

VI.A.4 Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity

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Objectives

- Explore the quaternary phase space between sodium hydride (NaH), alane (AlH₃), transition metal or rare earth (M) hydrides (MH_z, where z= 1-3) and molecular hydrogen (H₂) to discover new complex hydride compounds capable of reversibly storing hydrogen to a capacity of ≥ 7.5 wt %.
- Demonstrate a methodology for computationally evaluating the thermodynamic stability of a wide range of possible structures having high hydrogen capacity.
- Determine the optimum synthesis route for obtaining stable compounds from (i) solid state processing (SSP), (ii) molten state processing (MSP) or (iii) solution based processing (SBP); and characterize their structures.
- Demonstrate the operability temperature and pressure range of these compounds and the sorption kinetics under various conditions.
- Determine the cyclic stability of these compounds.
- Determine the economics of scaling up these materials to full production.

Technical Barriers

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

- Weight & Volume
- Durability

- Refueling Time
- Hydrogen Capacity and Reversibility

Technical Targets

This project is designed to couple atomistic/thermodynamic modeling and varied synthesis techniques in the search for new high hydrogen capacity materials composed of mixed light metal/transition metal complexes having hydrogen capacities greater than 7.5 wt%. Insights gained from these studies will greatly add to understanding the phase relationships of mixed complex hydrides and the synthesis routes used obtain them. The scope of study is limited to materials that meet the 2010 hydrogen storage targets, especially specific energy, and energy density, charging time, minimum full flow rate, system fill time, transient response and storage system cost.

Approach

- Investigate compositional space $(Sm_i, Dm_j)(Pe_x H_y)_z$, where Sm are the s-electron metals (alkaline metals and alkaline earth metals), Dm are the d-electron metals (transition metals) and Pe are the p-electron elements (metals, semi-metals and non-metals).
- Perform combined first principles atomistic modeling and thermodynamic modeling to identify stable high hydrogen capacity compositions.
 - Perform structural analogue review to identify stable crystallographic structures and elemental components
 - Perform ground state atomistic modeling to determine minimum energy structures
 - Perform phonon analysis to determine finite temperature stability
 - Thermodynamic assessment to identify multi-component phase space
- Investigate synthesis methodologies.
 - SSP utilizing mechano-chemical milling of active starting materials
 - MSP employing combined high temperature and high pressure exposure and
 - SBP exploiting organic solutions of complex compounds and metathesis techniques to economically separate new high capacity compounds
- Undertake characterization and performance evaluations.
 - Perform XRD, conventional X-Ray diffraction to identify new phases and quantify phase composition
 - Perform neutron diffraction to determine crystallography, especially deuterium atomic positions
 - Perform high-resolution XRD to gain insight into details of crystallography
 - Perform time-resolved XRD to gain understanding of dehydrogenation phase kinetics and mechanisms
 - Perform pressure composition isotherm analysis to gain understanding of sorption kinetics as a function of temperature and pressure
- Support commercialization.
 - Develop manufacturing processes to reduce cost and scale-up production
 - Develop business analyses for the commercialization of hydrogen storage systems integrated with fuel cell power plants

