

IV.A.1j Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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Contract Number: DE-FC36-05GO15063

Project Start Date: April 1, 2005
Project End Date: February 28, 2010

- (A) System Weight and Volume
- (E) Charging/Discharging Rates
- (J) Thermal management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Accomplishments

- Synthesis and characterization of a library of novel of anionic transition metal borohydrides with potential to meet U.S. DOE targets.
- Identification of a borohydride that undergoes reversible dehydrogenation of 8 wt% H₂ to the corresponding boride.
- Confirmation of low level hydrogenation of aluminum in 2:1 CO₂/H₂ supercritical media by magic angle spinning (MAS) ²⁷Al nuclear magnetic resonance (NMR).
- Development an improved supercritical fluids (SCFs) medium for the hydrogenation of Al such that 5% of the Al is converted to AlH₃.
- Development of a low-temperature, organo-metallic method for high level, 16% loading of Al and Mg in carbon aerogels without host degradation.
- Demonstration of reversible hydrogenation of Mg intercalated carbon aerogels through four cycles.



Objectives

- Develop new materials with potential to meet the DOE 2010 kinetic and system gravimetric storage capacity targets such as novel borohydrides that can be reversibly dehydrogenated at low temperatures and Al and Mg nano-confined in carbon aerogels.
- Determine the mechanism of action of dopants for the kinetic enhancement of the dehydrogenation and re-hydrogenation of complex hydrides (Fiscal Year 2006 only).
- Develop a method for the hydrogenation of Al to alane, AlH₃, at moderate pressures in hydrogen containing supercritical fluids.

Technical Barriers

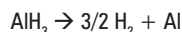
This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

Introduction

We are developing Group I and II salts of anionic transition metal borohydride complexes as hydrogen storage materials. These complexes have a higher hydrogen content (9-13 wt%) than neutral transition metal borohydrides. The anionic character of these materials may result in an increased stability and reduced volatility when compared to neutral transition metal borohydride complexes. Also, for some anionic complexes, the amount of diborane produced during dehydrogenation is very low. Finally, the thermodynamic parameters of these anionic complexes might allow reversibility.

We are also exploring new approaches for the incorporation of aluminum and magnesium into carbon aerogels. Intercalation into these nano-porous materials may change the thermodynamics and/or enhance the kinetics of the reversible hydrogenation of Al and Mg thus bringing them into the realm of practically viable hydrogen storage materials.

Additionally, a new task was recently initiated to target the use of alane as a hydrogen storage material. The dehydrogenation of alane follows the reaction:



This reaction provides 10 wt% of available hydrogen. In addition, the controllable dehydrogenation is possible at acceptable rates below 100°C with additives [1] or if ball milled [2]. We have been working in collaboration with the University of New Brunswick (UNB) to develop a new approach for reversing the dehydrogenation process of alane. This process will utilize the high solubility of hydrogen in supercritical fluids, which will reduce the requisite high pressures for aluminum hydrogenation. Our collaborators at UNB have previously demonstrated that the hydrogen pressure required for the re-hydrogenation of sodium alanate is dramatically lowered from 100 to 15 atm when it is carried out in a supercritical media. The hydrogenation Al/MgH_2 to $\text{Mg}(\text{AlH}_4)_2$ in supercritical fluids is also included in the scope of this new task.

Approach

We have developed a novel approach for the intercalation of Mg in carbon aerogel materials. This procedure achieves high, cyclable magnesium loadings in carbon aerogels without host degradation. Since this method is performed at relatively low temperatures, the pore size of the aerogel material is preserved without degradation. We have also begun to examine the effects of nano-confinement on the kinetics and thermodynamics of the dehydrogenation of MgH_2 .

In addition to the complexes $\text{MM}'(\text{BH}_4)_x$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}; \text{M}' = \text{Zn}, \text{Mn}, \text{and Zr}$), we have prepared $\text{MM}'(\text{BH}_4)_x$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}; \text{M}' = \text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Fe}, \text{Co}, \text{Ni}, \text{and Cu}$). These novel materials have been characterized by infrared, solid-state MAS ^{11}B NMR, and/or powder X-ray diffraction (XRD), and their hydrogen release and possible reversible uptake studied by thermal programmed desorption studies.

