

IV.A.1f Development of Metal Hydrides at Sandia National Laboratories

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Subcontractor:

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Project Start Date: January 2005

Project End Date: October 2010

- System Gravimetric Capacity: 0.06 kgH₂/kg system
- System Volumetric Capacity: 0.045 kgH₂/L system
- Fill Time (for 5 kg): 3 minutes

Accomplishments

Objectives

- Discover and develop new materials with potential to meet the DOE 2010 targets for system weight percent and charge/discharge rates.
- Theoretically predict and synthesize new materials that release hydrogen with favorable thermodynamics.
- Screen catalysts and additives for their efficacy in improving the kinetic performance of metal hydrides.
- Provide theoretical understanding on metal hydride kinetic and regeneration problems.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charge/Discharging Rates
- (J) Thermal Management

Technical Targets

Work is progressing on improving the reversibility of metal hydrides, predicting and synthesizing new metal hydrides with high hydrogen capacity and good thermodynamics, and understanding metal hydride kinetic and regeneration issues. The targets being addressed include:

- Determined the crystal structures and phase transitions of Ca(BH₄)₂ polymorphs at different temperatures.
- Found that desorption kinetics of Ca(BH₄)₂ is fast and ~7 wt% can be rapidly released within minutes upon choosing the right dopant.
- Discovered that the re-hydriding kinetics of Ca(BH₄)₂ at 100 bar H₂-pressures are slow and that ~3.5 wt% can be re-hydrided within one hour. However, it takes 12 hours to re-hydride up to 5 wt%. Higher wt% can be achieved at higher pressures, i.e. 700 bar.
- Prototype electrostatic ground state (PEGS) theory predicts two alkali borohydrides, NaK(BH₄)₂, and LiK(BH₄)₂, which were synthesized by mechanical alloying.
- PEGS provided the best candidate for the ground state crystal structure of Mg(BH₄)₂.
- Discovered four theoretical crystal structures of the polymorphs of Ca(BH₄)₂, found good confirmation with experiment.
- Used quantum chemistry calculations to identify several alane-amine complexes that should promote AlH₃ harvesting efforts by our Brookhaven National Laboratory (BNL) partner.
- An investigation of O₂ and H₂O reactivity with metal hydride surfaces (M = Li, Na, K) indicates that factors other than surface poisoning, such as material transport rates between phases, limit the reversibility of the corresponding alanates (MAlH₄).
- Identified major issues that have hindered the advancement of high throughput screening (HiTS) using second/third generation hotplate designs, yet successfully improved hotplate longevity and much higher sample operating temperatures without sacrificing calorimetric sensitivity.
- Modified the HiTS reactor array concept to a more conventional packed bed configuration for thermally treating samples, and investigated the modified HiTS reactor capability with energetically milled NaAlH₄.



Introduction

There are currently no materials that fully meet the DOE hydrogen storage performance targets. In order to address this problem, we at Sandia National Laboratories (SNL) have undertaken the prediction, synthesis and characterization of new high-hydrogen content complex metal hydrides for use as reversible hydrogen sorption materials. In addition, we have further modified these hydrides through catalyst doping and cation substitution in order to improve their reversibility and sorption properties. Computational modeling has assisted in directing these efforts, as well as understanding kinetic and regeneration issues for metal hydrides. We provide technical leadership and collaborate extensively with our partners in the Metal Hydride Center of Excellence (MHCoe).

Approach

The materials discovery process involves solid-state preparation methods, followed by extensive characterization. For the solid-state approaches, mainly traditional ball milling, as well as ball-milling in the high-pressure sintering environment ($P < 140$ MPa, $T < 773$ K) have been applied. 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 sintering vessel incorporating six sample holders has been proven to be an effective tool for discovering new hydrides and screening for optional reaction conditions in different ternary systems. Our synthetic studies are guided by theory and chemical intuition. Theoretical approaches include an improved Monte Carlo-based method for rapidly assessing compound stability as well as the more traditional density functional theory calculations. This year we have also initiated attempts to improve hydrogen storage reversibility by nano-engineering approaches; incorporation of hydride materials into nanoframeworks and nanoparticle synthesis by surfactant templating.