Accomplishments

- Developed and verified a methodology for atomistic and thermodynamic modeling to predict thermodynamic stabilities of various structures in the $\text{Na}_i\text{Ti}_j\text{Al}_k\text{H}_x$, $\text{Na}_i\text{Li}_j\text{Al}_k\text{H}_x$ and $\text{Na}_i\text{Mg}_j\text{Al}_k\text{H}_x$ & $\text{Na}_i\text{Li}_j\text{Mg}_k\text{Al}_x\text{H}_y$ with the predicted structure for $\text{Na}_2\text{LiAlH}_6$ given in Figure 1.
- Characterized the $\text{Na}_i\text{Li}_j\text{Mg}_k\text{Ti}_x\text{Al}_y\text{H}_z$, $\text{Na}_i\text{Li}_j\text{Mg}_k\text{Ni}_x\text{Al}_y\text{H}_z$, and $\text{Na}_i\text{Li}_j\text{Mg}_k\text{Co}_x\text{Al}_y\text{H}_z$ systems at 200 bar and temperatures ranging from 80 to 120°C using SSP.
- Characterized compounds in the $\text{Na}_i\text{K}_j\text{Al}_k\text{H}_x$, $\text{Na}_i\text{Ti}_j\text{Al}_k\text{H}_x$, $\text{Na}_i\text{Mg}_j\text{Al}_k\text{H}_x$ systems using MSP.
- Characterized compounds in the $\text{Na}_i\text{Ti}_j\text{Al}_k\text{H}_x$, $\text{Na}_i\text{Li}_j\text{Al}_k\text{H}_x$, $\text{Na}_i\text{Mg}_j\text{Al}_k\text{H}_x$, $\text{Na}_i\text{Li}_j\text{Mg}_k\text{Al}_x\text{H}_y$, and $\text{Na}_i\text{Li}_j\text{Mg}_k\text{Ti}_x\text{Al}_y\text{H}_z$ systems using SBP.
- Carried out quantitative X-ray diffraction assessment on the SSP, MSP and SBP synthesized material to understand the various phase relationships. Identified numerous hydrogen storage systems having *in-situ* reversible weight fractions to 5.6 wt.% hydrogen, but none meeting the 7.5 wt% goal.

Future Directions

- Perform combined atomistic and thermodynamic assessment of all potential high capacity hydrogen storage systems.
- Continue SSP, MSP and SBP analyses of combining Fe, Cr, Mn, N, B with $(\text{Sm}_i, \text{Dm}_j)(\text{Pe}_x\text{H}_y)_z$.

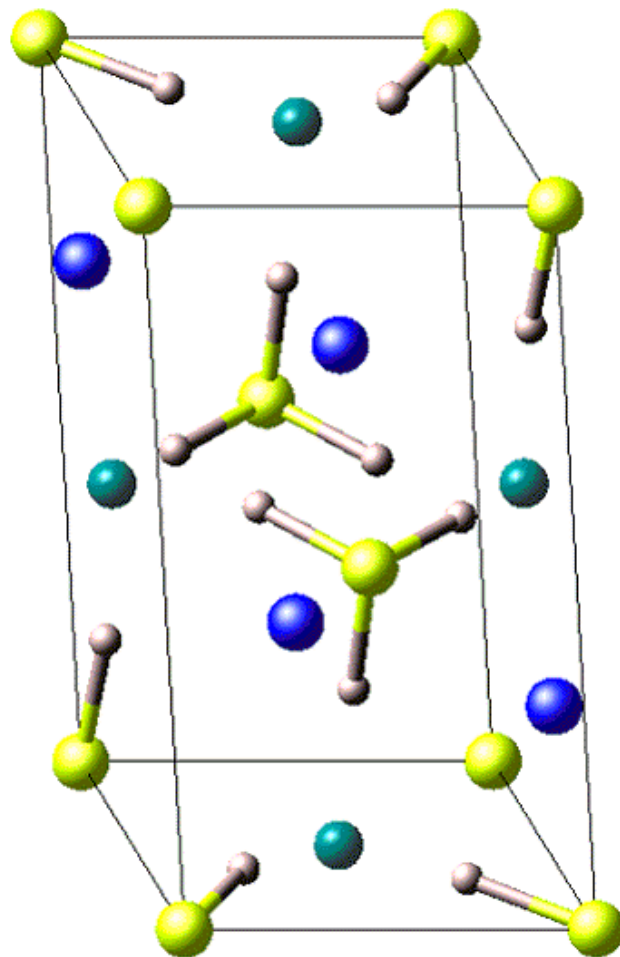


Figure 1. Predicted Lowest Energy Atomic Configuration for $\text{Na}_2\text{LiAlH}_6$ at 0K with Li-green, Na-blue, Al-yellow and H-white

Introduction

This project will identify new complex hydrides having weight fractions of retrievable hydrogen of greater than 7.5 wt% residing in the quaternary or higher phase space between alkaline metal hydrides (AmH), Alkaline earth metal hydrides (AeH_2) alane (AlH_3), transition metal (Tm) hydrides (TmH_z , where $z=1-3$) and molecular hydrogen (H_2). This will be done by first principal atomistic investigations along with collaborating empirical synthesis. Three synthesis routes for obtaining stable compounds include (i) solid state processing (SSP), (ii) molten state processing (MSP) and (iii) solution based processing (SBP). Investigation of all three

routes will yield a high probability of successful compound extraction.

