

## Hydride Development for Hydrogen Storage

*Karl J. Gross (Primary Contact), Weifang Luo, Eric Majzoub, Greg Roberts, Scott Spangler, Daniel Dedrick, Terry Johnson, Jennifer Chan*

*Sandia National Laboratories*

*P.O. Box 969*

*Livermore, CA 94551*

*Phone: (925) 294-4639; Fax: (925) 294-3410; E-mail: kjgross@sandia.gov*

*DOE Technology Development Manager: JoAnn Milliken*

*Phone: (202) 586-2480; Fax: (202) 586-9811; E-mail: JoAnn.Milliken@ee.doe.gov*

### Objectives

- Develop new complex hydride materials with >6 weight percent system hydrogen capacity at below 100°C.
- Improve the kinetics of absorption and desorption and thermodynamic plateau pressures of Ti-doped sodium alanate metal hydrides.
- Improve processing and doping techniques of Ti-doped sodium alanate to lower cost.
- Help develop state-of-the-art hydrogen storage/delivery systems by determining important materials engineering properties of these complex hydrides.

### 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 R,D&D Plan:

#### On-Board Hydrogen Storage

- A. Cost
- B. Weight and Volume
- C. Efficiency
- D. Durability
- E. Refueling Time
- F. Codes and Standards
- G. Life Cycle, and Efficiency Analyses

#### Reversible Solid-State Material Storage Systems (Regenerated On-Board)

- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption
- O. Test Protocols and Evaluation Facilities
- P. Dispensing Technology.

### Approach

We employ a parallel approach through work in each of the following areas:

- Investigate new complex hydrides to achieve higher capacities.
- Develop new doping process to improve both rates and capacity.

- Experimentally characterize the material properties using analytic techniques such as X-ray and neutron diffraction, electron spin resonance (ESR), nuclear magnetic resonance (NMR), etc.
- Determine the hydriding mechanisms through experimental analysis and modeling.
- Determine important engineering materials properties of the alanates to ensure that complex hydrides are on track for eventual commercialization.

### **Accomplishments**

- Ti-doped  $\text{Mg}_2\text{FeH}_6$  has been investigated as an analog to the alanate system.
- Preliminary investigation of Li-based complex hydrides has been performed.
- Using Sandia's direct synthesis and doping approach, it was found that Ti-halides (Cl, F, Br) all successfully enhance kinetics with  $\text{TiCl}_2$  providing the best results.
- It was also determined that non-reactive precursors ( $\text{TiH}_2$  and pre-reacted halides) improve kinetics, opening up new routes to improve capacity.
- Through collaborations with universities and other labs, we have performed in-depth NMR, neutron diffraction, and ESR measurements studies. These have aided in furthering our understanding of the Ti-doping mechanism.
- Pressure composition temperature isotherm (PCT) measurements have been performed on Na alanate. These measurements indicate that Ti-doping modifies the thermodynamic stability of the materials as well as the kinetics of hydrogen sorption.
- Detailed pressure- and concentration-dependent kinetics measurements have been made. This provided the basis for a more complete kinetics model that now allows the calculation of hydrogen sorption behavior over a broad range of conditions.
- Instrumentation has been completed and experimental work has been started to measure engineering materials properties of the complex hydrides, including thermal and electrical conductivity, volume expansion, and porosity. This work is critical for the ultimate commercialization of this technology.

### **Future Directions**

- New complex hydrides: Continue work to achieve higher hydrogen storage capacities with reasonable kinetics compared with current sodium alanates.
- Search for new  $\text{AlH}_6$ -based alanates: Achieve higher hydrogen storage capacities by discovering new highly coordinated aluminum-hydrogen compounds.
- Structure properties and mechanisms of Ti-doped sodium alanates: Continue work to fully understand how transition metal doping affects the bulk structure properties that lead to enhanced kinetics of sodium alanates.
- Materials synthesis improvements and scale-up: Improve materials synthesis processes for the scale-up and commercialization of the state-of-the-art alanates.
- Effect of contaminants on performance of complex hydrides: Determine the degree to which low-level contaminants in a hydrogen gas supply will impact the performance of complex hydride storage materials.
- Materials compatibility and safety studies: Ensure materials compatibility of the complex hydride storage systems.
- Engineering material properties characterization: Experimentally investigate and report material properties of current state-of-the-art Ti-doped sodium alanates to enable engineering design solutions for hydrogen storage systems.

- Complex hydride systems life cycle analysis: Investigate the technology scale-up effects of potential systems used for solid-state hydrogen storage.

## Introduction

The purpose of this project is to develop and demonstrate the next generation of practical hydrogen storage materials. This task will focus on complex metal hydrides with high reversible hydrogen storage capacities and novel approaches to on-board hydrogen storage.