The kick-off meeting for the new task was held at the UNB on September 12, 2007. Prof. Sean McGrady presented an overview of our collaborative efforts to date. He revealed that low-levels of hydrogenation (~3% of the aluminum) had been achieved through the reaction of Ti-doped Al with supercritical CO_2/H_2 at 70°C. This conclusion is supported by solid-state MAS ^{27}Al NMR analysis of the hydrogenated material which indicates that the amount of alane present in the Al (prepared from dehydrogenated alane) increases following supercritical charging. Additionally, isothermal desorption studies and gas chromatographic analysis the desorbed gas confirm that hydrogen is absorbed and about 3% of the aluminum undergoes hydrogenation. However, X-ray analysis of the material

following hydrogenation does not reveal any crystalline alane phases, thus the AlH_3 that formed is highly amorphous and perhaps limited to the surface of the aluminum.

Results

Task 1. Characterization of the Active Titanium Species in Ti Doped NaAlH_4

This task has been completed.

Task 2. Spectroscopic Studies of Complex Hydrides

The characterization of anionic borohydride compounds can not be generally accomplished by XRD due the highly amorphous nature of the material. Alternatively, MAS ^{11}B NMR spectroscopy allows detection and differentiation of all the borohydride species that are present (Figure 1). In collaboration with the University of Geneva, characterization has also been possible by infrared and Raman spectroscopy. Infrared and Raman spectra of $\text{LiSc}(\text{BH}_4)_4$ and $\text{Zr}(\text{BH}_4)_4$ provide fingerprints of the compounds and reveal details of the coordinative interaction of the BH_4 ligands to the transition metal center (Figure 2).

The lithium salt of the $[\text{Sc}(\text{BH}_4)_4]^-$ complex was synthesized according to the following reaction:

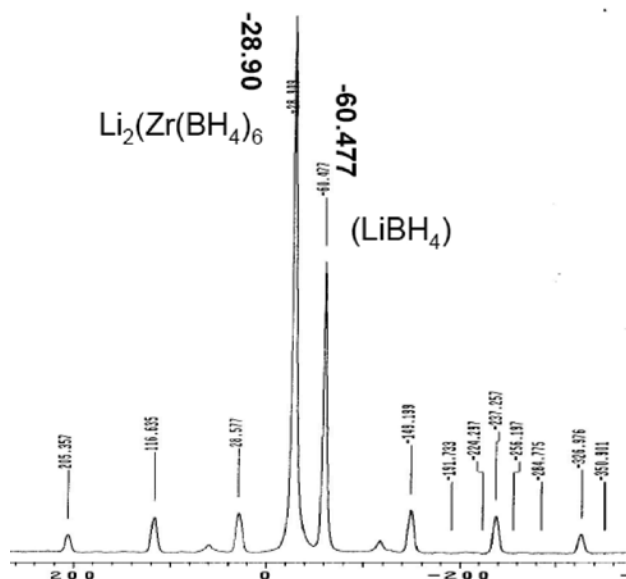


FIGURE 1. ^{11}B NMR spectroscopy allows detection and differentiation of all the borohydride species that are present.

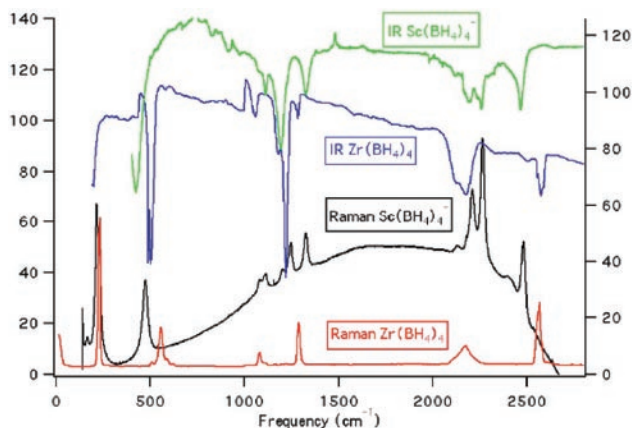


FIGURE 2. Infrared and Raman spectra of $\text{LiSc}(\text{BH}_4)_4$ and $\text{Zr}(\text{BH}_4)_4$ provide fingerprints of compounds and reveal details of the coordinative interaction of the BH_4 ligands to the transition metal center.

