IV.A.5a Development of Metal Hydrides at Sandia National Laboratories

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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 testing 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 helps direct these efforts, in collaboration with our Metal Hydride Center of Excellence (MHCoE) colleagues.

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 high-energy ball milling in combination with high-pressure sintering (pressure [P] <140 MPa, temperature [T] <773 K) has 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 in different ternary systems.

Realizing that a breakthrough material is needed, in FY 2007 we developed and demonstrated a new high-throughput synthetic and characterization approach employing micro-hotplate technology. With this new methodology, we will rapidly synthesize and characterize *in situ* new metal hydride storage materials.

Many of our synthetic studies are guided by theory. Theoretical approaches include an improved Monte Carlo (MC)-based method for rapidly assessing compound stability as well as the more traditional density functional theory (DFT) calculations. As part of our MHCoE lead activities, we have also provided technical leadership (setting directions, evaluating results) for the MHCoE Theory Group, particularly in the areas of materials kinetics.

Structural characterization of the new materials is performed by X-ray diffraction (XRD), neutron diffraction, synchrotron X-ray diffraction, Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and single crystal X-ray diffraction. Hydrogen adsorption/desorption behavior is characterized with Seivert's apparatus. For fundamental studies, we have also applied low-energy ion scattering (LEIS) spectroscopy to elucidate hydrogen bonding to surfaces of interest.

Results

Theoretical Predictions for New Materials

Obtaining accurate enthalpy estimates of potential new hydride decomposition reactions is a necessary means of identifying which materials systems we should attempt to synthesize. We have developed a MC global optimization algorithm to perform crystal structure prediction of complex anionic hydrides. These compounds consist of molecular anionic units such as (AlH_4^-), (AlH_6^{3-}), (BH_4^-), (NH^{2-}), and (NH_2^-), charge-balanced by a cation matrix consisting of the alkali or alkaline earth metals. The predicted crystal structures are used in first-principles calculations of reaction enthalpies.

Our global optimization algorithm utilizes distance scaling (DSM) to smooth the potential energy surface (PES). We attempt to find the electrostatic ground state of a collection of anions and cations using the DSM-MC approach. First-principles DFT methods are used to calculate quantum mechanical T = 0 K energies from the MC algorithm output. Structural relaxation of the MC-generated structures is performed using standard DFT energy functionals. These first-principles energies are used to obtain enthalpy estimates at 0 K. Lattice vibration contributions to the enthalpy can be calculated for finite temperature effects where necessary.

In FY 2007, advances made in the algorithm used for MC structure searching have yielded major

and surprising improvements. Figure 1 shows initial and final first-principles DFT energies of structures of $Ca(BH_4)_2$ generated with and without using the DSM-MC technique we have developed. The DSM-MC generated structures show a clear and dramatic improvement over single-run MC minimization. The algorithm has recently found the ground state structure of $NaAlH_4$, illustrating a major success of the code. We did not anticipate that the algorithm would be able to find ground state structures of complicated molecular crystals due to the size of the configuration space. Further use of the improved algorithm found a crystal structure for $LiAlH_4$ which is significantly lower in total energy at 0 K than the experimentally observed structure, which is likely stabilized at nonzero temperature due to lattice vibration contributions to the free energy. These new results give us added confidence that the MC approach is producing crystal structures that are likely very close to ground state energies, and therefore that the enthalpy estimates derived from the subsequent calculations may be more accurate than we anticipated. 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, and K-Ca.

We have also begun 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. We will continue the first-principles calculations to obtain physical parameters for use in the MC structure searching algorithm.

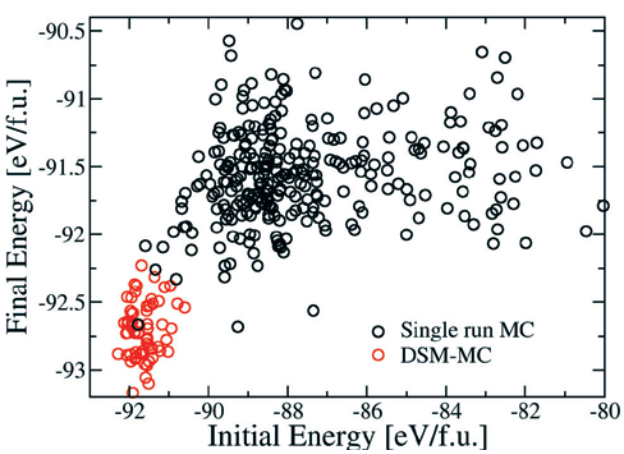

FIGURE 1. First principles energies for $Ca(BH_4)_2$ calculated from single run MC (black circles) and DSM-MC (red circles) methods. The initial energy (abscissa) is the calculated DFT energy before relaxation using the DFT energy functional. The DSM-MC generated structures show marked improvement over single run MC.