Approach

This project combines theoretical, experimental, analytical, manufacturing and business disciplines to identify, optimize, and implement hydrogen storage systems based upon stable complex hydride compounds that have a reversible hydrogen capacity of 7.5 wt % or higher. The compositional space defined for investigation here include $(\text{Sm}_i, \text{Dm}_j)(\text{Pe}_x\text{H}_y)_z$, where Sm are the s-metals (alkaline metals and alkaline earth metals), Dm are the d-metals (transition metals) and Pe are the

p-elements (metals, semi-metals and non-metals). Identification of specific high capacity hydrogen storage materials will be accelerated with the use of combined first principles atomistic modeling and thermodynamic modeling to identify stable high hydrogen capacity compositions. Simultaneously, the team will apply multiple synthesis methodologies to isolate new hydrides, and couple thermodynamic predictions and structural characterizations to verify structures of newly identified phases. Multiple synthesis methods incorporated here include (i) Solid State Processing, SSP, utilizing mechanico-chemical milling of active starting materials, (ii) Molten State Processing, MSP, employing combined high temperature and high pressure exposure and (iii) Solution Based Processing, SBP, exploiting organic solutions of complex compounds and metathesis techniques to economically separate new high capacity compounds. The team will conduct three levels of performance evaluations to select compositions for further development, optimize dehydrogenation-hydrogenation catalysis with spectroscopic mechanistic studies and first-principles screening simulations, develop manufacturing processes to reduce cost and scale-up production, and develop business analyses for the commercialization of hydrogen storage systems integrated with fuel cell power plants.

Results

Atomistic Modeling

The implementation of coupled predictive methodologies provided a new capability to survey, simulate, and evaluate new candidate hydrogen storage compounds, prior to their identification or preparation in the laboratory. The coupled predictive methodologies joined together ground state minimizations with density functional theory, thermodynamic property predictions with direct method lattice dynamics, and phase stability predictions with chemical thermodynamics. The key parallel developments required for implementation of these methodologies, included: a) approaches for proposing input candidate structures, b) criteria for down-selection and refinement of candidate phases, c) methods for assessment and incorporation of newly predicted thermodynamic data alongside

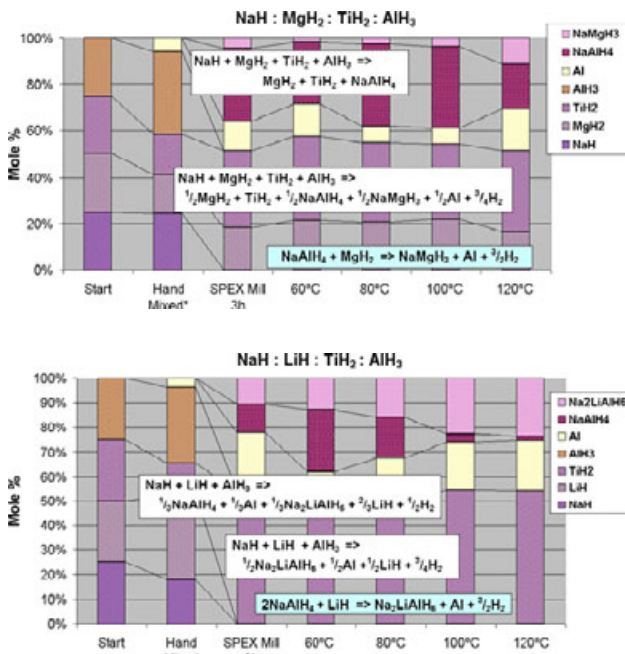
experimental data, and d) procedures to predict the relative phase stability of the candidates compared to existing known phases, over a wide range of temperatures and pressures. To prepare for deployment, the coupled predictive methodologies were validated by demonstrating excellent agreement between the predicted and experimentally measured thermodynamic properties for sodium alanate and other well-known compounds.

