Introduction

We have developed methods of doping sodium aluminum hydride, NaAlH₄, 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.

Approach

1. Studies of Ti dopants in NaAlH₄ 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 NaAlH₄ and related materials through anelastic spectroscopy, (collaboration with the University of Rome), nuclear magnetic resonance spectroscopy, and position annihilation studies (collaboration with AIST, Tsukuba, Japan) and muon spin resonance studies (collaboration with KEK, Tsukuba, 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.

Results

Task 1. Characterization of the Active Species in Doped Complex Hydrides – The majority of the Ti in cycled, Ti-doped NaAlH₄ 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 NaAlH₄. Synchrotron x-ray and extended x-ray absorption fine structure analysis (EXAFS) studies have previously identified this material to be either cubic Al₆Ti or a solid solution of Al₉₋₆Ti₁₋₀₇. Although an excellent fit was observed between our spectra of the major Ti species and cubic Al₆Ti, it was not distinguishable from...
orthorhomic Al$_3$Ti. It should, however, be possible to obtain better spectra and/or deconvolution of the data such that the cubic and orthorhomic 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 (~5x10$^7$ 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$_3$AlH$_6$ 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.

$^1$H 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 $^1$H 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. The values of $\Delta H_{\text{dehyd}}$ are determined to be -6.0±1.5, +3~+5 and -1.0±0.5 kJ/molH$_2$ for the $\alpha$, $\gamma$ and $\beta$ 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 dehydridding reactions both in the $\alpha$ and $\gamma$ phases during milling, but there is no drastic change in the $\beta$ phase.

\[ \Delta H (\text{kJ/molH}_2) \]

\[ \text{Al} \quad \gamma \quad -1.0 \pm 0.5 \]

\[ \text{milling} \]

\[ \alpha \quad -6.0 \pm 1.5 \]

FIGURE 2. Enthalpies of dehydrogenation of the $\alpha$, $\beta$, and $\gamma$ 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** – TiCl₃ has been found to have a pronounced effect on the kinetics of the dehydrogenation of MgH₂/2LiBH₄. 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 TiCl₃ added. Similar effects have been found with upon addition of TiCl₃ to LiBH₄ (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 LiBH₄ and Ti dopants. All efforts to hydrogenate Mg₂Si (with or without Ti additives) have been unsuccessful.

**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 NaAlH₄ 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 NaAlH₄. The observation of an isotopic shift in the low temperature spectrum NaAlD₄ provides direct evidence that the defects in the hydride are a hydrogen containing species.

**Future Directions**

**FY 2006 only**

- Complete fundamental studies of alanates.
  - Characterize the minority Ti species in Ti-doped NaAlH₄ in the grain boundary regions that are not associated with the segregated Al₃Ti 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 NaAlH₄.
  - Continue studies of the anomalous, highly mobile population of hydrogen in NaAlH₄ by $^1$H and $^2$H 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


Invited Presentations