As part of our Center lead activities, we have also provided technical leadership (setting directions, evaluating results) for the MHCoe Theory Group (TG). The TG makes use of first-principles methods to predict new materials and their thermodynamic properties, and suggests new directions for experimentalists and interpretation of their results. The TG consists of researchers at six institutions: SNL, University of Pittsburgh, Georgia Tech, University of Illinois at Urbana-Champaign, the National Institute of Standards and Technology and United Technologies Research Center (UTRC). To make maximum use of the different areas of expertise, joint TG efforts are guided by SNL not only in terms of technical direction, but also to

ensure that TG efforts are complementary and have an effective synergism with experimentalists. As a part of the TG activity, Sandia has been conducting quantum chemical studies of the binding of Lewis bases to aluminum as reagents for AlH_3 (alane) stabilization and harvesting. These studies are performed in collaboration with our MHCoe partner BNL.

Realizing that a breakthrough material is needed, we have been developing a new high-throughput synthetic and characterization approach employing micro hotplate technology. With this new methodology, our aim is to synthesize and characterize in situ new metal hydride storage materials.

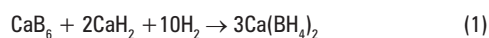
Structural characterization of the new materials is performed by X-ray diffraction (XRD), neutron diffraction, synchrotron XRD, Raman spectroscopy, Fourier transform infrared spectroscopy, and single crystal XRD. Hydrogen adsorption/desorption behavior is characterized with a Sievert's apparatus. Our characterization work is performed in-house, in collaboration with our MHCoe partners, and through international collaborations.

Results

Borohydrides: Experiment and Theory

As part of our lead lab activities, we lead Project B "Complex Anionic Materials". Results of individual research group efforts are described in the annual operating plans for the various groups. In this section, we discuss a collaborative effort, initiated and led by SNL in Fiscal Year 2006.

Since FY 2006, we have been keenly interested in the hydrogen storage properties of calcium borohydride ($\text{Ca}(\text{BH}_4)_2$). In FY 2006 we demonstrated a new solid-state route to prepare $\text{Ca}(\text{BH}_4)_2$ from a mixture of the decomposition products ($\text{CaB}_6/\text{CaH}_2$):



In FY 2007 we were able to optimize reaction conditions with additives. In FY 2008 we explored the crystal structures of different polymorphs of $\text{Ca}(\text{BH}_4)_2$, labeled α , α' and β , at different temperatures in collaboration with European Synchrotron Radiation Facility (ESRF), thus gaining valuable insight into the decomposition pathway, which is important for developing other borohydrides as well.

Figure 1 illustrates the phase transitions during heating and Figure 2 shows the crystal structures of the α , α' and β polymorphs of $\text{Ca}(\text{BH}_4)_2$. The desorption products were confirmed to be CaB_6 and CaH_2 , however, nuclear magnetic resonance analysis by the Jet Propulsion Laboratory (JPL) and Caltech indicated formation of an intermediate species, identified

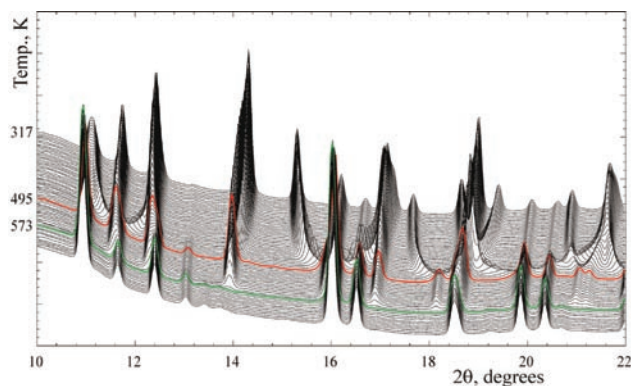


FIGURE 1. In situ synchrotron powder diffraction data of $\text{Ca}(\text{BH}_4)_2$ collected at 317-573 K, $\lambda = 0.711385 \text{ \AA}$ (at ESRF, France). Completion of the α -to- α' and α' -to- β transitions is highlighted in red and green, respectively.