The coupled predictive methodologies were used to survey well over 200 proposed phases in five quaternary spaces, formed from various combinations of Na, Li Mg and/or Ti with Al and H. In the first task, over 170 phases in the quaternary spaces encompassing known alanate phases: Na-Ti-Al-H, Li-Ti-Al-H, and Na-Li-Al-H, were evaluated. No new candidate phases were identified in these systems. However, thermodynamic predictions were made for the lesser-known $\text{Na}_2\text{LiAlH}_6$ phase, which has been incompletely characterized. This provided a test-case opportunity for implementing phase stability and reaction predictions for this mixed-alkali phase, with respect to known alanate phases and other disproportionation products. This analysis identified temperature-pressure conditions for *in-situ* reversibility accessing 5.2 weight % hydrogen in the Na-Li-Al-H system, with $\text{Na}_2\text{LiAlH}_6$ serving as a lower pressure intermediate hydride phase, compared to Na_3AlH_6 . The calculated ground state structure for $\text{Na}_2\text{LiAlH}_6$ is given in Figure 1. In the second task, over 50 candidate phases were simulated within the Na-Mg-Al-H and Li-Mg-Al-H quaternary systems. In each system, numerous favorable ground-state minimized candidate structures were identified for the compound stoichiometries $\text{Am}_2\text{MgAlH}_7$ and AmMgAlH_6 , where Am represent the alkaline metals Na or Li. Thermodynamic property predictions were made for a number of these candidates, as well as competing lower order phases. Thermodynamic databases have been established for both of these systems. An in-depth study of phase stability and reaction calculations is currently underway to assess the reaction reversibility for these candidates and the most favorable disproportionation products. The most favorable reactions will determine the potential for reversible hydrogen content for these compounds.

Solid State Processing

Solid State Processing, SSP, has been used to characterize the $\text{Na}_i\text{Li}_j\text{Mg}_k\text{Al}_x\text{H}_y$, $\text{Na}_i\text{Li}_j\text{Mg}_k\text{Ti}_x\text{Al}_y\text{H}_x$, $\text{Na}_i\text{Li}_j\text{Mg}_k\text{Ni}_x\text{Al}_y\text{H}_x$, and $\text{Na}_i\text{Li}_j\text{Mg}_k\text{Co}_x\text{Al}_y\text{H}_x$ systems at 200 bar and temperatures ranging from 80 to 120°C. SSP utilizes high energy attrition ball milling of mixed powders of metal hydrides and metals. Subsequent exposure to high pressure hydrogen at moderate temperatures is used to aid the kinetics in the formation of high hydrogen capacity materials. X-ray diffraction, XRD, was used to quantitatively evaluate the composition of reactants and products. To date, no new ordering phenomenon have been identified; however, a number of relatively high single step hydrogen storage reactions have been identified which are apparently reversible between 80 and 120°C.

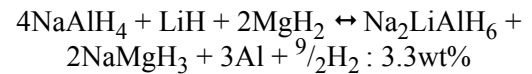
The results from 1:1:1:1 combinations of $\text{NaH}:\text{MgH}_2:\text{TiH}_2:\text{AlH}_3$ are given in Figure 2a, which resulted in a reversible reaction of:



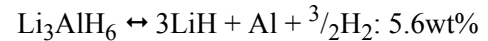
The results from 1:1:1:1 combinations of $\text{NaH}:\text{LiH}:\text{TiH}_2:\text{AlH}_3$ are given in Figure 2b, which resulted in a reversible reaction of:



The results from 1:1:1:1 combinations of $\text{NaH}:\text{LiH}:\text{MgH}_2:\text{AlH}_3$ are given in Figure 2c, which resulted in a reversible reaction of:



The results from 1:1:1:1 combinations of $\text{LiH}:\text{MgH}_2:\text{AlH}_3$ are given in Figure 2d, which resulted in a reversible reaction of:



While none of these reactions is in the 6-7% range to meet the DOE goals, it is interesting to note the complex interaction between various known complex hydrides. Single step 3-5 wt% reactions are common, and result from mixed alkaline metal hydrides and alanes as products. Based on these findings, a comprehensive investigation is being conducted into the thermodynamics of solid state

