a new bialkali borohydride

A new bialkali borohydride of $NaK(BH_4)_2$ has been predicted to be almost stable by the Monte-Carlo technique (Eric Majzoub, UMSL) and was recently synthesized via a ball milling technique to introduce a potentially new candidate for a hydrogen storage material. The material was characterized using X-ray diffraction and Raman spectroscopic techniques. Raman spectroscopic measurements, see Figure 4, indicate the presence of strong B-H bending and stretching vibrations at 1265 cm^{-1} and 2320 cm^{-1}, respectively-- values intermediate to the B-H vibrations of KBH_4 and $NaBH_4$. X-ray diffraction analysis of the material present new diffraction peaks at Bragg angles of 24, 27.5 and 39.2 to indicate the formation a new crystal phase most likely the result of the formation of the new product. 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 $NaBH_4$.

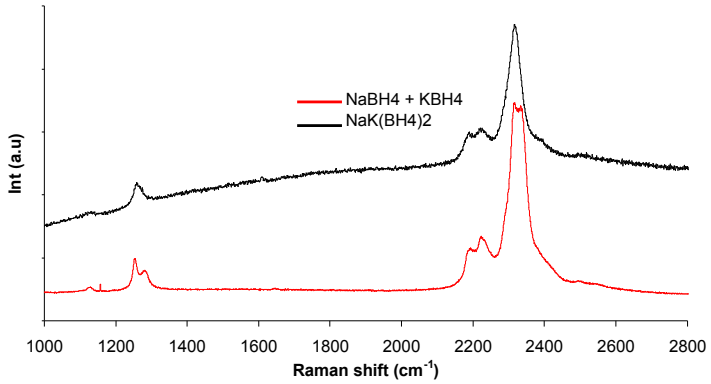

Figure 4. Raman spectra of a sample mixture of $NaBH_4$ and KBH_4 ($NaBH_4$ + KBH_4), and the new hydride, $NaK(BH_4)_2$. The unique spectral shape of the B-H vibrational peaks in $NaK(BH_4)_2$ indicates that it contains a different crystal feature from a mere mixture of the starting materials.

Investigation of thin film samples of Li-B-Mg-Ti and Ca-B

Raman spectra from thin film samples of Li-B-Mg-Ti composite on Si were taken and compared with similarly prepared samples which were hydrided at 450psi, 200ºC for 90 minutes. The hydrided samples show low wavenumber peaks indicating there may have been formation of a hydride compound. We are also exploring thin films of Ca-B multilayers with catalysts in between to find the best catalyst for hydrogenation of these films. Work is ongoing, and is being done in collaboration with Darshan Kundaliya, at Intematix.

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 metal 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. XRD analysis was done on the 30 samples. Up until now, two high pressure experiments were done on the Sc samples (No. 1-12) at 400ºC and 15000 psig for about 24 hours. Initial TG/DSC studies are showing formation of $Ca(BH_4)_2$ and $LiBH_4$ and not the transition metal borohydrides we had anticipated. The new phases could not be detected by XRD analysis so the reaction time was increased to 72 hours. The longer reaction time resulted in new white crystalline products in reactants containing MgB_2 and MnB_2 or ScB_2 with $TiCl_3/NiCl_2$ as catalysts. From the TGA/DSC studies on the Mg-Sc-B-H and Mg-Mn-B-H systems we observed that the product contains new hydrogen containing materials, likely the anticipated Mg-Sc and Mg-Mn borohydrides. As can be seen in Figure 5, hydrogen is released in a broad interval between 300-400ºC upon phase transitions which has to be investigated further. XRD and FTIR analysis is underway to confirm reaction products.

a) b)

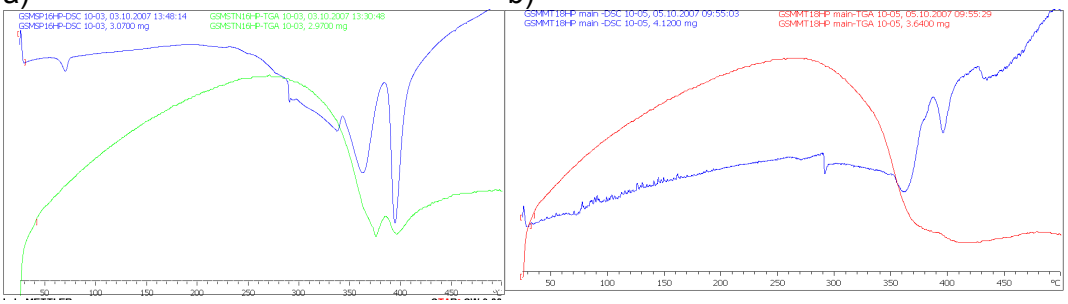

Figure 5. DSC and TGA curves of samples: a) MgB_2 + ScB_2 + catalysts TGA (green), DSC (blue) b) MgB_2 + MnB_2 + catalysts TGA (red), DSC (blue)

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 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 continuing exploring new systems and as reported recently found new compounds in the ternary Ge and Mn systems. Reproduction and analysis is in progress, but focus was not on this group of material during this quarter because of limited staff resources.

Monte Carlo - DFT structure prediction for new materials searching:

We have submitted a paper to Physical Review B titled "Prototype Electrostatic Ground-State (PEGS) Approach to Predicting Crystal Structures of Ionic Compounds: Application to Hydrogen Storage Materials." The publication summarizes the Monte Carlo method (PEGS) employed and highlights the results we have obtained on alanate-based hydrides, including both tetrahydrides and hexahydrides. The method finds ground state or observed crystal structures for alanates in over 80% of the compounds searched. In some cases, notably LiAlH4, the method finds an undiscovered ground state, which is destabilized by vibrational contributions at finite temperature, where the observed structure obtains a lower total free energy.