Synthesis and Characterization of New Hydrogen Storage Materials

In FY 2006, we discovered a new phase in the Ca-B-H system by attempting a previously untried solid-state reaction path that was predicted by theoretical calculations to result in a reaction enthalpy of ~53 $kJmol^{-1}$ and 9.6 wt% reversible storage:

(1) $CaB_6 + 2CaH_2 + 10H_2 \rightarrow 3Ca(BH_4)_2$

This year (FY 2007), we explored different synthesis routes to optimize the yield of this reaction. We discovered that it was possible to prepare calcium borohydride, $Ca(BH_4)_2$ by following a specific synthesis route, previously not reported in the literature. We were able to prepare $Ca(BH_4)_2$ with a yield of ~60% by using Sandia's high-pressure station that enables hydrogen pressures of <140 MPa and temperatures <773 K. It was crucial to add a catalyst to improve the yield. During FY 2007 we identified the Ca-B-H phase to be $Ca(BH_4)_2$ by performing Raman spectroscopy at Sandia and neutron vibrational spectroscopy with our MHCoE partner National Institute of Standards and Technology (NIST) (Dr. Udovic). Both the Raman and the neutron vibrational spectra showed that the samples contain BH_4^- groups, indicating that we indeed had formed $Ca(BH_4)_2$. XRD analysis clearly showed that the structure of the Ca-B-H phase is in accordance with the structure of $Ca(BH_4)_2$ published by Miwa et al (Phys. Rev. B, **74** 155122 (2006)), further confirming that we were successful in preparing $Ca(BH_4)_2$.

In FY 2006, we had observed hints of reversibility, but only for <1 wt% hydrogen. To understand why this material is not reversible, although theoretical calculations predicted favorable thermodynamics, we investigated the desorption mechanism. At Sandia, we performed thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analyses of $Ca(BH_4)_2$. Figure 2 shows two phase transitions at 140°C and 350°C, and hydrogen being released at the higher temperature. Since the anticipated desorption

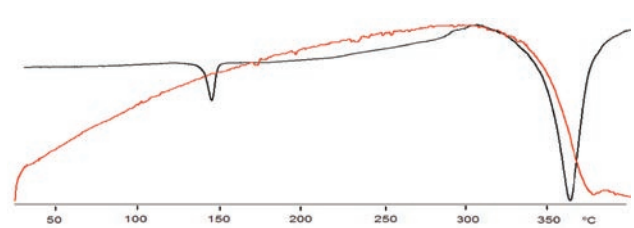

FIGURE 2. Desorption behavior of $Ca(BH_4)_2$ investigated by DSC and TGA. The DSC curve (black) and TGA curve (red) show two endothermic phase transformations at 140°C and 350°C, and the release of hydrogen at 350°C.

products are CaB_6 and CaH_2, the same as the starting materials, $Ca(BH_4)_2$ can be considered a partially reversible hydrogen storage material. To confirm this and to get more details on the structural transitions during desorption, we prepared and sent samples to our MHCoE partner, University of Nevada, Reno, (Prof. Chandra) for *in situ* XRD during desorption. Their analysis confirmed the phase transition from an alpha to a beta-phase at 140°C and further hydrogen release at 350°C upon detection of CaB_6 and CaH_2.

We also continued screening for new materials using our six-crucible high-pressure technique and focused on searching for new complex hydrides in the ternary/quaternary A-Mn-H system (A=Li, Na, Mg, Ca) in collaboration with Prof. Klaus Yvon of University of Geneva. However, we have not yet been able to find any non-reported materials. We also investigated A-Ni-H (A=Li or Na) and A-Ti-H, A-Nb-H (A=Li, Na, Mg) and analysis is in progress. We have identified a new phase in the ternary Na-Ge-H system from XRD, TGA and DSC analysis showing a new phase(s) and one major endothermic phase transition associated with a weight-loss at 370°C, thus indicating the formation of a new hydride material. Hydrogen content and reversibility in this material will be explored during FY 2008.

