

IV.A.4m Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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Approach

1. Studies of Ti dopants in NaAlH_4 through: electron paramagnetic resonance spectroscopy (in collaboration with the University of Denver), synchrotron x-ray diffraction (Institute for Energy Technology, Norway), and tunnelling electron microscopy (collaborations with the Norwegian Institute of Technology and University of Illinois).
2. Studies of point defects in Ti-doped NaAlH_4 and related materials through anelastic spectroscopy, (collaboration with the University of Rome), nuclear magnetic resonance spectroscopy, and position annihilation studies (collaboration with AIST, Tskuba, Japan) and muon spin resonance studies (collaboration with KEK, Tskuba, Japan).
3. Determine the enthalpies of dehydrogenation of advanced complex hydrides through differential scanning calorimetry (collaboration with University of South Florida) and differential thermal analysis of thermal gravimetric data (collaboration with Tohoku University).
4. Studies of the effects of doping and ball milling on the hydrogen cycling kinetics of “thermodynamically tuned” binary hydrides developed by HRL.

Introduction

We have developed methods of doping sodium aluminum hydride, NaAlH_4 , with titanium and/or zirconium that have given rise to state-of-the-art hydrogen storage materials. However, less than ~5 weight percent hydrogen can be reversibly released from these materials under conditions that are required for the practical operation of an onboard fuel cell. In light of this and other practical limitations, it has become apparent that improved variations of this material must be produced to achieve commercial viability. It has been found that the phenomenon of kinetic enhancement upon transition metal doping extends to other complex hydrides. However, all candidate alanates, amides, and borohydride hydrogen storage materials still have unacceptable dehydrogenation-rehydrogenation kinetics. A better understanding of the fundamental basis of the enigmatic kinetic enhancement of reversible dehydrogenation of the doped materials in the solid state would be invaluable to the effort to improve the hydrogen cycling kinetics of these materials. Therefore, our efforts have been focused on gaining a fundamental understanding of the nature of the dopants and the structural effects they exert on alanates and related materials.

Results

Task 1. Characterization of the Active Species in Doped Complex Hydrides – The majority of the Ti in cycled, Ti-doped NaAlH_4 has been found by electron paramagnetic resonance spectroscopy, synchrotron x-ray diffraction, x-ray absorption fine structure, and tunnelling electron microscopy to be an Al-Ti alloy that is catalytically inactive. This implies the enhanced hydrogen cycling kinetics are due to a minority Ti species. Thus our efforts are currently focused on the characterization the active, minority Ti species through tunneling electron microscopy studies (collaboration with University of Illinois). **Ti species will be identified** on the basis of comparison to the electron energy loss spectroscopy (EELS) spectrum of standards of known Ti species as seen in Figure 1. We have obtained the of the major Ti species in a doped and cycled sample of NaAlH_4 . Synchrotron x-ray and extended x-ray absorption fine structure analysis (EXAFS) studies have previously identified this material to be either cubic Al_3Ti or a solid solution of $\text{Al}_{0.93}\text{Ti}_{0.07}$. Although an excellent fit was observed between our spectra of the major Ti species and cubic Al_3Ti , it was not distinguishable from

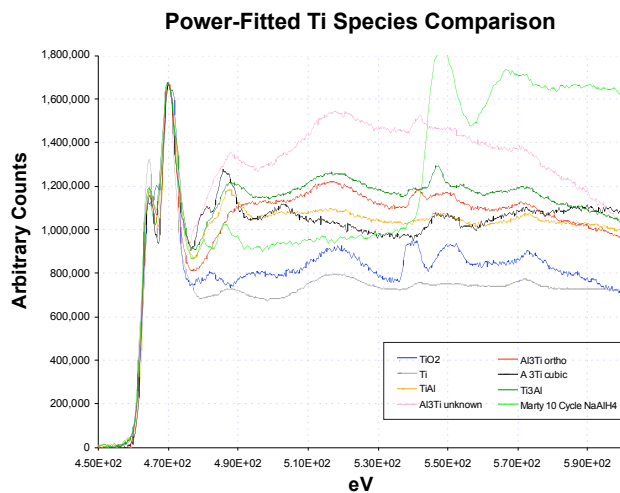


FIGURE 1. Comparison of EELS Spectra of various Ti Species

orthorhombic Al_3Ti . It should, however, be possible to obtain better spectra and/or deconvolution of the data such that the cubic and orthorhombic phases can be differentiated. Once the majority Ti species can be unambiguously identified, we will examine the minor Ti species in the grain boundary regions that are not associated with the segregated alloy crystallites.