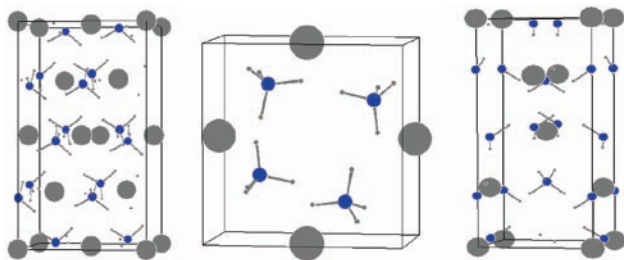


FIGURE 2. Crystal Structures of α , β and α' - $\text{Ca}(\text{BH}_4)_2$ Polymorphs

as $\text{CaB}_{12}\text{H}_{12}$. Moreover, we investigated kinetics at lower pressures and temperatures, showing partial reversibility of $\sim 5 \text{ wt\%}$ at 620 K and 100 bar. From the hydrogen desorption and adsorption curves in Figure 3, it can be seen that desorption kinetics are fast, but re-hydrogenation is much slower. We are currently performing a pressure-composition-temperature measurement and if the experimental enthalpy is close to the near ideal theoretical value (40 kJ/mol), we will embark on improving kinetics.

We have decided to discontinue our previous attempts to explore the ternary Si and Ge systems, due to their poor hydrogen content. Instead, in FY 2008, we directed our focus towards the discovery of new materials in the bialkali borohydride and the mixed alkali-transition metal borohydride, $\text{AT}(\text{BH}_4)_x$, systems. During our theoretical/synthetic search, we were able to discover two new bialkali borohydrides, $\text{NaK}(\text{BH}_4)_2$ and $\text{LiK}(\text{BH}_4)_2$. Unfortunately, $\text{NaK}(\text{BH}_4)_2$ proved to be unstable and $\text{LiK}(\text{BH}_4)_2$ was too stable (did not release H_2 below 773 K). As a consequence, the bialkali borohydride system did not seem to be very promising to pursue further.

In collaboration with Prof. Craig Jensen of the University of Hawaii at Manoa, we have been investigating reversibility of mixed alkali-transition

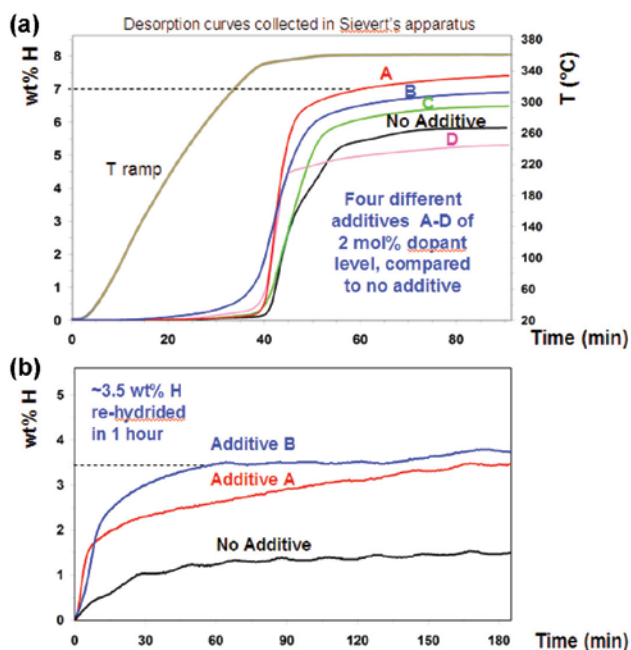


FIGURE 3. (a): Desorption curves of $\text{Ca}(\text{BH}_4)_2$ with and without (black curve) 2 mol% dopant collected in a Sievert's apparatus at 633 K in vacuum. (b): Absorption curves of $\text{Ca}(\text{BH}_4)_2$ with and without (black curve) 2 mol% dopant collected in a Sievert's apparatus at 120 H_2 -pressures and 623 K.

metal borohydrides. This type of borohydride desorbs considerable amounts of hydrogen at low temperatures, below 323 K, and so far we have seen partial reversibility in one particular system (patent in progress). We also attempted to re-hydrate the TiCl_3 -doped $\text{ScH}_2\text{-LiBH}_4$ system in collaboration with JPL and Caltech, at 896 bar H_2 -pressure and 733 K. We observed limited LiBH_4 formation from a mixture of $\text{ScB}_2 + 2\text{LiH}$, indicating a small reversibility effect. During FY 2009, we will continue our collaboration with our MHCoe team to further explore the other mixed alkali-transition metal borohydride systems.