We completed our studies of amide syntheses in collaboration with Prof. Ping Chen at the National University of Singapore. Li_3AlH_6-$LiNH_2$ mixtures with Li_3AlH_6:$LiNH_2$ molar ratio of 1:3 and 1:2 were investigated, respectively. Mechanical milling the starting materials at two given energy levels resulted in totally different reaction paths for hydrogen desorption. In the case of the low-energy mechanical milling, hydrogen was first desorbed by the thermal decomposition of Li_3AlH_6, then via the interaction of resulting LiH and $LiNH_2$. Li_2NH and Al were the solid products of dehydrogenation. High-energy mechanical milling induced direct interaction between Li_3AlH_6 and $LiNH_2$, as a result, considerable amount of hydrogen evolved in the milling process. Heating the post-milled samples to high temperatures led to more hydrogen desorption. In total, ~10 and ~8 H atoms (per formula unit) were detached from Li_3AlH_6-$LiNH_2$ (1:3) and (1:2) sample, respectively. In related studies, HY-Energy performed pressure, composition, temperature measurements of Li_3AlH_6-$LiNH_2$ mixtures in support of our University of Utah partner (see report by Utah). Although the Sandia synthetic efforts in the amide materials are currently paused, we remain available to our MHCoE partners (i.e. Utah) for characterizations of amide systems.

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

Realizing that a breakthrough material is needed, we at Sandia have created a new synthetic methodology that uses an array of micro-hotplates integrated into a high pressure vessel as a means to rapidly synthesize 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.

The development of the combinatorial HTS concept has progressed well in the nine months since DOE approved this activity. 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. The 2 kpsi Parr reactor contains a small, fully instrumented 2.75" outside diameter conflat flange assembly that has four sample hotplates and one thermal conductivity detector (TCD). 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 five 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. Figure 3 depicts the 2 kpsi Parr reactor and flow system (top), hotplates affixed to a circuit board assembly (bottom right), and the conflate flange mounted assembly (bottom left).

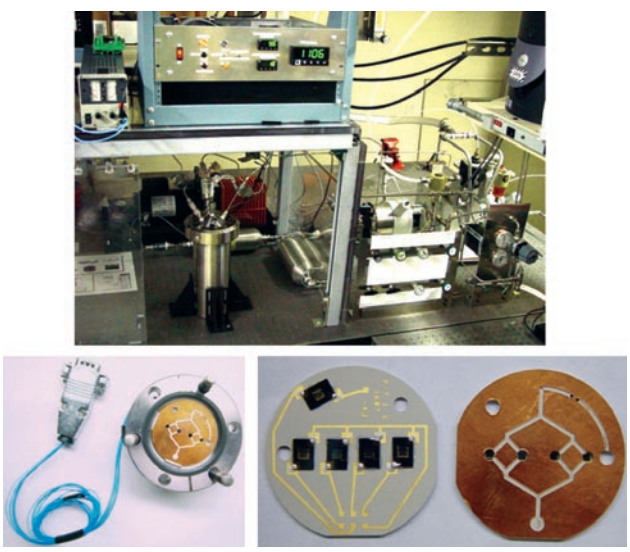

FIGURE 3. Flow system, 2 kpsi Parr reactor, and control electronics (top); four sample hotplate with one TCD hotplate PCB assembly (bottom right) and conflat flange mounted assembly (bottom left).