Task 2. Spectroscopic Studies of Complex Hydrides – The results of our anelastic spectroscopic studies have provided insight into the mechanism of the reversible dehydrogenation of Ti-doped NaAlH_4 . The studies conducted in FY 2005 showed that highly mobile ($\sim 5 \times 10^3$ jumps/s at 70K) **point defects arise** upon thermal treatment of Ti-doped NaAlH_4 . During FY 2006, we have **observed an isotopic shift in the low temperature spectrum NaAlD_4** . The finding of this deuterium isotope effect provides direct evidence that the defects in the hydride are a hydrogen containing species. We have also found that the generation of the highly mobile hydrogen species occurs in concert with Na_3AlH_6 and takes place at much lower temperatures upon Ti doping of the hydride. Thus it can be concluded that the **fundamental role of the Ti dopants in enhancing the kinetics of the dehydrogenation processes is to decrease the energy barrier to breaking the Al-H bond and increase the population of the mobile hydrogen species**. In light of the insight that has been gained into the reversible dehydrogenation of Ti-doped NaAlH_4 , we are extending our studies to lithium and magnesium amides.

^1H nuclear magnetic resonance (NMR) spectroscopy provides **further evidence for the presence of a mobilized population of hydrogen**. The spectrum of NaAlH_4 consists of an expected broad component with a very long, 2,000 sec, T_1 relaxation time and an

anomalous sharp component with a short, 240 ms relaxation time indicating that it corresponds to highly mobile population of hydrogen. The sharp component is often ascribed to residual solvent. However, the ^2H NMR spectrum of NaAlD_4 that is prepared in protio-solvents also contains an analogous sharp component. We have also eliminated the possibility that the sharp component is free H_2 gas as its spectrum consists of a resonance that is much narrower and has a T_1 of 13 msec. Thus it appears that the mobile hydrogen species is molecular hydrogen H_2 that is lightly bound within the bulk of the hydride.

Task 3. Thermodynamic Properties of Complex Hydrides – Attempts were made to determine if the thermodynamics of the reversible dehydrogenation of alanates are altered upon doping through the determination of enthalpies of dehydrogenation through differential scanning calorimetry (collaboration with University of South Florida) in January. Unfortunately, the data that was obtained was flawed by contributions from exothermic reactions between the hydride and contaminant oxygen in the glove box system. A second round of experiments will be conducted once a higher performance glove box system is installed at USF this summer.

The enthalpy of the α , β , and γ phases of alane, AlH_3 both before and after mechanical modification have been determined through differential thermal analysis of thermal gravimetric data (collaboration with Tohoku University). The values of ΔH_{dehyd} are determined to be -6.0 ± 1.5 , $+3 \sim +5$ and -1.0 ± 0.5 kJ/mol H_2 for the α , γ and β phases, respectively. As illustrated in Figure 2, the milling-time dependences of the powder x-ray diffraction measurement and thermal analyses indicate the occurrence of the dehydrating reactions both in the α and γ phases during milling, but there is no drastic change in the β phase.

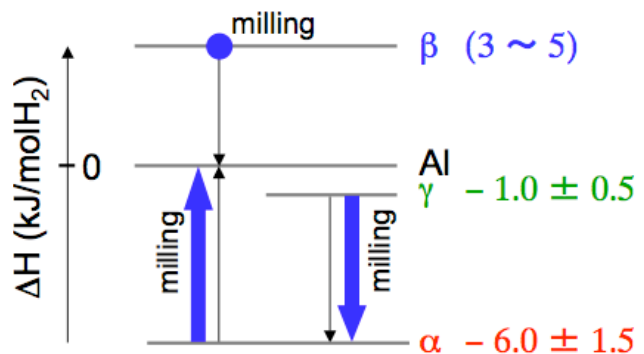


FIGURE 2. Enthalpies of dehydrogenation of the α -, β - and γ -phases of alane and schematic representation of mechanical milling effects on the thermal stabilities of the phases.

Task 4. Kinetically Enhancement of “Thermodynamically Tuned” Binary Hydrides – TiCl_3 has been found to have a pronounced effect on the kinetics of the dehydrogenation of $\text{MgH}_2/2 \text{LiBH}_4$. However, no enhancement is observed during re-hydrogenation or on the second cycle of dehydrogenation. The amount of rapidly released hydrogen during the first dehydrogenation has been found to have a linear relationship with amount of TiCl_3 added. Similar effects have been found with upon addition of TiCl_3 to LiBH_4 (M. Au and A. Jurgensen *J Phys. Chem.* **2006**, *110*, 7062). As seen in Figure 3, our results show that the kinetic effect is due to **stoichiometric** reaction between LiBH_4 and Ti dopants. All efforts to hydrogenate Mg_2Si (with or without Ti additives) have been unsuccessful.