This material was found to be unusually crystalline and its molecular structure, seen in Figure 3, has been determined by synchrotron power XRD data in a collaborative effort with the University of Geneva and the Institute for Energy Research (Norway). This study confirmed the asymmetric η^3 -coordination of the BH_4 ligands in the Sc complex that was predicted by the spectroscopic studies.

Task 3. Thermodynamic Properties of Complex Hydrides

This task has been completed.

Task 4. Kinetic Enhancement of “Thermodynamically Tuned” Binary Hydrides

Our efforts have focused on the synthesis of Al and Mg intercalated carbon aerogels. Initial syntheses utilized carbon aerogels with an average pore width of 4.1 nm that were supplied by center partner, HRL. The aerogels were intercalated with Et_3Al precursor and then heated to 200°C to eliminate the organic groups from the aluminum. The resulting materials were analyzed by solid-state, MAS ^{27}Al NMR. The materials that we initially obtained were found to contain major amounts of oxidized Al. We reasoned that this was due to the presence of absorbed water in the carbon aerogels. Therefore, in the next round of experiments, the as received carbon aerogels were preheated to 200°C for 10 h under high vacuum before use. Following treatment of the aerogels with the Et_3Al precursor and subsequent thermal analysis, there was a clear indication that Al had been intercalated into the aerogel as the weight of the sample was found to have increased by 10.9 wt%. Furthermore, MAS ^{27}Al NMR analysis of the material showed that the aluminum is present only as aluminum metal in these materials. Powder XRD

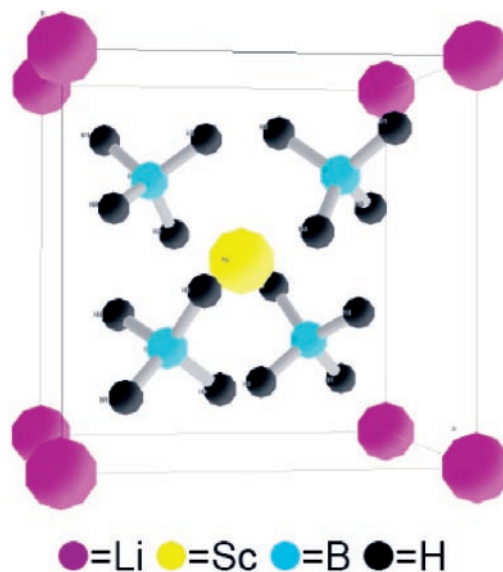


FIGURE 3. Crystal structure of $\text{LiSc}(\text{BH}_4)_4$ determined by synchrotron X-ray data confirms the asymmetric η^3 -coordination of the BH_4 ligands to Sc.

studies of the material performed by center partner, HRL, confirmed the presence of Al metal in the aerogel. Thermogravimetric analysis that was also carried out by HRL indicated that 7.3 wt% Al has been intercalated into the aerogel which is in approximate agreement with our observed weight gain.

Then we examined whether these materials could be hydrogenated. These studies involved pressurizing the Al intercalated carbon aerogels with 120 atm of hydrogen at temperatures ranging from 80 - 150°C for 24 h. No measurable drop in hydrogen pressure was observed during any of our experiments. Following the attempted hydrogenation, the materials were subjected to isothermal heating in a thermal volumetric analyzer (pressure-composition-temperature). These studies gave no indication of gas evolution and thus indicated that hydrogenation of the Al had not occurred. Similarly, analysis of the materials by MAS solid-state ^{27}Al NMR also gave no indication that hydrogenation had occurred.