Two key demonstration milestones of the HTS approach using arrays of micro-hotplates are the ability to both rapidly synthesize and characterize complex metal hydrides from their respective elemental and/or hydride precursors. We effectively demonstrated both capabilities this FY using the aforementioned 2 kpsi Parr reactor. Plotted in Figure 4 are the hotplate temperature and power profiles measured during a programmed thermal desorption experiment with MgH_2 as a test material. During desorption, the reactor was held at atmospheric pressure with a constant flow of argon through the system. The sample hotplate temperature containing MgH_2 was ramped at 180°C/min while holding the TCD hotplate temperature fixed at 400°C. At 160 seconds (which corresponds to a conductor temperature of approximately 580°C) the rate of hydrogen desorption from the sample peaks (as indicated by the TCD signal). Both the calorimeter and TCD respond in kind and provide three essential pieces of information, (1) area under the sample hotplate power curve is representative of the total enthalpy change (in this case an endothermic transition from MgH_2 to Mg and H_2), (2) area under the TCD curve quantifies the total amount of H_2 liberated by the reaction, and (3) the temperature at the peak rate of H_2 production is indicative of the kinetics associated with the desorption reaction. Therefore, within a few hundred seconds, we are able to record essential information about the thermal stability, hydrogen capacity, and kinetics of the sample material. Subsequent to the desorption experiment, depleted Mg metal was hydrided by holding the hotplate temperature at 500°C (corresponding to a sample temperature of approximately 400°C) and pressurizing the Parr reactor to 1.8 kpsi H_2 for 15 minutes, then allowing the material to cool to room temperature under H_2. We can continually cycle between MgH_2 and Mg, thus validating the synthesis approach for a simple binary hydride that admittedly requires high temperature and moderate pressure to process.

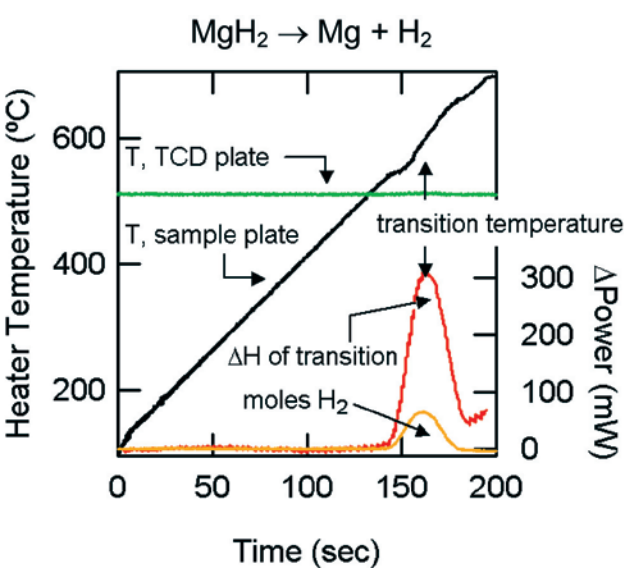

FIGURE 4. Sample Plate Temperature and Zero-Referenced Power Curves for the TCD and Sample Plates during a Programmed Thermal Desorption Experiment on MgH_2

A similar synthesis and hydrogen-cycling experiment was also performed using powdered sodium alanate precursors. For this particular sample preparation, Al, NaH, and $TiCl_3$ powders were mixed in the appropriate proportions and ball-milled in argon for 30 minutes at low energy. This powder mixture was subsequently pressed into small pellets, loaded into the 2 kpsi hotplate fixture, and then exposed to 1.8 kpsi H_2 at hotplate temperatures varying from 200 to 250°C over a range of times from 15 to 60 minutes. XRD patterns obtained from the post-treated precursor pellets are shown in Figure 5(a) and indicate the presence of $NaAlH_4$, thereby confirming the assertion that the HTS apparatus incorporating micro-hotplates can successfully synthesize complex metal hydrides. The data in Figure 5(b) summarize the *in situ* diagnostic results, plotting hotplate temperatures and power requirements, for both sample and TCD hotplates, measured over several thermal desorption cycles. Here again, these results indicate that the HTS methodology as implemented is a valid approach to rapidly synthesizing and characterizing complex metal hydride materials. What remains to be demonstrated is to achieve experimental conditions (20 kpsi hydrogen and 800°C sample temperature) such that we can verify the melt or near-melt approach to synthesizing complex metal hydrides without ball milling.

Work in the past three quarters has also focused on design, modeling, and preliminary fabrication of novel silicon, high-temperature hotplate structures. These improvements were motivated by our discovery 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. Work is in progress on these advanced hotplate designs.