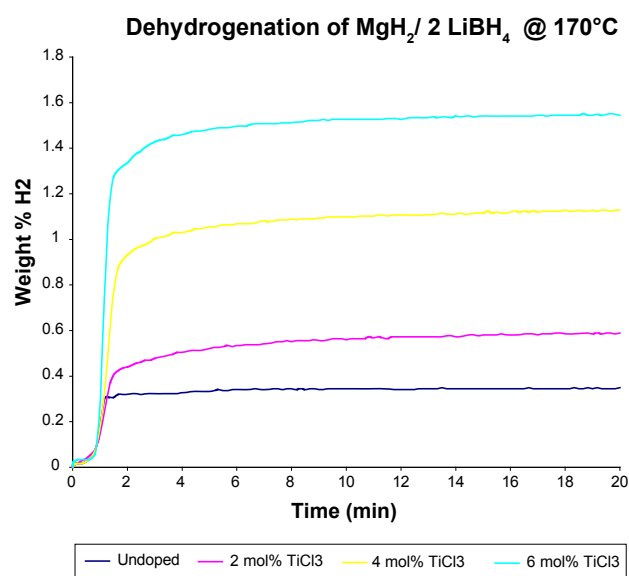


FIGURE 3. Comparison of dehydrogenation of samples of $2\text{LiBH}_4/\text{MgH}_2$ containing varied amounts of TiCl_3 .

Conclusions

1. Our studies of alanates will conclude this year with an effort to identify minority Ti species in the grain boundary regions of Ti-doped NaAlH_4 that is likely to be the species that is responsible for the enhanced kinetics.
2. Anelastic spectroscopy has proven to be a powerful tool for the detection of the hydrogen containing point defects whose generation is greatly promoted in the Ti-doped NaAlH_4 . **The observation of an isotopic shift in the low temperature spectrum NaAlD_4 provides direct evidence that the defects in the hydride are a hydrogen containing species.**

The generation of the highly mobile hydrogen species occurs in concert with Na_3AlH_6 and takes place at much lower temperatures upon Ti doping of the hydride. **Thus it can be concluded that the fundamental role of the Ti dopants in enhancing the kinetics of the dehydrogenation processes is to decrease the energy barrier to breaking the Al-H bond and increase the population of the mobile hydrogen species.** ^1H NMR spectroscopy provides further evidence for the presence of a mobilized population of hydrogen and indicates that it is molecular hydrogen H_2 which is lightly bound within the bulk of the hydride.

3. The enthalpy of the α , β , and γ phases of alane, AlH_3 both before and after mechanical modification have been determined through differential thermal analysis of thermal gravimetric data.
4. The kinetic effect of TiCl_3 dopant on the dehydrogenation of $\text{LiBH}_4/\text{MgH}_2$ has been found to arise from a **stoichiometric** reaction between LiBH_4 and Ti dopants.
5. The scope of work at UH has been extended to borohydrides, amides, and alane.

Future Directions

FY 2006 only

- Complete fundamental studies of alanates.
 - Characterize the minority Ti species in Ti-doped NaAlH_4 in the grain boundary regions that are not associated with the segregated Al_3Ti crystallites by EELS (collaboration with U. Illinois).
 - Carry out positron annihilation (collaboration with AIST, Tskuba and muon spin resonance studies (collaboration with KEK, Tskuba) to further characterize point defects in Ti-doped NaAlH_4 .
 - Continue studies of the anomalous, highly mobile population of hydrogen in NaAlH_4 by ^1H and ^2H NMR spectroscopy.

FY 2006 and continuing in FY 2007

1. Initiate studies of point defects in doped Group I and II amides by anelastic spectroscopy (collaboration with University of Rome and University of Nevada).
2. Identify and optimize catalysts for HRL reversible borohydride based materials and novel materials discovered by Hawaii Hydrogen Carriers, LLC in the UOP led US DOE EERE project for the development of hydrogen storage materials.