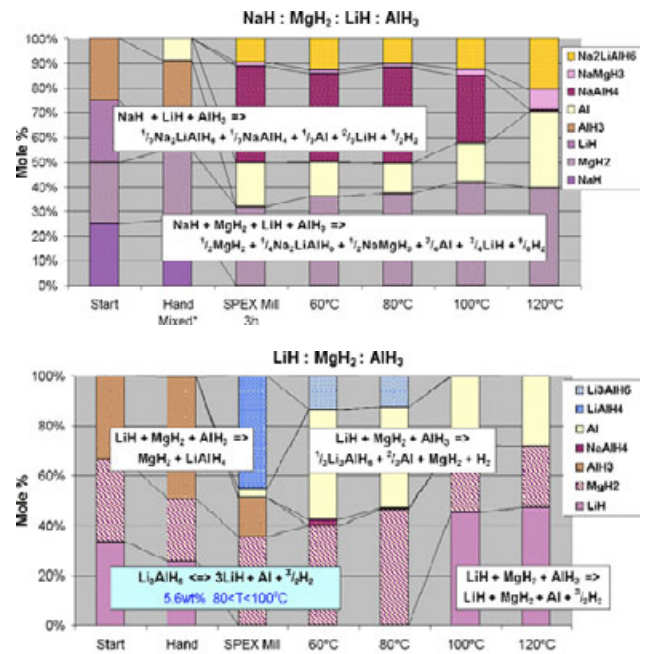


Figure 2. Results of XRD analysis of mixed Am and Ae hydrides with AlH_3 after various processing and charging treatments for 20 hours at 200 bar at the indicated temperatures. Reversible reactions are observed with mixed AmAe hydrides as products having weight fractions ranging between 2.6 and 5.6 wt%.

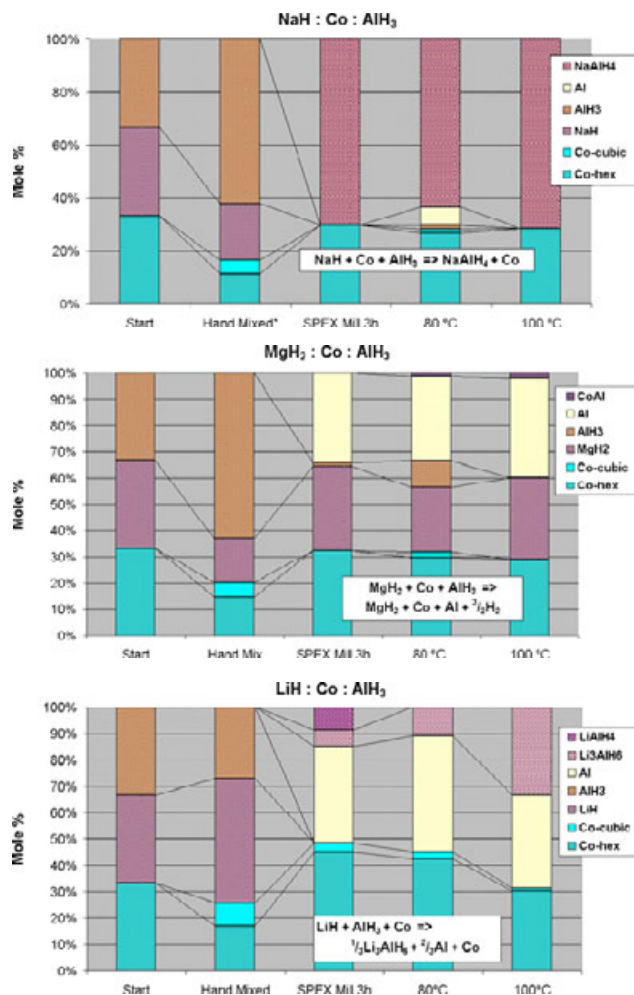


Figure 3. Results of XRD analysis of mixed Am and Ae hydrides, Tm powders with AlH_3 after various processing and charging treatments for 20 hours at 200 bar at the indicated temperatures. No interaction with alkaline metals, alkaline earth metals Ni, Co and aluminum hydrides have been observed under the thermal and pressure conditions tested.

hydride combinations to identify *in-situ* rechargeable systems having high capacity.