Fundamental Studies of Hydrogen Adsorption and Binding on Light Metal Surfaces

The surface condition of a hydrogen storage material affects the kinetics of hydrogen uptake and release. Contaminants can impede H_2 uptake/release kinetics while some types of foreign atoms can function as catalysts and improve the kinetics. As part of an effort to understand the influence of contaminants and catalysts, we examined several model systems using the surface-specific technique of LEIS, which can detect and identify top-layer atoms (including hydrogen and its isotopes) as well as provide information about local atom arrangement on ordered surfaces.

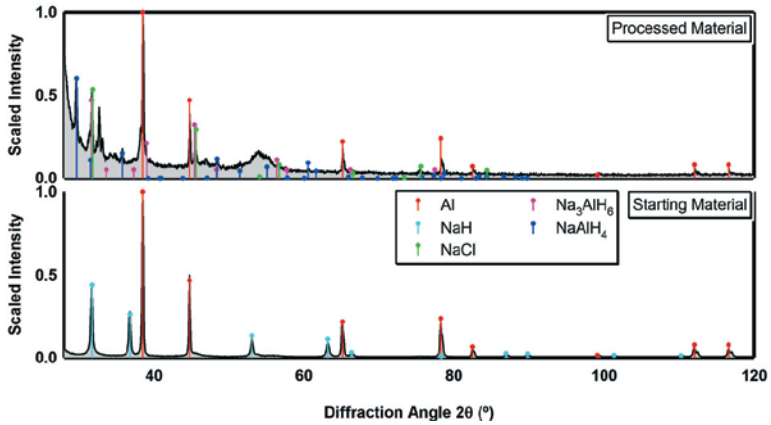

FIGURE 5(A). XRD patterns of a ball-milled powder sample containing Al, NaH, and $TiCl_3$ prior to processing in the hotplate fixture (bottom), and a pattern of the same material after processing at 1.8 kpsi H_2 in the hotplate fixture (top). Note the appearance of $NaAlH_4$ features in the processed sample.

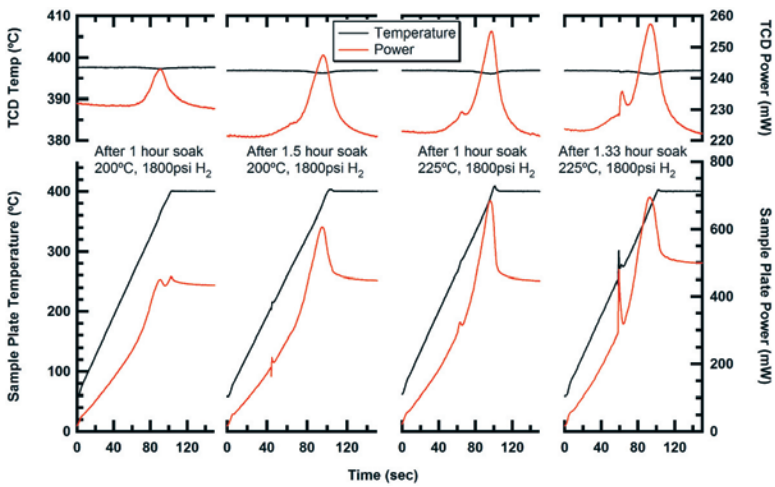

FIGURE 5(B). Hotplate Temperatures and Power Required to Maintain Setpoint for TCD (top) and Sample Hotplate (Bottom) During Thermal Desorption and Subsequent Hydrogen Cycling of Sodium Alanate

Considering the high current interest in nanoconfinement of MgH_2 , the use of MgH_2 in destabilized borohydride systems and $Mg(BH_4)_2$ itself, we focused on Mg and MgB_2 surfaces. On Mg, we studied the binding site location of hydrogen on the pure crystalline surface to provide baseline data for subsequent work concerning the effect of contaminants and catalysts. On MgB_2, we measured the surface composition of MgB_2 powders prior to hydrogenating to determine their cleanliness and stoichiometry. We also examined the rate of adsorption of atomic and molecular hydrogen on the prepared surface.

The surface of Mg(0001) was probed with a 2 keV Ne^+ beam and the energy distribution of scattered and recoiled ions was measured as a function of sample orientation. Over 6,000 spectra were recorded at selected polar and azimuthal angles, from which it was possible to construct a real-space map of both Mg and H surface atoms, as shown in Figure 6. This is the first time adsorbed hydrogen has been directly imaged on Mg. Adsorbed hydrogen was found to occupy 3-fold hollow sites, in agreement with DFT calculations. In the future, we plan to obtain similar data on surfaces with adsorbed impurities or transition metal atoms to see how their presence affects hydrogen binding.