Applying the PEGS method to mixed cation borohydrides resulted in the prediction of two structures of sufficiently low total energy which suggested they may be stable. We have prepared these materials and currently characterizing their structure and thermal properties. We are preparing a publication to highlight the formation of a brand-new structure, predicted by theory. We continue our search for bi-alkali borohydride systems, including but not limited to, Li-Mg, Li-Ca, Li-Na, Li-K, Na-Mg, Na-Ca, Na-K, K-Mg, K-Ca. The success rate for prediction of ground-state structures in borohydrides is lower than alanates. We believe that vibrational entropy may be more important in the borohydrides and may be the cause of this discrepancy. Solving this problem for the borohydrides will likely be very important for applying the PEGS method to nanoparticle complex hydrides, which is a planned part of the program for MHCOE.

We have used the PEGS method to find a low energy structure for $Mg(BH_4)_2$. This structure is currently of interest and synthesis and structural investigations of this compound have been carried out by General Electric Co. and Yvon, and co-workers. Experimental studies of both

groups find a common structure for both the room temperature and elevated temperature structures, which contain 30 and 64 formula units per conventional cell, respectively. $Ca(BH_4)_2$, by comparison has only 2 formula units in the primitive cell at room temperature. The complicated unit cell of magnesium borohydride is fascinating and unexpected. The PEGS method finds a 4 formula unit structure, which is lower in total energy at T=0K, than the experimental structures, and has nearly identical local order to the experimental structures. Vibrational calculations for the experimentally observed structures are time consuming to perform due to the size of the unit cells and have not been calculated. A publication is in preparation discussing the PEGS method applied to magnesium borohydride.

New materials search in Si/Ge-H based systems:

We previously reported calculations of potential structures in the Na-Si-H, Li-Si-H, K-Si-H, Na-Ge-H, Li-Ge-H, and K-Ge-H systems. The calculations indicate that some stable hydrided compounds may be prepared in the system consisting of SiH_6 and/or GeH_6 anions. Experimental attempts to prepare these materials have met with some success, but the results are not conclusive. Experimental work is ongoing.

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 fourth quarter of FY07 (Jul-Sep 2007), and will focus primarily on efforts to achieve three major project milestones. These are: (1) design and fabrication of instrumentation to establish the HTS capability, (2) integration and testing of the overarching software architecture developed to efficiently manage the HTS system, and (3) Sandia strategies for implementing the HTS approach.

Micro-reactor array design, fabrication, and diagnostics

The development of the combinatorial HTS concept has progressed markedly well in the 12 months since DOE approved this task. We have taken a fairly aggressive approach to establishing method credibility by making use of a small Parr reactor operating at 2 kpsi hydrogen pressure to test operational concepts, validate diagnostics, and engineer methods to interface hotplate dies with support and control fixtures. In parallel, we have designed a high pressure vessel capable of operating at or above 20 kpsi hydrogen pressure that is large enough to hold a first-generation micro-reactor array assembly with 15 sample hotplates and 5 TCDs (vessel footprint of order 7 inches outside diameter with minimal plumbing and electrical requirements). We have also made progress on the design and fabrication of second generation hotplates which will be more mechanically stable than the current suspended silicon nitride planar membrane technology, as well as provide for better thermal contact between heater and sample material thus improving the efficiency of heat transfer in the system.

With the aforementioned fully instrumented 2 kpsi pressure vessel, equipped with a four element sample array and single TCD, we demonstrated the sensitivity and utility of the in-situ diagnostics, as well as performed proof of concept experiments thereby satisfying a key project milestone. We have also made significant progress on the design of a 20 kpsi vessel, which we fully expect to have fabricated and tested for manned operation before the end of calendar year 2007. Illustrated in 6 is a solid rendition of this vessel. It will be constructed of high yield stress, heat-treated A286 stainless steel. Electrical power lines are passed into the chamber using two commercial 10-pin, pressure rated feedthroughs (45 kpsi) mounted into high pressure Autoclave Engineers fittings. Gas inlet and outlet fittings are also Autoclave type. A PC board capable of holding 15 sample hotplates and 3 TCDs (also pictured in 6 showing three flow rails with 5 sample hotplates per rail) will be sandwiched between top and bottom flanges of the vessel and sealed using a commercial metal “C” seal. We are also considering a higher throughput concept board (not pictured) that has five flow rails with 3 sample hotplates and 1 TCD hotplate per rail. This configuration will provide for greater experimental throughput (multiplexing 5 flow rails per run versus 3).

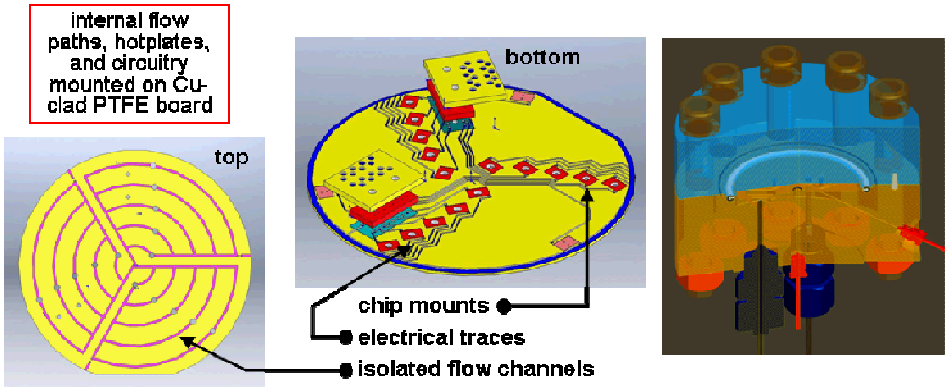

Figure 6. Schematic diagrams of PCB assembly (left) and solid rendition of 20 kpsi vessel (right).