Transition metal additions have also been investigated with 1:1:1 mixtures of $\text{AmH}:\text{AeH}_2:\text{Tm}:\text{AlH}_3$ where Tm have thus far been Ni and Co. Results of these experiments with Co are shown in Figure 3 and have shown no interaction of either Ni or Co in the hydride formation process.

Molten State Processing

Sodium aluminum hydride (SAH) was mixed in excess with LiH and NaH and processed in the

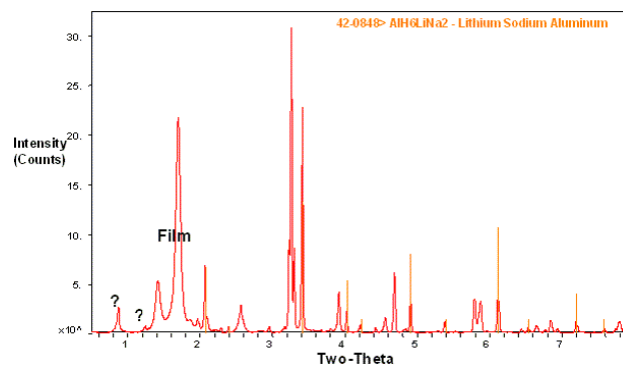


Figure 4. XRD Analysis of SBP NaH, NaAlH_4 and LiH Showing a High Yield $\text{Na}_2\text{LiAlH}_6$

molten state. The resultant product was analyzed by XRD, shown in Figure 4, and the compound, $\text{Na}_2\text{LiAlH}_6$ was detected. SAH mixed with LiH, NaH, and KH and melt processed showed that ionic exchange occurring in the melt, since KAlH_4 was detected by XRD as shown in Figure 5. SAH mixed with MgH_2 produced XRD evidence that NaMgH_3 was formed by melt processing seen in Figure 6. Mixing SAH with TiH_2 unfortunately produced no reaction.

Solution Based Processing

SBP has been used to look for unique compositions using scalable routes. Systems targeted were quaternary metal alانات systems. These systems include the following:

Ti/Na/Al/H System

The initial alenate target was the Ti/Na/Al/H system (titanium doped SAH). We used $\text{TiCl}_3(\text{THF})_3$ as our dopant based on its high solubility in THF.



Doped NaAlH_4 having Ti at 2, 4, 10, and 33% levels were prepared. By way of gas evolution monitoring, the results were consistent with formation of TiAl_3 . Hydrogen storage performance of these compounds has thus far been inferior to the corresponding ball-milled materials, presumably due to the larger particle size. The thermal behaviors of these compounds have been investigated by DSC (differential scanning calorimetry). No new ordered phases have been observed.