We also analyzed pressed pellets of MgB_2 powder, which was found to consist of oxidized Mg with almost no B present. Even after sputter cleaning the surface composition was $Mg_{0.7}O_{0.2}B_{0.1}$. We monitored the cleaned material's reactivity to both molecular and atomic hydrogen. There was no uptake of molecular D_2, but when the sample was exposed to a flux of atomic D, noticeable uptake of D occurred. An accompanying drop in scattering intensity from Mg suggested that D chemisorbs on surface Mg atoms. Our initial LEIS measurements demonstrate how it is possible to monitor in great detail the surface condition of model hydrogen storage materials and their reactivity with hydrogen. We plan to apply this technique to $Ca(BH_4)_2$ as samples become available.

MHCoE Theory Group, Joint Kinetic Studies

The Theory Group (TG) of the MHCoE makes use of first-principles methods to conduct materials discovery, provide thermodynamic and kinetic data for use by engineering and modeling efforts, and suggest new directions for experimentalists and interpretation of their results. The TG consists of researchers at five MHCoE partner institutions, comprising effectively of four groups: Sandia National Laboratories, Carnegie Mellon University (CMU) and the University of Pittsburgh (Pitt), University of Illinois at Urbana-Champagne (UIUC) and NIST. 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.

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,

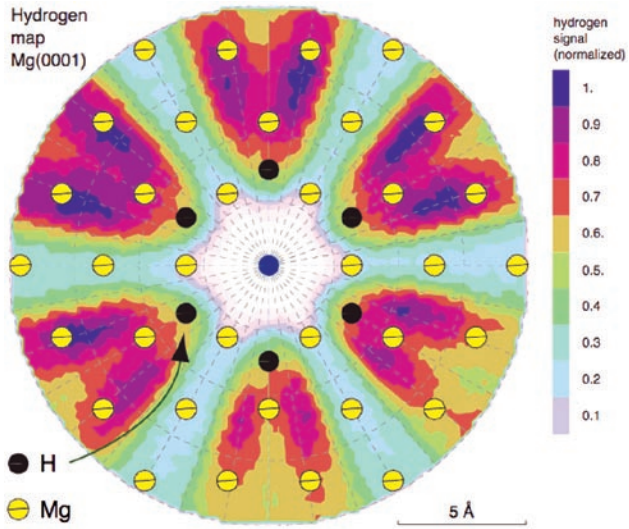

FIGURE 6. Hydrogen Atom Map of the H/Mg(0001) Surface Obtained from LEIS

initiated and led by SNL in FY 2007, to probe the effects of surface poisoning on the kinetics of alanate ($MAlH_4$) rehydrogenation.

The TG conducted extensive discussions this year to identify one or more metal hydride systems to serve as the focus of an investigation of kinetics-related issues. Although kinetic factors are suspected of limiting the reversibility of a number of metal-hydride systems, the specific reasons behind the limitation are rarely clear. Thus, we established criteria for selecting a system for investigation: 1) evidence of reversibility, 2) relevant crystal structures should be known, and 3) known thermodynamics of the relevant reactions. Few systems meet all three criteria. However, the series $MAlH_4$ (M = Li, Na, K) comes closer than any other we are aware of. The reactions of concern are:

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

(3) $M_3AlH_6 \leftrightarrow 3\ MH + Al + 3/2\ H_2$

Within this series it is particularly intriguing that $KAlH_4$ is known to be reversible without a catalyst, $NaAlH_4$ becomes reversible if a catalyst is added, but $LiAlH_4$ is not reversible. This trend suggests that in making the transition from K to Li, something changes systematically that raises an activation barrier and inhibits rehydrogenation. Crystal structures for the relevant compounds are available and the thermodynamics for the reactions are known as well (either measured or calculated). Consequently, the $MAlH_4$ system was suggested by SNL as an excellent initial starting system for identifying and understanding kinetic limitations. It furthermore has the advantage that $LiAlH_4$ has a high weight-percentage of hydrogen (10.6 wt%). Thus, if the kinetic limitation can be overcome, $LiAlH_4$ has the potential to be a useful storage system.