The high pressure vessel is compact and portable, so that precursor powders can be loaded into the hotplates in a glove box, the vessel sealed, and then transported to another location where the flow system and gas compressor are housed. We have nearly completed the design of this vessel. Numerical finite element analysis has been performed to determine areas of high mechanical stress within the part, and results used to improve the design such that a safety factor of 3.5 is expected to be achieved at 20 kpsi hydrogen pressure. What remains is to finalize the PC board and associated internal fixtures (not pictured), then send the design out to bid and then fabrication.

Work in the final quarter of FY07 also focused on design, fabrication, and testing of novel silicon, high-temperature hotplate structures. We had discovered early in FY07 that the suspended silicon nitride membrane devices had certain deficiencies that needed to be remedied if we were going to achieve operating conditions with sample temperatures approaching 800 °C and 20 kpsi hydrogen pressure. The second generation hotplate devices are constructed from highly doped silicon on insulator (SOI) wafers to form three dimensional heating structures, as shown in the SEM images of 7. Plasma etching processes are used to selectively remove silicon and form the joule heating and three dimensional powder containment structures. The top layer of the SOI wafer consists of 10 microns of single crystal silicon, and forms the device's joule heating layer. Electrical contact to this heating layer will be made using bond pads formed from silicon doped aluminum. The backside silicon will be etched to form a variety of powder containment structures, ranging from thin containment walls to internal heat-spreading features. A buried layer of silicon dioxide will from a membrane between the two layers to prevent accidental electrical conduction from the bond pads to the powders or the interface board.

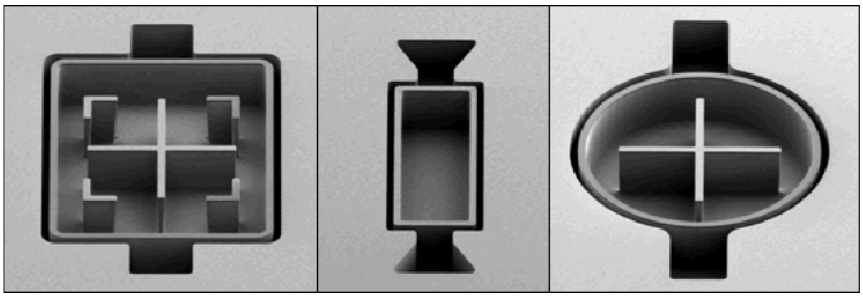

Figure 7. SEM images of design concepts for second generation hotplate illustrating 3-D heating structures and suspended sample well.

Devices were fabricated in parallel at both an external foundry and at Sandia's MESA facility. Devices from the external foundry were completed first, while fabrication work at Sandia is still ongoing into FY08. Completed wafers hold nine different device iterations with varying bridge shapes, tab lengths, and 3D heat-spreading structures. Figure 8 shows the nine different device iterations.

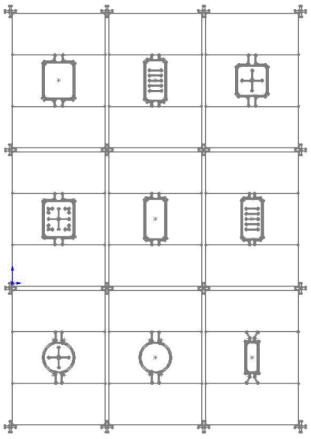

Figure 8. Schematic illustration of the design mask for second generation hotplates, internal 3D heat-spreading structures can be seen in greater detail in the SEM images of Figure 7.

Device testing focused on establishing the upper limits of device performance, and determining the approximate relationship between voltage and temperature for various device iterations. Many conductors have a linear relationship between the temperature of the conductor and its resistance: this relationship is known as the temperature coefficient of resistance (TCR). The TCR for doped silicon is nonlinear, and varies with temperature, making it difficult to derive the average temperature of the device by monitoring resistance. To address this issue, thermal imaging was used to derive the relationship between average device temperature and the resistance. Figure 9 shows an image of a device heated by a 9V DC potential, exhibiting an average temperature of around 400 °C. In application *sample* temperatures, which lag the

device temperature, will be calibrated against solids with known melting points (such as In, Sn, Zn, and Al) subjected to various voltage ramp rates and overpressure conditions. We expect to derive a fairly robust relationship between hotplate voltage and actual sample temperature.

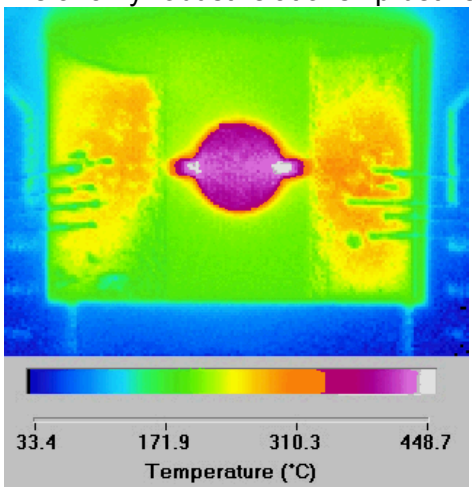

Figure 9. Thermal imaging of second generation hotplate under power at 9V DC showing good thermal isolation of sample well from die body, as well as local hotspots near tabs.