Our studies were expanded to include the nano-confinement of magnesium in carbon aerogel materials. The preparation of magnesium intercalated carbon aerogels was studied by utilizing organo-magnesium precursors in a unique synthetic procedure. Our novel, “neat” organo-metallic approach achieves high, cyclable magnesium loadings in carbon aerogels without host degradation. This method is performed at relatively low temperatures to preserve the pore size of the aerogel material. The loading procedure begins with carbon aerogel submerged and stirred in neat liquid. Next, organo-metallic $\text{Mg}(\text{C}_4\text{H}_9)_2$ is added to the mixture. The

aerogel intercalated with organo-metallic $\text{Mg}(\text{C}_4\text{H}_9)_2$ is filtered from the suspension and heated to 200°C . Subsequently, the organic groups are reductively eliminated. This preparation method has yielded high (9-16 wt%) Mg loadings without degradation of the aerogel. Reversible hydrogenation of the material has been demonstrated through four cycles (Figure 4).

Task 5. Synthesis and Evaluation of Anionic Borohydrides

Our studies showed that some anionic borohydride complexes evolve hydrogen at relevant temperatures ($\sim 100^\circ\text{C}$) with low levels of diborane contamination. For example, $\text{NaMn}(\text{BH}_4)_4$ undergoes rapid dehydrogenation of >3 wt% at 130°C with 50:1 $\text{H}_2/\text{B}_2\text{H}_6$ molar ratio observed in the eliminated gases. Also, $\text{Na}_2\text{Zr}(\text{BH}_4)_6$, unlike $\text{Zr}(\text{BH}_4)_4$, is non-volatile and undergoes rapid elimination of 2-3 wt% H_2 at 40 - 110°C with no detectable B_2H_6 contamination. In order to test the reversibility of the dehydrogenation of $\text{LiM}(\text{BH}_4)_x$ $M = \text{Sc, Mn, and Zr}$, the hydrogenation of mixtures of LiH/MB_2 and LiB_2/MB_2 was attempted at 15,000 psi in collaboration with Dr. Ronnebro at Sandia National Laboratories. The attempts proved to be unsuccessful as the only observed product was LiBH_4 . Further attempts using CaH_2 and CaB_2 also failed to yield anionic transition metal borohydride complexes. In continuing these studies, a “new borohydride” has been found that undergoes reversible dehydrogenation to the corresponding boride. The following reaction takes place at 1,000 atm H_2 and 230°C as follows:

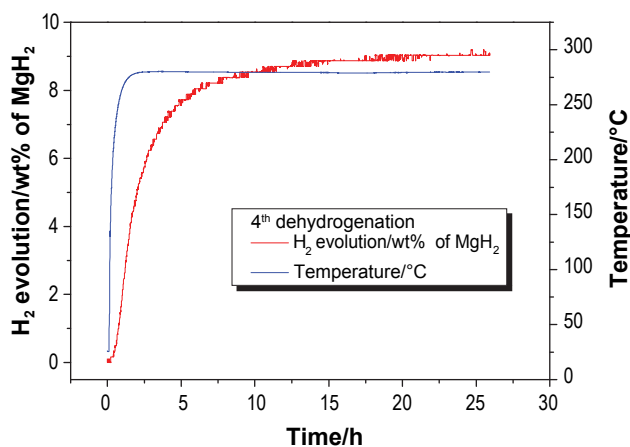


FIGURE 4. Reversible hydrogenation of Mg-intercalated carbon aerogel has been demonstrated through four cycles.

Task 6. Recharging of Light Metal Hydrides through Supercritical Fluid Hydrogen

The phase boundary between liquid and gas phases disappears in SCFs providing a material which has different physical properties than gases and liquids. Collaborators at the UNB have previously shown that an 80% yield of NaAlH_4 from NaH/Al is obtainable at 80°C in supercritical CO_2/H_2 .

Our initial studies focused on the hydrogenation of titanium-doped aluminum in 2:1 supercritical CO_2 - H_2 . Isothermal desorption from hydrogenated Al at 110°C indicates that 3% of the Al was hydrogenated (Figure 5). Gas chromatography (GC) analysis shows that hydrogen is evolved only from the Al subjected to the SCF (Figure 6). The hydrogenation of aluminum in 2:1 supercritical CO_2 - H_2 has been confirmed by MAS ^{27}Al NMR. As shown in Figure 7, the NMR shows a clean Al peak prior to hydrogenation. After 4 hours in 2:1 supercritical CO_2 - H_2 at 60°C , an alane peak is revealed. Presumably, the low-level hydrogenation occurs on the surface of the powder. In order to screen