Reaction 3 appears to be the slow step in the rehydrogenation process, based on experimental evidence. The question raised by the TG was, is the reaction of water and/or oxygen with the surface of LiH the cause of irreversibility of this reaction? Existing thermodynamic data (NIST) for bulk materials indicate that the reaction $MH + H_2O \rightarrow MOH + H_2$ is exothermic for M = Li, Na, and K, but is the most exothermic for Li, suggesting that the lack of reversibility in MH is caused by reaction with environmental water. van't Hoff plots from the NIST data indicate vanishingly small equilibrium pressures of O_2 over MH as well. Thus, the thermodynamics alone indicate that the most likely environmental contaminants are capable of poisoning these materials. These conclusions, however, are based on bulk thermodynamics and do not account for the energetics of the exposed surfaces of the material. DFT methods employed by two of the four TG groups are an excellent tool for probing surface thermodynamics and can also be used to identify transition states (and thus determine activation barriers).

To date, the TG has examined the thermodynamics of H, H_2, O_2, O, and H_2O adsorption on LiH, NaH, and KH surfaces. To assess this, calculations were performed by the Pitt/CMU group to identify the most thermodynamically stable surface. Of the various surfaces examined, including (100), (111), (110), and (121), the (100) surface is the most stable in all three cases. Thus, all calculations of adsorbate energies were performed using the (100) MH surface as the starting point.

Not surprisingly, the calculations indicate that H_2 interacts only weakly with all three MH (100) surfaces, with adsorption energies no larger than 4.0 kJ/mol. This corresponds to weak physisorption at best. In contrast, O_2 reacts with MH surfaces without a barrier (i.e., the reaction is spontaneous) to form strongly bonded surface OH groups. The adsorption energy depends on the initial site for the adsorption. For illustration, the surface structures predicted for LiH and NaH are shown in Figure 7(a).

DFT predicts that H_2O adsorbs exothermically to MH surfaces; however, an energy barrier must be surmounted for dissociation to occur. Binding without dissociation to LiH(100) is the weakest (0.35 eV vs. 0.62 eV on KH). Alternatively, coadsorption of OH and H leads to either H_2O on the LiH surface or adsorbed OH and H_2, depending to the initial adsorption sites. Using DFT molecular dynamics to predict what will happen at finite temperatures of 600-700 K, we find that H_2O will dissociate on the LiH and NaH surfaces to form bound OH and gas-phase H_2. The results suggest the need for additional calculations to determine: 1) barriers to dissociation of H_2O and 2) barriers to diffusion of H_2

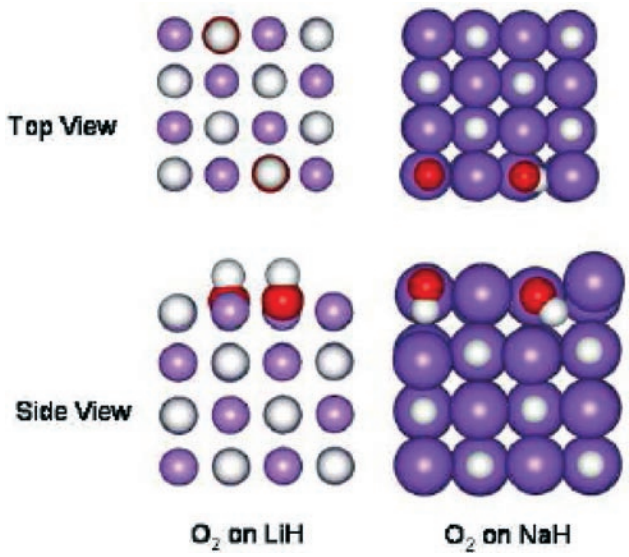

FIGURE 7(A). The optimized structures of 25% O_2 coverage on LiH(100) and NaH(100). Purple denotes the metal ion (Li or Na), white denotes hydrogen and red denotes oxygen. Calculations performed by Pitt/CMU.