As testing has progressed, we have also identified the primary failure mechanism for these devices which appears to be the plastic deformation, and ultimate stress failure, of the bridge tabs. Figure 10 shows a SEM image of a deformed bridge after it was heated and cooled; the cause of the deformation is that silicon changes from a brittle to a ductile material at ~600 °C. The site of the bridge deformation corresponds with a localized hotspot, shown by IR imaging in the previous figure, on the bridge near the paddle. The plastic deformation of the bridge tabs allows for stress relief of the suspended structure (which is good and likely makes the device more robust), however continued heating at the point of deformation will ultimately cause material failure. At this point it is unclear whether or not daily operations of the HTS will require such excessive device heating but this issue may be addressed in the third generation hotplate design.

In addition to device fabrication and testing, we developed a computational fluid dynamics (CFD) model to simulate the flow of desorbed hydrogen through the microfluidic channels that are milled into the PC board fixture which supports the hotplates. The goal of this model is to optimally design the flow channels as well as develop appropriate flow conditions to minimize holdup of desorbed hydrogen. The CFD approach provides an efficient means to visualize desorbed gases in the fixture as well as rapidly test prototypical configurations. Figure 11 shows a snapshot in time of a flow simulation where 0.25 µg of hydrogen is desorbed over 0.5 sec period. This simulation reveals that the cavity containing metal hydride serves as a stagnation zone trapping the desorbed hydrogen and causing holdup which bleeds out over

Figure 10. SEM image illustrating out of plane movement of bridge and paddle during heating treatment. This ductile transformation of the silicon relieves stress in the suspended structure.

tens of seconds into the bulk channel flow. Efforts are underway to model different well configurations and flow regimes to maximize the injection of hydrogen into the flow channels.

Figure 11. CFD simulation illustrating hydrogen holdup in sample well cavity. CFD simulations will be used to optimize microfluidic behavior of PC board.

Finally, another major activity initiated in the first quarter of FY07, which was finally resolved in this last quarter, involved navigating the Sandia Environmental Safety and Health bureaucracy to establish operational guidelines for this new activity. Pressure Safety and Site Operations experts were consulted to gain approval to construct and operate this new capability in a manned environment. This will enable the experiment to be conducted outside a concrete-reinforced test cell (coveted space within Sandia that could potentially limit free access to the system and thereby hinder progress). The experimental plan, vessel design, engineering controls, and administrative controls developed for this experiment were successfully amended to the laboratory Standard Operating Procedures (SOP) document thereby clearing the way for full, manned operation in the CRF laboratories.

C *e the HTS system*

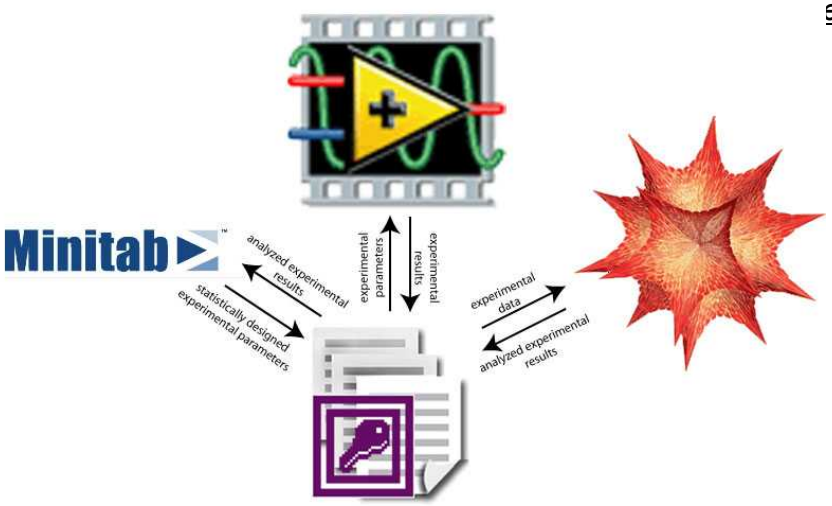

Figure 12. Schematic illustrating connectivity between the relational database, which represents the entire body of HTS experiments, and several applications used to design and execute experiments, as well as analyze the results.

An important part of the combinatorial method is to rapidly acquire, analyze, and manage a very large amount of data emanating from multiple analog channels, especially if we scale to 30 or more sample hotplates in the second generation of the 20 kpsi vessel. In the final quarter of FY07 we focused on developing the requisite software architecture to facilitate experimental design, automate and control the physical devices to execute the experiments, store the data, and manipulate and analyze results. The operational concept is founded on a relational database model of the experimental system which we developed using traditional methods of database design within the Microsoft Access environment. Applications such as Minitab, LabView, and Mathematica communicate with the database through SQL queries and are respectively used to design, execute, and analyze an HTS experiment. The application-to-database connectivity is illustrated schematically in Figure 12.

Minitab is a software tool designed to perform statistical functions and is often used in conjunction with the implementation of Six Sigma, CMMI and other statistics-based process improvement methods (Sandia holds a multi-seat site license to this software). Minitab is SQL-92 compliant and we use several features of this software to design experiments (primarily factorial design) as well as resolve statistical correlations between experimental sets, analyze variance, and track the quality of our various calibration methods. Essentially, experimental variability is captured within Minitab, an efficient design space is then produced with the appropriate number of variants and replicates, and the output from this process in the form of

detailed instruction sets to prepare material compositions and execute experiments is written back into the database.

LabView is used to build software for experimental control, automation, and data acquisition. We acquired a database connectivity toolset from National Instruments which is used to query the database for the appropriate instruction sets (e.g. flow rate, vessel pressure, hotplate controls). The software then executes experiments with little user intervention and the database is updated with raw data streaming from the data acquisition platform.