The PEGS method was employed in FY 2008 to search for undiscovered compounds, and to address crystal structure issues in newly discovered compounds. As described above, two bialkali borohydrides, $\text{NaK}(\text{BH}_4)_2$, and $\text{LiK}(\text{BH}_4)_2$, were predicted and synthesized, but discarded due to undesirable stability issues. PEGS provided the best candidate for the ground state crystal structure of $\text{Mg}(\text{BH}_4)_2$ in FY 2008, finding a low-energy structure in symmetry $I42m$, 5 kJ/mol formula unit below the experimentally observed structure in symmetry $P61$ [1]. Four crystal structures of the polymorphs of $\text{Ca}(\text{BH}_4)_2$ were predicted. Two low-temperature phases including the observed structure in symmetry $Fddd$, a potentially new ground state, and two high-temperature polymorphs, including the correctly identified structure of the β phase, confirmed with

Rietveld refinements. The unreported phases appear to be observed in synchrotron diffraction experiments.

Remarkably, the PEGS method has also produced high-symmetry low-energy crystal structures in the $\text{LiSc}(\text{BH}_4)_4$ system, indicating that the method may address mixed transition-metal alkali borohydrides, and even transition metal hydrides. Other transition metal containing hydrides are under investigation with other MHCoe partners. In FY 2009 the method will be actively used for structure searching in amide/imide containing materials, and in mixed anion materials such as $\text{Mg}(\text{AlH}_4)(\text{BH}_4)$.

Nanostructured Materials

It has been shown in the literature how incorporation of metal hydrides in carbon aerogels and nanostructured materials can improve reversibility. Thus, we have this year initiated two new approaches to nano-engineer our promising materials: 1) incorporation of hydride materials in catalyzed nanoframeworks, and 2) synthesis of nanoparticles by surfactant templating.

By teaming with UTRC, HRL and others, we are exploring routes to infiltrate calcium borohydride into nanoframeworks. Our first trial, utilizing Sandia's high-pressure station, indicated that calcium borohydride can wet the surface of a carbon aerogel under high-pressures by melting at elevated temperatures, thus showing promise towards incorporation.

Low-temperature synthesis of nanoparticle hydrides using surfactant templating began in late FY 2008. Briefly, micelles are formed by surfactant in a nonpolar solvent and then mixed with small volumes of polar solvent saturated with NaBH_4 . The polar solvent is then extracted from the interior of the micelle to obtain small crystals of complex hydride. Dynamic light scattering was applied to monitor the sizes of the micelles being formed in the solution, and transmission electron microscopy (TEM) was used to observe the obtained nanoparticle sizes after the solvent extraction treatment. The TEM images in Figure 4 show the particles that were harvested after the solvent extraction. Figure 4 shows an abundant amount of spherical material with diameters near 7 nm. Based on these preliminary experiments, surfactant templating appears to be a very promising method to develop nanomaterials of metal hydrides.

Theoretical Modeling

Oxidation of MH Surfaces: Reversibility and Kinetics

As part of our lead lab activities, we coordinate and contribute to the MHCoe TG. Results of individual research group efforts are described in the annual operating plans for the various groups. In this section, we discuss a group-wide effort, initiated and led by SNL

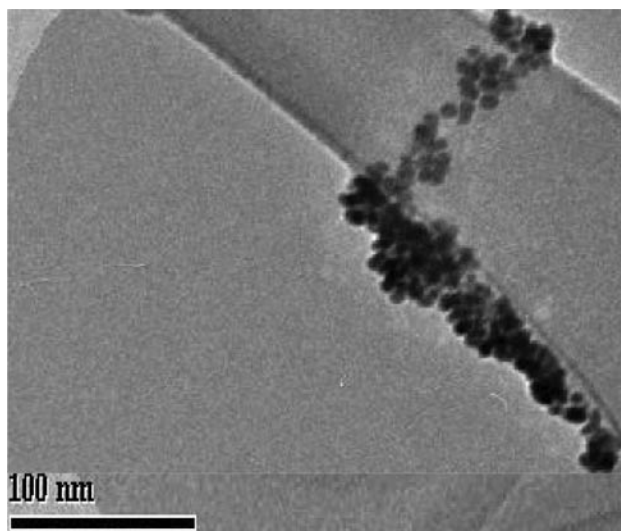


FIGURE 4. TEM images of NaBH_4 containing micelles after solvent extraction. Gray and dark colored particles may be empty micelle shells and NaBH_4 particles.

in FY 2007 and completed in FY 2008, to probe the effects of surface poisoning on the kinetics of alanate (MAlH_4 ; $\text{M} = \text{Li}, \text{Na}, \text{K}$) re-hydrogenation.