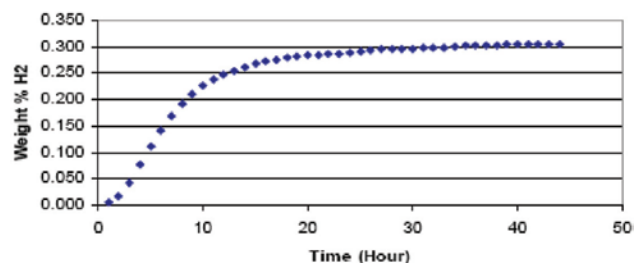


FIGURE 5. Isothermal desorption from hydrogenated Al at 110°C indicates that 3% was hydrogenated.

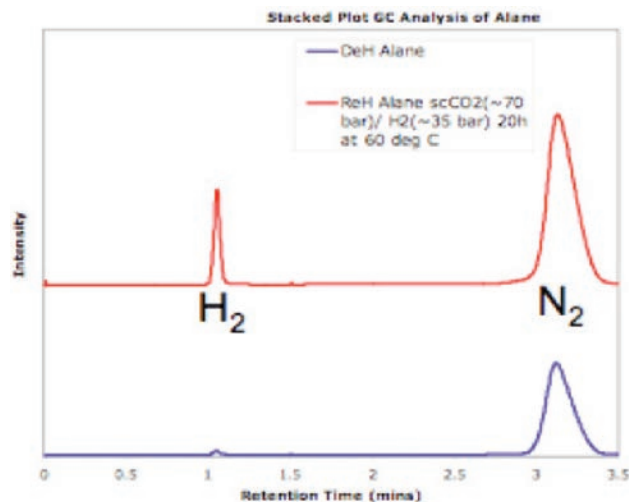


FIGURE 6. GC analysis shows that hydrogen is evolved only from the Al subjected to the supercritical fluid. N_2 was utilized as carrier gas for analysis.

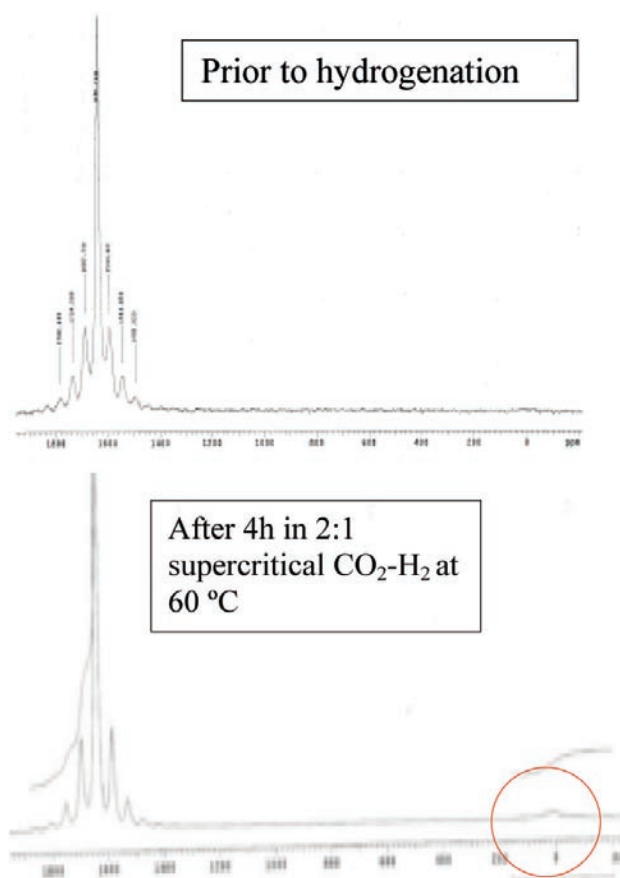


FIGURE 7. Hydrogenation of aluminum in 2:1 supercritical $\text{CO}_2\text{-H}_2$ is confirmed by MAS ^{27}Al NMR.

Al hydrogenation in alternative SCFs, a dedicated SCF reaction station has been constructed at the UNB. Preliminary experiments indicate that higher levels, >5% of Al hydrogenation can be achieved in an alternative SCF.