Mathematica is a powerful analysis and data visualization tool which we use to extract the raw experimental data from the database, apply the appropriate manipulation and analysis methods, and then write the results back into the database thus completing the application-to-database connectivity. At any point in this process, the user can search the database and draw statistically relevant correlations, for example, between an experimental condition/observation and the analyzed result. We envision making this database available to MHCoE partners in future if sufficient interest develops.

Strategy for implementing high throughput combinatorial approach

A statistically-based approach using Design of Experiments methodology (making use of the Minitab software as discussed in the previous section) will be used to generate possible sample formulations from promising stoichiometries, which have been identified by theoretical predictions (a separate MHCoE activity). We will initially target alkali and alkaline earth metal-based borohydrides. Currently Sandia (as well as other Center partners) is theoretically evaluating 7 of the 10 possible $A_xB_y(BH_4)_z$ combinations formed from the elements (A, B = Li, Na, Mg, K, Ca). These calculations are searching the phase-pure space for a material with the potential to meet DOE program targets. In order to efficiently survey the domain encompassing the 7 possible pure-phase borohydrides currently under theoretical scrutiny, as well as mixtures thereof, we will use complex mixing rules that are best represented on a phase-like diagram. Illustrated in Figure 13 is a triangle that looks to be a phase-diagram but simply represent a means to apportion mixture fractions of hydride and borohydride precursors in a systematic way. At the vertex of the triangle is the pure precursor. Moving along the sides of the triangle will create compositions of the $A_xB_y(BH_4)_z$ space with the potential to synthesize phase-pure material of various stoichiometry (e.g., $Li_2NaB_3H_{12}$, $LiNa_2B_3H_{12}$, and/or $LiNaB_2H_8$ which are stable structures identified by theory) or mixtures of the same. Moving into the interior will potentially create mixtures of bi-alkali compounds with different A and B cations in various proportions or perhaps tri-alkali compounds.

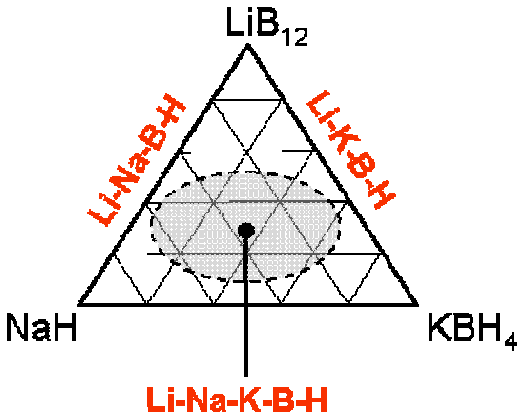

Figure 13. Triangle diagram illustrating method from which precursor-mixing rules will be derived and graphically displayed.

Ultimately kinetics will govern what reactions take place, but our belief is that the combinatorial experiments executed with the HTS approach will result in a thorough survey of the $A_xB_y(BH_4)_z$ system, with (A, B = Li, Na, Mg, K, Ca). It has yet to be determined what information will be presented in the phase-like diagrams, but presumably it will be linked to one or more performance metrics such as peak desorption temperature, hydrogen capacity, and/or total enthalpy observed during the desorption process. It is also anticipated that the exact mixture composition for any particular point in the diagram will remain unknown unless there is sufficient reason to resolve it based on observed hydrogenation and dehydrogenation behavior. In such cases XRD or other more sophisticated chemical analysis will be employed.

Subtask 2.3 – MHCoE Project C: Amides/Imides Storage Materials
Effort on hold, work on Li/Mg material suspended.

Subtask 2.4 – MHCoE Project E: Engineering Analysis and Design
Effort on hold

Subtask 2.5 – Cross-cutting Theory and Contamination Studies

2.5.1 – Cross-cutting Theory

This task is focused on theoretical issues that have impacts across the center's various projects. Results applicable only to individual projects are described within that project's report. The MHCOE Theory Group (TG) is coordinating its efforts to make the best use of resources,

maintain effective communication, and take advantage of synergies and complimentary expertise among the different organizations. The Theory Group continued its ongoing series of discussions this quarter concerning the kinetics of $MAlH_4$ systems. Prof. Bruce Clemens (Stanford) is now regularly participating in these calls, providing an experimental perspective on issues relating to nanoscale materials effects. Dr. Suzanne Opalka (UTRC) joined the TG and is representing the project concerning catalyzed nano-frameworks. Group conference calls were held 8/1/07 and 9/10/07.

Reaction kinetics.

The group is continuing to focus its efforts concerning reaction kinetics on the factors limiting reversibility in the series $MAlH_4$ (M = Li, Na, K). The reactions of concern are:

$$MAlH_4 \leftrightarrow 1/3\ M_3AlH_6 + 2/3\ Al + H_2 \quad (1)$$
$$M_3AlH_6 \rightarrow 3\ MH + Al + 3/2\ H_2 \quad (2)$$

This quarter computations of the activation barriers for physisorption and chemisorption of H_2O on MH surfaces were completed by the group at U. Pitt. The results show that water weakly physisorbs on all three surfaces and that a barrier exists to dissociative chemisorption, i.e.,

$$MH + H_2O \rightarrow OH(surface) + H_2(surface) \quad (3)$$

The adsorbed H_2 is weakly bound and would be released to the gas phase at any finite temperature (calculations were performed at 0 K). The activation barriers are 23.0, 13.8, and 18.4 kJ/mol for LiH(100), NaH(100), and KH(100) respectively, including zero-point energy corrections. These low barriers suggest a high reaction rate at realistic temperatures. For example, preliminary calculations using simple transition-state theory the turnover frequency at 300 K for reaction (3) indicate values of $9.9x10^8$ site^{-1} s^{-1}, $4.0x10^{10}$ site^{-1} s^{-1}, and $6.3x10^9$ site^{-1} s^{-1} for LiH(100), NaH(100), and KH(100) respectively. These results indicate that water reacts very rapidly with all three surfaces and that, although the three activation barriers are not the same, all three are small. Therefore, we do not believe that differences in the rate constants for reaction (3) are sufficient to explain the differences in reversibility behavior for the three $MAlH_4$ systems.