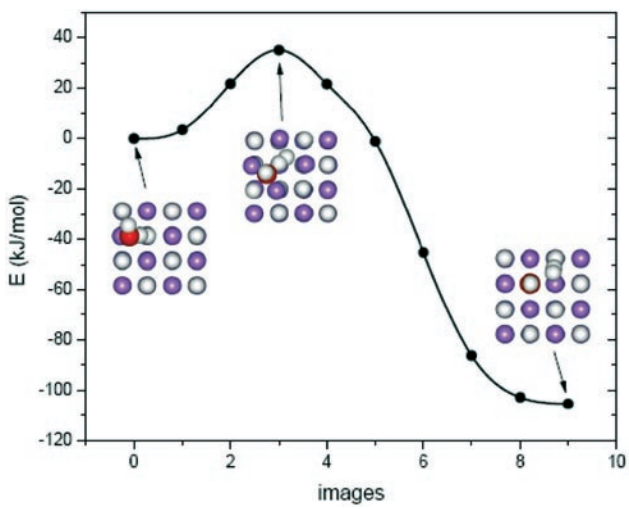

FIGURE 7(B). Energetics of dissociative adsorption of H_2O on the LiH(100) surface predicted by the NEB/DFT method of the Pitt/CMU group. The left side corresponds to the unreacted H_2O/LiH(100) system. The right side is the reacted final state.

through the three MOH layers. One such calculation performed by the Pitt./CMU group is shown in Figure 7(b), who used the nudged elastic band (NEB) method of determining reaction pathways on surfaces using DFT. In this case, a barrier height of 35.2 kJ/mol is predicted for the reaction of H_2O with the LiH(100) surface.

Conclusions

- MC approach improved, ground state structures being found.
- Bialkali borohydrides explored with MC method, new promising materials predicted.
- New solid-state synthesis route and characterization of $Ca(BH_4)_2$.
- Showed partial reversibility of $Ca(BH_4)_2$ at high H_2-pressures (<700 bar).
- Completed phase stability study of Li-B-H system (with UIUC).
- New ternary Na-Ge-H compound obtained by high P, T sintering.
- Completed study of $LiNH_2/Li_3AlH_6$ system (with the National University of Singapore).
- Developed HTS synthesis strategies for rapidly assessing promising hydrides.
- Built 130 bar, two hotplate HTS prototype system for initial evaluation.
- Designed 2,000 bar, 18 hotplate system for eventual HTS use.
- Validated diagnostics (H_2 gas detection and calorimetry) for HTS approach.
- Demonstrated HTS synthesis capability with MgH_2, $NaAlH_4$.
- Determined geometric structure of hydrogen adsorption on Mg(0001).
- Found that the (100) surface is the most stable plane of LiH, NaH, and KH.
- Whereas H_2 interacts weakly with (100) MH surfaces, O_2 reacts spontaneously with MH(100) to create strongly bound OH.

Future Directions

- Continue MC theoretical search for promising mixed cation borohydrides.
- Begin search for promising mixed anion compounds such as $Ca(AlH_4)(BH_4)$.
- Synthesize predicted bialkali borohydrides and explore their reversibility.
- Continue optimizing performance of calcium borohydride at lower P, T.
- Discover new complex anionic materials guided by theory.
- Build 15 hotplate HTS reactor for 800°C, 20 kpsi studies.
- Examine surfaces of $Ca(BH_4)_2$ and their dehydrogenation using LEIS.
- Use HTS to screen promising alkali and alkaline earth metal-based borohydrides.
- Explore possibilities to design alternative nanostructured metal hydrides to improve hydrogen storage properties.
- Complete the TG investigation of the reversibility of $MAlH_4$ surfaces.

- Initiate new TG effort to probe nanoscale effects in hydrogen storage.

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 filed 02/12/2007.

2. W. Luo and K. Stewart, "Reactor for removing Ammonia", SD-8574, Patent application filed 07/13/06.

FY 2007 Publications/Presentations

1. E. Rönnebro, E. H. Majzoub, "Crystal structure, Raman Spectroscopy and ab-initio Calculations of a New Bialkali Alanate K_2LiAlH_6", J. Phys. Chem. B. 110(51); 25686-25691, 2006.

2. E. Rönnebro, "Overview of Metal Hydride Center of Excellence (MHCoE) Activities and Sandia's Recent Progress on Discovering New Complex Hydrides", invited seminar at Arizona State University, Tempe, AZ on June 8, 2006.

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4. E. Rönnebro, "Complex Metal Hydrides", Lawrence Berkeley National Laboratory, July 21, 2006.

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