Conclusions and Future Directions

In summary, high Mg loadings of carbon aerogels without host degradation can be achieved using a relatively low temperature, “neat organo-metallic” method. Additionally, reversible hydrogenation of the material has been demonstrated through four cycles.

Our studies have also shown that anionic transition metal borohydride complexes can be conveniently prepared from the ball milling of alkali metal borohydrides with transition metal chlorides or transition metal borohydrides. These anionic complexes, unlike most neutral transition metal borohydrides, are non-volatile and highly stable at ambient temperatures. These materials have been found to undergo rapid elimination of 2-8 wt% hydrogen at relevant ($\sim 100^\circ\text{C}$) temperatures. In addition, anionic

manganese and zirconium borohydride complexes have been found to undergo elimination of hydrogen at low temperatures with little or no tandem elimination of diborane. Recently, a new borohydride has been found that undergoes reversible dehydrogenation to the corresponding boride.

Finally, the reaction of Ti-doped Al with scCO_2/H_2 under relatively mild conditions leads to low-level hydrogenation, presumably on the surface of the powder. The occurrence of hydrogenation have been confirmed by isothermal desorption studies, gas chromatography, and MAS ^{27}Al NMR. A dedicated SCF reaction station has been constructed at UNB. Preliminary experiments indicate high levels of hydrogenation can be achieved in an alternative SCF.

Our future work will focus on the following points:

- Mg-intercalated carbon aerogels:
 - Determine pressure-composition-temperature isotherms to determine if nano-confinement alters ΔH_{dehyd}
 - Conduct isothermal kinetic studies to determine if nano-confinement alters dehydrogenation kinetics.
 - Utilize carbon aerogels with a variety of pore sizes to optimize Mg loadings.
- Borohydrides:
 - Determine ΔH_{dehyd} through differential thermal analysis.
 - Continue high-pressure re-hydrogenation studies in collaboration with Dr. Ronnebro at Sandia National Laboratories.
 - Explore variation in catalysts.
- Alane:
 - Exploration of improving levels of hydrogenation by conducting reaction in alternative SCFs.
 - Explore hydrogenation of activated Al rather than dehydrogenated alane.
 - Screen a variety of initiators/catalysts.
 - Explore SCF synthesis of $\text{Mg}(\text{AlH}_4)_2$.
 - Supercritical hydrogenation to be carried out at UNB.
 - Product characterization (XRD, MAS ^{27}Al NMR) and analysis/quantification of desorbed hydrogen to be carried out at UH.

FY 2008 Publications/Presentations

Publications

1. Pressure Induced Structural Phase Transition in NaAlH_4 . R.I. Kumar, A.I. Cornelius, O. Tshauner, M.P. Sulic, C.M. Jensen. *Phys. Rev. B.* **2007**, *75*, 174110.