In light of these results, we are considering two alternative explanations. First, the lattice constants of the three hydrides compared with their corresponding hydroxides are not the same. A simple comparison of the a, b, and c lattice constants indicates that the mismatch is smallest for LiH vs LiOH (~ 0.4 Å in each case) vs the Na and K cases in which the differences are as large as 1.95 Å. This suggests that if a hydroxide layer forms on a NaH or KH surface due to contamination, poisoning may not occur because cracks that form as a result of the lattice mismatch enable H_2 to penetrate the layer and react with the underlying hydride. In contrast, the relatively close match in the LiH case may result in an impenetrable barrier and thus no reversibility. We note, however, that rotation of the MH and MOH lattices with respect to each other can bring the two materials into better atomic register with each other, so this result is not definitive. We are exploring possible differences in lattice energies, however, using the bond-counting method developed by Bruce Clemens to estimate surface energies.

A second possible explanation does not involve surfaces at all, namely, that in order for reaction (2) to be reversible, the heat of reaction must be sufficient to melt the material, creating a liquid phase that wets the heterogeneous Al phase so that further (presumably rapid) reaction can occur. This is thought to be a requirement for solid-state oxidation reactions, such as those involved in combustion-synthesis processes used to produce various refractory materials (see for example the work of Arvind Varma at Purdue University). The melting points of LiH, NaH,

and KH are 689 °C, 800 °C, and 360 °C, respectively, indicating that the most reversible system, $KAlH_4$ is also the one that most readily forms a liquid phase upon recharging with H_2. It is also interesting to note that the melting points of LiOH, NaOH, and KOH are 450–470 °C, 318 °C, and 360 °C, respectively. An alternative explanation for the lack of Li_3AlH_6 reversibility, therefore, is that formation of a liquid hydroxide layer is necessary to achieve a reasonable H_2 diffusion rates to the underlying MH solid. The low melting points of NaOH and KOH enable this, but the higher melting point of LiOH prohibits it.

We are investigating both alternative mechanisms at this time. A manuscript describing the DFT results for MH surfaces is currently in preparation and we anticipate submitting it for publication in *J. Phys. Chem. B* next quarter.

Nanoscale effects. The TG devoted substantial portions of the conference calls this quarter to a discussion of nanoscale effects and ways that the TG could contribute to understanding how these could be manipulated to yield improved materials for hydrogen storage. Some members of the TG are either already working in this area or have addressed nanoscale effects as part of their research in other areas. In particular, Suzanne Opalka (UTRC) is employing force field and DFT calculations to examine interactions between hydride materials and porous supports, Duane Johnson's group has performed DFT calculations using VASP to predict geometries for transition-metal clusters, and Clemens and Sholl have developed a simple bond-counting model for estimating surface energies. Calphad calculations performed by U. Kattner (NIST) of the TG can also be adapted to model nanoscale systems.This quarter's discussions were motivated in part by intriguing results published by de Jongh et al. suggesting that very small Mg cluster (< 20 atoms) are destabilized relative to the bulk; preliminary experimental results presented at the Hawaii meeting (Oct. 2006) appeared to support this calculations. However, at the hydrogen-storage Gordon conference this summer, de Jongh indicated that these results were not due to pure Mg as previously reported. Thus, this prediction remains to be confirmed by experiment. The Goddard group (Caltech) recently published new parameters for their ReaxFF reactive force field applicable to MgH_2 systems (*J. Phys. Chem. A*, **109** (2005), 851). They predict a relationship between grain size and MgH_2 heat of formation. The results suggest that Mg particles formed by ball milling in the 20 – 100 nm range are not sufficiently small to exhibit nanoscale effects and confirm the notion that nanoporous materials for synthesizing small clusters will be necessary to take advantage of nanoscale effects. ReaxFF offers a potential route to predicting stability of clusters within matrices, and could perhaps be used in conjunction with quantum-chemistry or DFT calculations to identify specific clusters sizes or compositions that would be favorable for hydrogen storage. K. Johnson (U. Pitt.) has an existing collaboration with the Goddard group involving ReaxFF and has the code running in his group. He will contact them to determine the range of materials for which this tool is applicable and report back to the TG, allowing the TG to determine whether this will be a useful tool for examining cluster-scaffold interactions.

2.5.2 – Study of Surface Contamination and Catalysts on Hydrogen Storage Materials

Effort on hold.

PLANS FOR NEXT QUARTER

Subtask 2.1 – MHCoE Project B: Complex Anionic Materials

Subtask 2.1.1 – Metal Borohydrides

We have moved our high-pressure facility to a new location and we are now able to perform sintering experiments again. This caused delays in our work on synthesis and re-hydriding materials, but we are now back on track. We will aim at showing full reversibility of $Ca(BH_4)_2$ at lower H_2-pressures than 70MPa. We will prepare a series of samples with different catalysts and investigate the features with XRD, NMR, *in-situ* NMR, Raman, *in-situ* Raman and TGA/DSC. The sample which show the best features, with respect to product yield and desorption temperature, will be investigated by the PCT-instrument. Further, we will also take another approach and prepare $Ca(BH_4)_2$ from an Aldrich sample by removing the solvent and then mill the sample with catalysts before measuring PCT-isotherms at 100bar and required temperatures.

In collaboration with our partner GE (Zhao et al), we will aim at re-hydriding the decomposition products of magnesium borohydride.