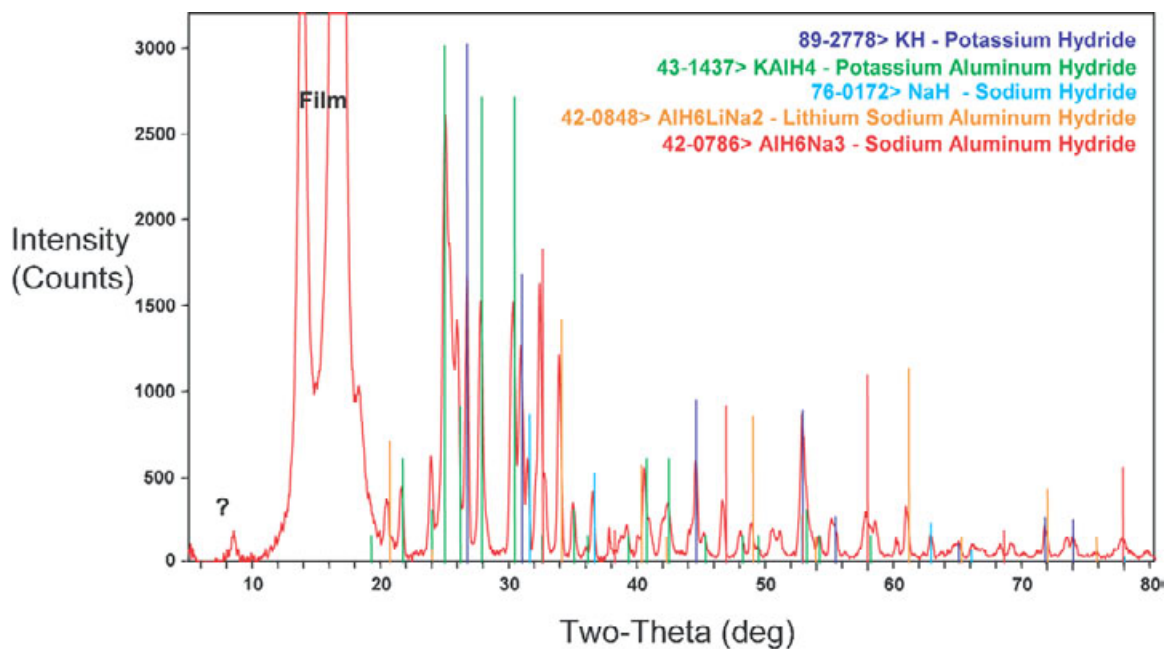


Figure 5. Formation of KAlH₄ Illustrated by XRD Analysis Resulting from SBP Processed Mixture of NaAlH₄ and KH

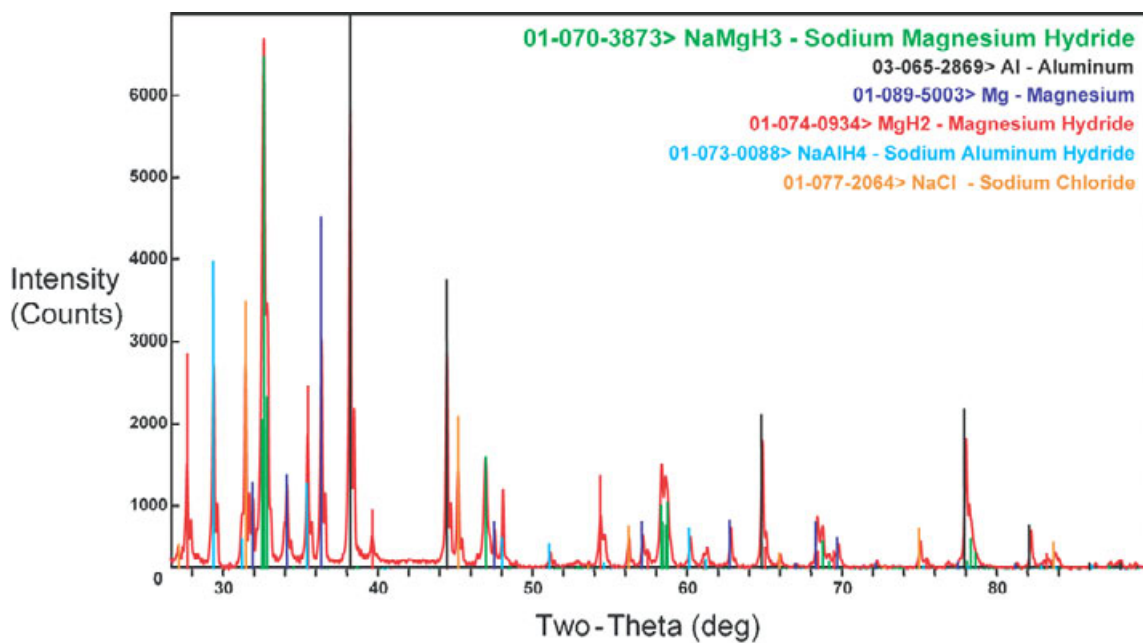


Figure 6. Formation of NaMgH₃ Illustrated by XRD from Mixture of MSP Processed NaAlH₄ and Mg

Li/Mg/Al/H System

The target quaternary compounds of Li/Mg/Al/H were made from the product of MgCl_2 , LiAlH_4 and NaAlH_4 in Et_2O . Use of NaAlH_4 was a key finding that allowed a more complete removal of chloride-containing by-products.



Three products described by the formula $\text{Li}_x\text{Mg}(\text{AlH}_4)_{2+x}$, where $x = 1, 2,$ and 2.4 , have been isolated. Thermal, structural, and performance properties of these compounds are under investigation.