2. Synthesis and Crystal Structure of β -AlD₃. H.W. Brinks, W. Langley, C.M. Jensen, J. Graetz, J.J. Reilly, B.C. Hauback. *J. Alloys and Comp.* **2007**, 433(1-2), 180.
3. Crystal Structure of γ -AlD₃. H.W. Brinks, C. Brown, C.M. Jensen, J. Graetz, J.J. Reilly, B.C. Hauback. *J. Alloys and Comp.* **2007**, 441(1-2), 364.
4. NMR Studies of Aluminum Hydride Phases and their Stabilities. S-J. Hwang, R.C. Bowman, J. Graetz, J.J. Reilly, W. Langley, C.M. Jensen. *J. Alloys and Comp.* **2007**, 446-447, 290.
5. Dynamics of Defects in Alanates. R. Cantelli, O. Palumbo, A. Paolone, C.M. Jensen, M.T. Kuba, R. Ayabe. *J. Alloys and Comp.* **2007**, 446-447, 260.
6. Thermal Properties of AlH₃-etherate and its Desolvation Reaction into AlH₃. T. Kato, S. Orimo, Y. Nakamori, T. Komuro, C. Brown, C.M. Jensen. *J. Alloys and Comp.* **2007**, 446-447, 276.
7. High Throughput Screening of the Ternary LiNH₂-MgH₂-LiBH₄ Phase Diagram. G.J. Lewis, J.W.A. Sachtler, J.J. Low, D.A. Lesch, S.A. Faheem, P.M. Dosek, L.M. Knight, C.M. Jensen, J. Yung, A. Sudik, D.J. Sigel, D. Halliday, A. Drews, R. Carter, C. Wolverton, V. Ozolins, S. Zhang. *J. Alloys and Comp.* **2007**, **2007**, 446-447, 355.
8. EELS standards for Identification of Catalytic Species in NaAlH₄ Hydrogen Storage Materials. D.D. Graham, L.F. Culnane, M. Sulic, C.M. Jensen, I.M. Robertson. *J. Alloys and Comp.* **2007**, 446-447, 255.
9. Complex Hydrides for Hydrogen Storage. S. Ormio, Y. Nakamori, J. Eliseo, A. Zuttel, C.M. Jensen. *Chem. Rev.* **2007**, 107, 4111. (Invited contribution for topical "Hydrogen" issue).
10. "The Role of Hydrogen Bonding in the Dehydrogenation Kinetics of Sodium Alanate". R. Kadono, K. Shimomura, K.H. Satoh, S. Takashita, A. Koda, K. Nishiyama, E. Akiba, R.M. Ayabe, M. Kuba, C.M. Jensen; *Phys. Rev. Lett.* **2008**, 100, 26401.
5. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials", University of Sydney, Sydney, Australia; 6/21/07.
6. "Chemisorbed Hydrogen" Community Focus Day, Hydrogen Storage Session, Australian Nuclear Science and Technology Organization, Menai, Australia; 6/22/07.
7. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials", Hydrogen in Materials LANSCE Neutron Scattering School; Los Alamos National Laboratory, New Mexico; 7/16/07.
8. "Development of Anionic Transition Metal Borohydride Complexes as Hydrogen Storage Materials", International Energy Agency, Hydrogen Storage Experts Workshop, Egmond aan See, The Netherlands; 9/5/07.
9. "Alane as a Hydrogen Storage Material", BASF, Mannheim, Germany; 9/6/07.
10. "Development of Anionic Transition Metal Borohydride Complexes as Hydrogen Storage Materials"; University of New Brunswick, Canada; 9/12/07.
11. "Hydrogen Storage via Reversible Dehydrogenation of Organic Liquids by Dihydroido Iridium PCP Pincer Complexes"; General Motors Corporate Research Center, Warren, Michigan; 9/16/07.
12. "Development of Anionic Transition Metal Borohydride Complexes as Hydrogen Storage Materials", Materials Science & Technology 2007 Conference and Exhibition; Detroit, Michigan; 9/17/07.
13. "I. Recharging of Light Weight Metal Hydrides Through Hydrogenation in Supercritical Fluids. II. Anionic Transition Metal Borohydride Complexes as Hydrogen Storage Materials"; LANL/NEDO/AIST Workshop on Fuel Cell Performance Improvement & Hydrogen Storage Materials; Tokyo, Japan; 10/30/07.
14. "Exploration of Direct Synthesis of Alane in Supercritical Fluid Media"; Materials Innovations in an Emerging Hydrogen Economy, organized by the American Ceramic Society and American Materials Society; Cocoa Beach, Florida; 2/28/08.
15. "Recent Results in the Development of Anionic Transition Metal Borohydride Complexes as Hydrogen Storage Materials"; International Energy Agency, Hydrogen Storage Experts Workshop; Saint-Alex-des-Monts, Quebec, Canada; 3/5/08.

Presentations

1. "Development of Anionic Transition Metal Borohydride Complexes as Hydrogen Storage Materials", Studies of Matter at Extreme Conditions, 2007 meeting; Symposium on Hydrogen Storage Materials; Miami Beach, Florida; 4/17/07.
2. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials", Users Week 2007, Argonne National Laboratory; 5/7/07.
3. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials", Griffith University, Brisbane, Australia; 6/19/07.
4. "Advanced Complex Hydrides: Development and Fundamental Studies of Promising New Hydrogen Storage Materials", Australian Nuclear Science and Technology Organization, Menai, Australia; 6/20/07.

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