Re-hydrogenation kinetics strongly limits the usefulness of many metal hydrides. In FY 2007 the TG completed an investigation of surface poisoning by oxygen and water on MH surfaces ($\text{M} = \text{Li}, \text{Na}, \text{K}$), which we hypothesized is the rate-limiting reaction in the re-hydrogenation of alanates. Calculations were performed on the (100) surfaces of LiH , NaH and KH surfaces, which we find is the lowest-energy surface in all three cases. The dissociation pathways and energetics of oxygen and water on the (100) face of each of surface were then computed. No substantial differences in the initial kinetics of poisoning of the three surfaces by either O_2 or H_2O were found. The results indicate that our hypothesis is not correct and that other factors, such as material transport rates between phases, limit the reversibility.

In FY 2008, we took the results of these calculations and constructed a microkinetic model for H_2O dissociation on the MH(100) surfaces, using the computed transition-state energetics for dissociative adsorption of H_2O . One interesting manner in which these results can be used is to search for the time at which each surface becomes 90% site occupied by OH species at the condition of interest. Using this metric, it can be seen from Figure 5 that at 100% saturation concentration of H_2O the NaH surface is occupied nearly 160 times faster than at 1% of saturation humidity. The behavior of the $\text{KH}(100)$ surface is similar to the $\text{Na}(100)$ surface. Although the LiH surface reacts significantly slower than either NaH or KH , the calculations indicate the surface is still

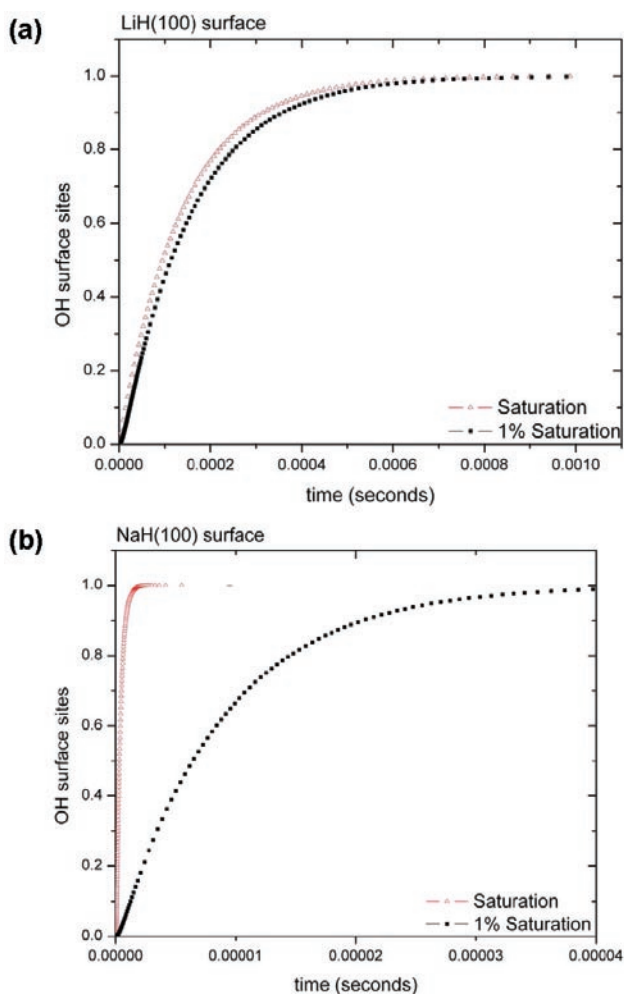


FIGURE 5. The time evolution of the MH(100) (M=Li, Na) surfaces as measured by conversion to surface MOH sites when exposed to H₂O saturation concentrations and 1% saturation concentrations at 298 K.

saturated with OH sites under these conditions and is converted to LiOH almost instantaneously. We have also performed these calculations at the much lower H₂O concentrations typical of glove boxes used to handle metal hydrides. In this case, we expect the H₂O partial pressure to be of the order 1 ppm. Even at this concentration, however, the model predicts that MH surfaces are saturated within ~10 msec. This suggests that the surfaces of at least these materials should not be considered to be free of oxygen. More generally, this may be true of all metal hydrides, since they are all known to be highly reactive with water