In collaboration with Dr. Martin Dornheim, GKSS, Germany, we will perform in-situ Raman measurements on their destabilized calcium borohydride system.

We will summarize our findings regarding the 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 2.1.2 – New Hydrogen Storage Materials

We will continue our experimental efforts on screening for new materials. We will also reproduce and characterize the newly discovered phases in the ternary Ge and Mn systems. 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.

Subtask 2.2 – Exploratory Routes to Materials Discovery

Two main tasks will be undertaken in the first quarter FY08, (1) finalize material testing and designs of the high pressure vessel and PC board; fabricate and complete installation, (2) embark on the investigation of the Li-Na-K-B-H system using the 2 kpsi capability and ultimately transitioning to the 20 kpsi reactor.

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

- Complete and submit journal article describing DFT modeling of MH surfaces
- Assess applicability of ReaxFF to modeling nanoscale phenomena relevant to hydrogen storage
- Identify area related to nanoscale phenomena where the TG can make a significant contribution to MHCOE efforts and initiate computations.
- Initiate computational effort at Sandia in support of the alane project.

Subtask 2.4.2 - Study of Surface Contamination and Catalysts on Hydrogen Storage Materials

Effort on hold

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:

R. Bastasz, W. P. Ellis, R. Stumpf, and J. A. Whaley, "Effect of hydrogen on the stability of Ti on an Al surface", presented at the AVS 53rd Annual Symposium, San Francisco, November 13, 2006.

E. Rönnebro, E. Majzoub, "Crystal structure, Raman Spectroscopy and ab-initio calculations of a new bialkali alanate K_2LiAlH_6", J. Physical Chemistry B, 110(51), 2006, 25686-25691.

E. Majzoub, "Global optimization of Complex Hydride Crystal Structures", presented at the International Symposium on Metal Hydrogen Systems, Maui HI, October 3, 2006.

E. Majzoub, "Predicting New Hydrides: Global optimization of Complex Hydride Crystal Structures", presented at the NEDO Workshop on Advanced Hydrides, Yokohama, Japan, October 24, 2006.

E. Majzoub, "Enthalpy Estimates from Global optimization of Complex Hydride Crystal Structures", presented at the MRS Fall Meeting, Boston MA, November 30, 2006.

E. Rönnebro, "On the Challenge to Synthesize New Metal Hydrides and Potential for High-Pressure Materials", Invited presentation, Gordon Research Conferences, Hydrogen-Metal Systems, Colby College, Waterville, ME, July 9, 2007.

E. Rönnebro, "Synthesis and Structural Characterization of New Metal Hydrides and Borohydrides", Invited presentation, Meeting of the American Crystallographic Association, Salt Lake City, Utah, July 24, 2007.

E. Rönnebro, E. Majzoub, "Discovery and Development of Metal Borohydrides", presented at the IEA HIA Task 22 Experts workshop, Egmond an Zee, Netherlands, September 4-7, 2007.

E. Rönnebro, "Synthesis and Characterization of New Metal Hydrides and Borohydrides", Invited presentation at University of Geneva, Switzerland, September 10, 2007.

E. Rönnebro, "Synthesis and Characterization of New Metal Hydrides and Borohydrides", Invited presentation at University of Göttingen, Germany, September 12, 2007.

E. Rönnebro, "Chemical Bonding in Complex Metal Hydrides", Invited tutorial lecture at University of Göttingen, Germany, September 13, 2007.

E. Rönnebro, "Synthesis and Characterization of New Metal Hydrides and Borohydrides", Invited presentation at GKSS, Germany, September 18, 2007.

E. Rönnebro, "Synthesis and Characterization of New Metal Hydrides and Borohydrides", Invited presentation at Stockholm University, Sweden, September 27, 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 in contribution.

WEBSITES:

Password protected collaborative site (MHCoE QuickPlace):
https://sierra-nk.son.sandia.gov/QuickPlace/mhcoe/Main.nsf

Public website: http://www.ca.sandia.gov/MHCoE

COLLABORATIONS:

- Sandia is leading the team effort among the MHCoE partners of Project B-Complex Anionic Materials.
- We are working with U. Utah (Fang) on materials discovery using reactive milling in these systems: Mg-Ti-H and Li-Ti-H
- We are working with SRNL (R. Zidan) as we investigate melt processing in the HTS activity.
- A student from U. Hawaii (Jensen) has been visiting during July-October to utilize SNL's high-pressure technique to re-hydride transition metal borohydrides.
- We will continue collaborating with Klaus Yvon and Ravadan Cerny of U. Geneva, Switzerland, on new materials.
- Initiated collaborations with Martin Dornheim of GKSS, Germany, on destabilized calcium borohydride.

- Initiated collaborations with Dag Noréus and Karim Kadir at Stockholm University on Mg-containing materials.

- We have contacted Dr. Peter Edwards who is Professor and Head of Inorganic Chemistry at the University of Oxford, England; and is currently Coordinator of the UK Sustainable Hydrogen Energy Consortium. Thus far, a teleconference has been conducted and information exchanged detailing the MHCoE activities. In future, we anticipate visiting with Professor Edwards and perhaps negotiating a cooperative agreement between US and UK hydrogen storage activities.

- 10 members of the MHCoE met with the Berkeley Hydrogen Storage group (Jeff Long, Paul Alivasatos) on March 13, 2007. We discussed nano-approaches to improving the kinetics and thermodynamics of new materials. We agreed to collaborate as appropriate on developing metal hydride nanoparticle superlattices.