Publications

1. Electron Microscopy Studies of NaAlH₄ Doped with TiF₃: Hydrogen Cycling Effects. C.M. Andrei, J. Walmsley, H.W. Brinks, R. Homestad, C.M. Jensen, B.C. Hauback; *Appl. Phys. A* **2005**, *80*, 709.
2. Point Defect Dynamics and Evolution of Chemical Reactions in Alanates by Anelastic Spectroscopy. Oriele Palumbo, Rosario Cantelli, Annalisa Paolone, Sessa S. Srinivasan, Craig M. Jensen; *J. Phys. Chem. B* **2005**, *109*, 1168.
3. Effects of Milling, Doping and Cycling of NaAlH₄ Studied by Vibration Spectroscopy and X-ray Diffraction. S. Gomes, G. Renaudin, H. Hagemann, K. Yvon, M.P. Sulic, C.M. Jensen; *J. Alloys Compd.* **2005** *390*, 305.
4. Synthesis and Crystal Structure of Na₂LiAlD₆. H.W. Brinks, B.C. Hauback, C.M. Jensen, R. Zidan; *J. Alloys Compd* **2005** *392*, 27.
5. Synchrotron X-ray Studies of Al_{1-y}Ti_y Formation and Re-hydriding Inhibition in Ti-enhanced NaAlH₄. Hendrik W. Brinks, Bjørn C. Hauback, Sessa S. Srinivasan, and Craig M. Jensen; *J. Phys. Chem. B* **2005** *109*, 15780.
6. Characterization of Titanium Dopants in Sodium Alanate by Electron Paramagnetic Resonance Spectroscopy Meredith T. Kuba, Sandra S. Eaton, Christine Morales, and Craig M. Jensen; *J. Mater. Res.* **2005**, *20*, 3265.
7. Motion of Point Defects and Monitoring of Chemical Reactions in Sodium Aluminium Hydride. Oriele Palumbo, Rosario Cantelli, Annalisa Paolone, Craig M. Jensen, and Sessa S. Srinivasan; *J. Alloys Compd.* **2005**, *404-406*, 748.
8. Intrinsic and Mechanically Modified thermal Stabilities of α -, β - and γ -Aluminum Trihydride, AlH₃. S. Orimo, Y. Nakamori, T. Kato, C. Brown, C.M. Jensen; *Appl. Phys. A* **2006**, *117*, 27.
9. TiCl₃-enhanced NaAlH₄; Impact of Excess Al and Development of the Al_{1-y}Ti_y Phase During Cycling. Hendrik W. Brinks, Martin Sulic, Craig M. Jensen, and Bjørn C. Hauback; *J. Phys.Chem. B* **2006** *110*, 2740.
10. Fast H-vacancy Dynamics During Alanate Decomposition by Anelastic Spectroscopy: Model for Ti-induced Defect Transport. Oriele Palumbo, Rosario Cantelli, Annalisa Paolone, Martin Sulic, and Craig M. Jensen; *J. Phys. Chem. B* **2006**, *110*, 9105.
3. “Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material”, Symposium on Research Challenges for the Hydrogen Economy, Hydrogen Storage, 230th American Chemical Society National Meeting, Washington, D.C.; August 28, 2005.
4. “Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material”, Purdue University; October 17, 2005.
5. “Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material”, Department of Material Science and Engineering, University of Illinois at Urbana-Champaign; October 18, 2005.
6. “Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material”, Clean energy Research Center, University of South Florida; October 20, 2005.
7. “Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material”, WE-Heraeus-Seminar on Hydrogen Storage with Novel Nanomaterials, Bad Honnef, Germany; October 23, 2005
8. “Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material”, Nissan Research Center, Kanagawa, Japan; October 28, 2005.
9. “Detection and Characterization of Point Defects in Doped Sodium Aluminium Hydride”, Fall 2005 meeting of the Materials Research Society, Boston, MA; November, 2005.
10. “Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material”, Symposium on Metal Hydrides, Symposium on Metal Hydrides and Dihydrogen Complexes: Synthesis, Properties, and Applications in Catalysis and Hydrogen Storage, International Chemical Congress of the Pacific Basin Societies, Honolulu, Hawaii; December 19, 2005.
11. “Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material”, 7th International 21st Century Symposium on Integrated EcoChemistry, Honolulu, Hawaii; December 20, 2005.
12. “Monitoring Point Defect Complexes Arising in the Dehydrogenation of Sodium Aluminum Hydride by Anelastic Spectroscopy”, Symposium on Advanced Materials for Energy Conversion III, 2006 TMS Annual Meeting, San Antonio, Texas; March 21, 2006.

Invited Presentations

1. “X-ray and Neutron Diffraction Diffraction Studies of Ti-doped Sodium Aluminum Hydride, a Promising NewHydrogen Storage Material”, American Crystallographic Association 2005 meeting, Orlando, Florida, May 3, 2005.
2. “Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material”. IPHE International Hydrogen Storage Technology Conference, Lucca, Italy; June 19, 2005.