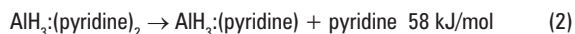
Lewis Base Donors to Promote AlH₃ Regeneration

Lewis Base molecules such as amines and ethers can be used to stabilize alane (AlH₃) in a form that could enable it to serve as a hydrogen-storage material. For example, a complex between AlH₃ and triethylenediamine (TEDA; N(C₂H₄)₃N) in solution can

reversibly desorb H₂ at room temperature [2]. However, in solid form the AlH₃:N(C₂H₄)₃N decomposition and reformation kinetics are very slow. It may be that the Al:N bond is too strong and therefore, a weaker complexation agent must be found to increase the kinetics to acceptable rates.

In support of the Alane Project (Project D) within the MHCoe, we performed quantum-chemistry calculations to predict dissociation energies for alane complexes with electron donor molecules such as amines and ethers. Calculations were completed for a series of amines, using the bond additivity correction (BAC) method methodologies developed by Sandia to determine the thermodynamics of individual molecular species [3]. Heats of formation and other temperature-dependent thermodynamic data for thirteen AlH₃:amine complexes were determined and are shown in Table 1.

The results show that among the 1:1 complexes (*i.e.*, one AlH₃ coordinated with one amine), complexes with triethylamine (N(C₂H₅)₃) have the weakest Al-N bonds. Al-N bonds to aromatic amines such as pyridine are also weaker than TEDA. Dialane complexes have the weakest Al-N bonds of all the complexes that were modeled. For example, the energy to dissociate (AlH₃)₂-pyrazine to 2AlH₃ + pyrazine is predicted to be 110 kJ/mol, while the energy to dissociate AlH₃:TEDA is 156 kJ/mol. Finally, it is found that bonding in 1:2 complexes (*i.e.*, AlH₃:(amine)₂ complexes is weaker in general than in 1:1 complexes. For example, the reaction enthalpies (298 K) of the sequential removal of pyridine molecules from AlH₃(pyridine)₂ are:



Assuming that decomposition of the complex occurs by sequential loss of amine groups, these results suggest that the rate-limiting decomposition step will be the loss of the second amine (reaction 3). These results

TABLE 1. Energies to Dissociate Alane:Amine Complexes Computed by the BAC Method

1:1 Complex	E(complex)*	1:2 Complex	E(complex)*
AlH ₃ :NH ₃	142.7		
AlH ₃ :NMe ₃	147.6	AlH ₃ :(NMe ₃) ₂	217.9
AlH ₃ :NEt ₃	118.6	AlH ₃ :(NEt ₃) ₂	158.7
AlH ₃ :TEDA	156.3	AlH ₃ :(TEDA) ₂	233.8
AlH ₃ :Quinuclidine	159.9	AlH ₃ :(Quinuclidine) ₂	236.7
AlH ₃ :pyridine	135.2	AlH ₃ :(pyridine) ₂	193.3
AlH ₃ :pyrazine	125.3	(AlH ₃) ₂ :pyrazine	110.4

* Energy (kJ/mol) to dissociate the complex into AlH₃ + (donor groups); *e.g.*, AlH₃(NMe₃)₂ → AlH₃ + 2 NMe₃. Me = CH₃, Et = C₂H₅.

have been shared with the alane group to assist them in selecting chemistries for stabilizing AlH_3 .

High Throughput Screening (HiTS) and Synthesis of Hydrogen Storage Materials

Our effort was focused on developing combinatorial methods to discover catalyzed light-weight, high-capacity metal hydrides. FY 2008 accomplishments include; (1) design and fabrication of instrumentation to scale up the HiTS capability, (2) development of a viable process workflow for sample preparation, and (3) efforts to derive and validate experimental protocols. In June of 2008, this activity was suspended at the recommendation of the MHCoe Coordinating Council, with the MHCoe materials screening efforts re-directed.

In FY 2007, both viability of the in situ diagnostics, including micro-calorimeter and micro-thermal conductivity detector (μ -TCD), and validation of the approach to material synthesis (except for the energetics of the multi-sample mixer mills) were demonstrated. Sensitivity to gas phase H_2 , with good signal-to-noise and in the concentration range of interest, was demonstrated for the μ -TCD. As a result of FY 2007 successes, the project resources, in FY 2008, were dedicated to scale up of the combinatorial approach with the objective focused on conducting experiments relevant to the materials and catalysts screening efforts that are ongoing in MHCoe Project B.