FY 2007 MILESTONE STATUS TABLE

FY 2007 Milestones/Deliverables	Planned Completion	Actual Completion	Comments
Subtask 2.1: MHCoE Project B: Complex Anionic Materials			
Subtask 2.1.1: Metal borohydrides			
Synthesize high-capacity borohydrides in the solid state guided by theory (1.2.1 Milestone Chart)	05/07		On track
Prepare higher yields of $Ca(BH_4)_2$ and $Mg(BH_4)_2$ in the solid state (1.2.2 Milestone Chart)	(1) 12/06 (2) 9/07 (new goal set for CaBH)	12/06 -- Delayed to 03/08 due to moving of experimental equipment	(1) Higher yield prepared on CaBH -- 75-85% yield obtained. No-go decision on MgBH. (2) New milestone set to continue exploring reaction route to obtain 100% yield on CaBH. -- Delayed to 03/08 due to moving of experimental equipment
Characterize hydrogen sorption properties and explore reversibility (1.2.3 Milestone Chart)	05/07		Delayed to 03/08 due to moving of experimental equipment
Investigate structural features with XRD, synchrotron and/or neutron diffraction, FTIR and Raman (1.2.4 Milestone Chart)	03/07	07/07 Paper in preparation	Deferred to 7/07 due to beam-time schedule at ESRF. Synchrotron measurements have been completed; analysis in route to SNL.
Generating stable structures of mixed alkali borohydrides with compositions $AB_2C_4X_{16}$, and ABC_3X_{12} using the Monte Carlo method (1.3.1 Milestone Chart)	02/07	02/07	Identified 2 potentially stable mixed cation borohydrides

FY 2007 Milestones/Deliverables	Planned Completion	Actual Completion	Comments
Calculate approximate compound stabilities and decomposition enthalpies based on the structures of the mixed borohydrides (1.3.2 Milestone Chart)	05/07	08/07	Calculations predict NaK borohydride would be stable, experimentally confirmed metastability
Solution based synthesis of solvent free metal borohydrides (1.4.1 Milestone Chart)	03/07		Milestone delayed due to lack of funding
Solution based synthesis of mixed borohydrides ($MM'(BH_4)_x(solv)_y$) (1.4.2 Milestone Chart)	09/07	12/06	Task completed, approach discontinued
Subtask 2.1.2: New Hydrogen Storage Materials			
Synthesize new complex metal hydrides in the ternary Si-system (2.1.1 Milestone Chart)	12/06	12/06	No-go on the Si-system. New hydrides had too low of a hydrogen content.
Investigate structural features with XRD, synchrotron and/or neutron diffraction, FTIR and Raman (2.2.4 Milestone Chart)	03/07		Task ongoing,
Characterize hydrogen sorption properties of potential candidates (2.2.5 Milestone Chart)	05/07		Work paused, awaiting more materials
Discover new complex metal hydrides guided by theory (2.3.1 Milestone Chart)	09/07	Ongoing	New hydride discovered in the Ge-system.
Subtask 2.2 : Exploratory Routes to Materials Discovery			
Design and fabricate microreactor with 2x5 element μHP array, validate in situ diagnostics (differential calorimetry and thermal conductivity)	12/06	1/07	Used 2 kpsi chamber to validate diagnostics.
Proof of principle experiments with known hydrides, choose a well characterized binary and complex metal hydride system	2/07	7/07	Used 2 kpsi chamber with molybdenum oxide conductor hotplate.
Formulate and acquire initial matrix of complex hydride precursor materials for FY07 combinatorial activities	3/07	8/07	Chemical inventory includes material precursors needed to

FY 2007 Milestones/Deliverables	Planned Completion	Actual Completion	Comments
			investigate the Li-Na-K-B-H system.
Acquire the software tools for combinatorial infrastructure	6/07	9/07	Software architecture needed to manage combinatorial system is in place and tested (see text).
Melt process and characterize simple Mg or Ca borohydrides	9/07		Change of scope from synthesis of Ca borohydrides to searching for effective catalysts.
Subtask 2.3: MHCoE Project C: Amides/Imides			
Complete PCT measurements confirming reversible adsorption, wt %	2/07		Deferred due to budget cuts
Complete theoretical assessment of enabling Li/Mg Amide	12/06	12/06	Completed
Complete theoretical Assessment of thermally enabling $LiNH_2$ /Li_3AlH_6	4/07		Deferred due to budget cuts
Extended cycling studies of $LiNH_2$/Li_3AlH_6	7/07		Deferred due to budget cuts
Complete PCT measurements of catalytically modified $LiNH_2$ /Li_3AlH_6	9/07		Deferred due to budget cuts
Subtask 2.4: Engineering Modeling			
Subtask 2.4.1 - Reaction Kinetics Model			
Develop generalized formulations for reaction kinetics	12/06		Deferred due to budget cuts
Subtask 2.4.2 - Engineering Modeling of Materials Requirements			
Determine material properties that meet dynamic target for loading hydride bed	3/07		Deferred due to budget cuts
Determine material properties and heat demand to meet fuel cell stack demand profiles	6/07		Deferred due to budget cuts
Subtask 2.4.3 - Engineering Design Study			
Model alternative heat transfer designs including fins	9/07		Deferred due to budget cuts

FY 2007 Milestones/Deliverables	Planned Completion	Actual Completion	Comments
Subtask 2.5: Fundamental Mechanisms and Modeling			
Subtask 2.5.2 - Develop and document a sample handling and measurement procedure for examining the surface composition of candidate storage materials using low-energy ion beam analysis.	12/06	12/06	Completed
Complete surface characterization of selected candidate storage material specimens	~~3/07~~ 9/07	09/07	Completed study of H adsorption on Mg(0001) surface
Complete kinetics study of the effects of a selected impurity species on hydrogen adsorption/desorption for a candidate storage material	9/07		Deferred to next FY due to budget cuts