Conclusions

Combined atomistic and thermodynamic modeling has been shown to yield accurate predictions of plateau pressures suitable for determination of *in-situ* rechargability. Numerous reversible hydrogen storage reactions have been identified via combinations of hydrides and alanates yielding *in-situ* reversible storage reactions of 2.6-5.6 wt%. Solution based processing can be used to readily synthesize mixed complex alanate compositions having high hydrogen capacity.

FY 2005 Publications/Presentations

- O. M. Lovvik, O. Swang, and S. M. Opalka, "Modeling alkali alanates for hydrogen storage by density-functional band-structure calculations" accepted for publication in *J. Mater. Res.*, Volume 20, Number 12, December 2005.
- C. Qiu, S. M. Opalka, G. B. Olson, and D. L. Anton, "The Na-H System: from First Principles Calculations to Thermodynamic Modeling," submitted to *Zeitschrift fur Metallkunde* in June 2005.
- O. M. Lovvik and S. M. Opalka, "First-principles calculations of Ti-enhanced NaAlH_4 ," *Phys. Rev. B* **71** 054103-1-10 (2005).
- C. Qiu, G. B. Olson, S. M. Opalka and D. L. Anton, "A Thermodynamic Evaluation of the Al-H System," *J. of Phase Equilibria and Diffusion* **25**(6) 520-527 (2004).
- O. M. Lovvik, S. M. Opalka, H. W. Brinks and B. C. Hauback, "Crystal structure and thermodynamic stability of the lithium alanates LiAlH_4 and Li_3AlH_6 ," *Phys. Rev. B* **69** 134117-134125 (2004).
- C. Qiu, G. B. Olson, S. M. Opalka, and D. L. Anton, "Thermodynamic Modeling of Sodium Alanates and the Effect of Ti," presentation to be given at the 2005 Fall MRS Meeting, Boston, MA, November 29-Dec. 3, 2005.
- O. M. Lovvik, O. Swang, S. M. Opalka, and P. N. Molin, "Alanates for Hydrogen Storage – Density Functional Calculations of Structural, Electronic, and Thermodynamic Properties," invited presentation to be given at the 2005 Fall MRS Meeting, Boston, MA, November 29-Dec. 3, 2005.
- S. M. Opalka, O. M. Lovvik, H. W. Brinks, B. C. Hauback, Paul W. Saxe, and D. L. Anton, "Combined Experimental-Theoretical Investigations of the Na-Li-Al-H System," *Materials Science & Technology 2005* to be held in Pittsburgh, PA, on September 25-28, 2005.
- C. Qiu, S. M. Opalka, D. L. Anton, G. B. Olson, "Thermodynamic Modeling of Sodium Alanates," *Materials Science & Technology 2005* to be held in Pittsburgh, PA, on September 25-28, 2005.
- O. M. Lovvik and S. M. Opalka, "First-principles calculations of Ti-enhanced NaAlH_4 ." Presentation at the International Symposium of Metal Hydrogen Systems (MH2004), Krakow, Poland, September 10, 2004.
- "Synthesis and crystal structure of $\text{Na}_2\text{LiAlD}_6$ " *J. Alloys and Compounds* Volume 392, Issues 1-2, 19 April 2005, Pages 27-30, H.W. Brinks, B.C. Hauback, C.M. Jensen and R. Zidasn
- "Synergistic effects of co-dopants on the dehydrogenation kinetics of sodium aluminum hydride" *J. alloys and compounds* Volume 391, Issues 1-2, 5 April 2005, Pages 245-255 J. Wang, A.D. Ebner, R. Zidan and J.A. Ritter
- "Effect of graphite as a co-dopant on the dehydrogenation and hydrogenation kinetics of Ti-doped sodium aluminum hydride" *J. Alloys and Compound*, in press, Jun Wang, Armin D. Ebner, Tanya Prozorov, Ragaiy Zidan and James A. Ritter
- Hydrogen Economy Workshop, *Invited Speaker*, for the Department of Energy, (1) Hydrogen Storage R&D Key Issues for the Hydrogen Economy, (2) Solid-State Hydrogen Storage Systems Cairo Egypt January 31 – February 2, 2005
- ASM Material Solution Conference, *Invited Speaker*, Development and Characterization of Complex Hydrides, Columbus, OH Oct. 18- 21 2004.