In FY 2008 we successfully designed the scale-up of the HiTS apparatus from a planned 15-sample, 3-detector configuration on a single board to stacking of two 12-sample, 4-detector boards into a smaller vessel. These modifications allowed for reduced volume, increased sample capacity per reactor, a greater number of simultaneous desorption experiments per cycle, and experimental flexibility.

In the interim period of time between fabrication of the high-density microfluidic cartridge and integration of second/third generation micro-hotplates into the HiTS platform, a series of experiments were undertaken to derive and validate experimental protocols. Absorption reactions were executed at up to 125 bar H_2 in the Parr reactor. Experiments were conducted on energetically milled samples of NaAlH_4 , a mixture of NaH , Al and TiCl_3 catalyst, $\text{Ca}(\text{BH}_4)_2$ with and without catalyst and a ternary Li-Na-K borohydride system.

Findings from the cycling (abs/des) of energetically milled NaAlH_4 experiments are: (1) the H_2 content of the “as received” material is much less than what is observed after cycling; (2) H_2 content and calorimetric behavior are somewhat variable but remain consistent between cycles at different sample soak times and temperatures; (3) adequate absorption conditions were identified, however, soak times could be decreased if the material was saturated. These experiments validated

the approach, in that complex metal hydrides (NaAlH_4) could be synthesized in situ using this approach (which was further corroborated via XRD by the presence of NaAlH_4). Initial validation studies were also conducted on $\text{Ca}(\text{BH}_4)_2$.

Over the course of the development effort, we also found major problems associated with integrating the second/third generation hotplates into the microfluidic platform and initiating full scale material studies. There were performance inconsistencies between the old, planar hotplate devices and the newest generation plates. Although the newest generation plates were neither beneficial nor entirely understood, we still succeeded in improving cycle longevity and operating at much higher sample temperatures without sacrificing calorimetric sensitivity to any great extent. However, these devices require significantly more power to achieve sample temperatures comparable to that of the planar devices, which produced other experimental difficulties.

Given the need to move beyond method development, and realizing that it would have taken more time and effort to work through the aforementioned issues, we decided to modify the reactor array concept to a more conventional packed bed configuration for thermally treating samples, and explore the performance. Essentially an array of packed bed reactors replaced the sample hotplates, keeping everything else the same (power supplies, support systems, software architecture), and continued use of the in situ diagnostic for measuring desorbed gas composition (μ -TCD). Fully validating this new experimental arrangement was in progress, when in June of 2008, this activity was suspended at the recommendation of the MHCoe Coordinating Council, with the MHCoe materials screening efforts re-directed.

Conclusions

- Crystal structure determination of the polymorphs of $\text{Ca}(\text{BH}_4)_2$ by a theoretical/experimental approach, *i.e.* PEGS-and Rietveld methods.
- In situ synchrotron data from ESRF showed second-order phase transition in $\text{Ca}(\text{BH}_4)_2$.
- Showed partial reversibility of $\text{Ca}(\text{BH}_4)_2$ to 5 wt% at 100 bar H_2 -pressures and 623 K.
- Desorption kinetics of $\text{Ca}(\text{BH}_4)_2$ is fast and ~6-7 wt% can be rapidly released at ~623 K within minutes upon choosing the right dopant.
- Re-hydriding kinetics of $\text{Ca}(\text{BH}_4)_2$ is slow and ca 3.5 wt% can be re-hydrided within one hour, but it takes 12 hours to re-hydride up to 5 wt%.
- PEGS predicted alkali borohydrides, $\text{LiK}(\text{BH}_4)_2$ and $\text{NaK}(\text{BH}_4)_2$, synthesized by mechanical alloying.
- Constructed a microkinetic model for H_2O dissociation on the $\text{MH}(100)$ surfaces, using the

- computed transition-state energetics for dissociative adsorption of H₂O.
- Used quantum chemistry calculations to identify several alane-amine complexes that should promote AlH₃ harvesting efforts by our BNL partner.
- Identified major issues that have hindered the advancement of HiTS using second/third generation hotplate designs, yet successfully improved hotplate longevity and much higher sample operating temperatures without sacrificing calorimetric sensitivity.
- Modified the HiTS reactor array concept to a more conventional packed bed configuration for thermally treating samples, and investigated the modified HiTS reactor capability with energetically milled NaAlH₄.

Future Directions

- Continue PEGS theoretical search for promising mixed cation borohydrides.
- Continue PEGS searching for transition-metal containing borohydrides.
- Begin studies of mixed ammonia borohydride and amide/imide borohydride complexes.
- Conduct additive screening studies in support of MHCoe Additive Screening program.
- Begin search for promising mixed anion compounds such as Ca(AlH₄)(BH₄).
- Optimize performance of Ca(BH₄)₂ at lower pressure and temperature.
- Incorporate Ca(BH₄)₂ and other hydride materials in catalyzed nanoframeworks.
- Explore possibilities to design alternative nanostructured metal hydrides to improve hydrogen storage properties.

Special Recognitions & Awards/Patents Issued

1. E.C.E. Rönnebro, E.H. Majzoub, “Solid-state Synthesis of Calcium Borohydride and Its Use for Reversible Hydrogen Storage”, Patent Application Serial Number 60/901,248 originally filed 02/12/2007.
2. W. Luo and K. Stewart, “Reactor for removing Ammonia”, SD-8574, Application # 11/487,527. Filed on 07/13/06.
3. E.C.E. Rönnebro, Craig M. Jensen, Godwin Severa, Technical Advance Disclosure filed on 06/06/2008.

FY 2008 Publications/Presentations

1. V. Ozolins, E.H. Majzoub, C. Wolverton, “Metal Borohydride Thermodynamics: Influence of B₁₂H₁₂²⁻ Anions,” manuscript in progress.

2. L. Seballos, E. Rönnebro, J.L. Herberg, E.H. Majzoub, “Metastability and Crystal Structure of NaK(BH₄)₂”, manuscript in progress.
3. B. Dai, R.B. Rankin, M.D. Allendorf, D.S. Sholl, N. Zarkevich, D.D. Johnson, J.K. Johnson, “Microkinetic Model of Metal Hydride Oxidation”, manuscript in progress.
4. E. Rönnebro, V. Stavila, M. Ulutagay-Kartin, “Hydrogen Sorption Properties of Doped Ca(BH₄)₂”, manuscript in progress.
5. E. Majzoub and E. Rönnebro, “The Crystal Structures of Ca(BH₄)₂: Theory and Experiment”, submitted, 2008.
6. R.D. Kolasinski, J.A. Whaley, and R. Bastasz, “Real Space Ion Scattering Maps of the Mg(0001) Surface,” submitted to Phys. Rev. B., 2008.
7. B. Dai, R.B. Rankin, M.D. Allendorf, D.S. Sholl, N. Zarkevich, D.D. Johnson, J.K. Johnson “Influence of Surface Reactions on Complex Hydride Reversibility,” submitted to J. Phys. Chem. C, 2008.
8. L. Seballos, J. Zhang, E. Rönnebro, J.L. Herberg, J., E.H. Majzoub, “Metastability and Crystal Structure of the Bialkali Complex Metal Hydride NaK(BH₄)₂”, accepted J. Alloys Compounds.
9. Y. Filinchuk, E. Rönnebro, D. Chandra, “Crystal Structures and Phase Transformations in Ca(BH₄)₂”, accepted Acta Materialia.
10. E. Rönnebro, E. Majzoub, Hydrogen Storage in Calcium Borohydride: Catalysis and Reversibility, J. Phys. Chem. B. Letters, 111 (42), 12045 -12047, 2007.
11. E. Majzoub, V. Ozolins, “Prototype Electrostatic Ground State Approach to Predicting Crystal Structures of Ionic Compounds: Applications to Hydrogen Storage Materials”, Phys. Rev. B, 77, 104115, 2008.
12. V. Ozolins, E. Majzoub, C. Wolverton, “First-principles Prediction of a New Ground State of Mg(BH₄)₂”, Phys. Rev. Lett, 100, 135501, 2008.
13. J. Purewal, S. Hwang, R.C. Bowman, E. Rönnebro, B.Fultz and C.Ahn, “Hydrogen Sorption Behavior of the ScH₂-LiBH₄ System: Experimental Assessment of Chemical Destabilization Effects”, J. Phys. Chem. C, 112, 8481–8485, 2008.
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