This research is based on achievements that Sandia has made in developing advanced Ti-doped Na alanates [1]. The discovery of enhanced hydrogen sorption by Ti-doped alanates opened up an entirely new prospect for lightweight hydrogen storage [2-3]. These materials have nearly ideal equilibrium thermodynamics, high capacities, and moderate kinetics. However, while the hydrogen capacity is 2 to 3 times better than commercial low-temperature hydrides, it does not meet the DOE/FreedomCAR storage capacity targets. Thus, other higher capacity reversible complex hydrides must be developed. At the same time, Na alanates continue to provide a good working model to better understand reversible hydrogen sorption in complex hydrides. Sandia's direct synthesis process and new Ti-doping methods have led to a dramatic improvement in the reversible hydrogen capacity and hydrogen absorption and desorption rates. These methods will be employed to seek out advanced complex hydrides with larger hydrogen storage capacities and better performance.

## Approach

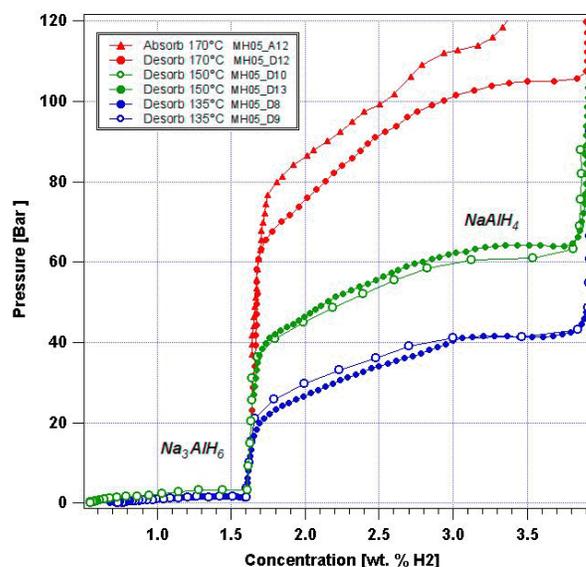
Ti-doped alanate samples were prepared by direct synthesis from NaH and Al powders doped with 4 mol.% of  $\text{TiCl}_3$ . These powders were mechanically milled for 30 minutes in an argon atmosphere. Samples were prepared, transferred and measured without exposure to air.

Thermodynamic measurements were performed on a fully automated commercial PCT instrument. Absorption and desorption kinetics measurements were obtained volumetrically using manual Sieverts' apparatus and a cylindrical 316 SS reactor (1.3 cm outer diameter by 0.12 cm wall thickness and length

of 12 cm) containing about 1.5 g of catalyzed samples. A thermocouple well in the center of the vessel allows for accurate temperature measurements during cycling. Data were recorded via computer, and measurements lasted from minutes to several days, depending on the  $\text{TiCl}_3$  level test pressure, and temperature conditions.

## Results

**Thermodynamics of Ti-doped alanates.** Our most recent measurements of the thermodynamic properties of the current generation of 4 mol.% Ti-doped alanates were performed using an automated PCT instrument (Figure 1). These measurements show the two plateau regions associated with the formation and decomposition of the  $\text{NaAlH}_4$ , the  $\text{Na}_3\text{AlH}_6$  phases. Absorption and desorption measurements of the  $\text{NaAlH}_4$  phase were made at 135, 150 and 170°C. These clearly show two distinct regions. One portion has a flat pressure plateau and the other is sloping. These results suggest that sample is composed of an inhomogeneous distribution of material with dissimilar kinetic and thermodynamic properties. One hypothesis is that

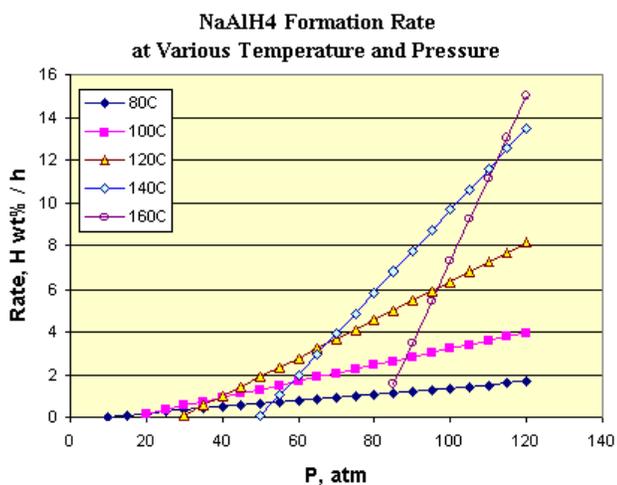


**Figure 1.** PCT measurements of Hydrogen Absorption and Desorption of  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$  at 135, 150 and 170°C

the Ti is not homogeneously distributed in the sample. If that is the case, then there is a direct link between the presence of Ti and a change in the thermodynamics of alanate formation.

Thermodynamics being a bulk property, this could only happen through introduction of Ti into the crystal lattice. Knowing whether Ti is at the surface or present in the bulk is fundamental to solving the mystery of the mechanism of the Ti-enhanced sorption properties. These preliminary results are being followed up with a more detailed analysis.

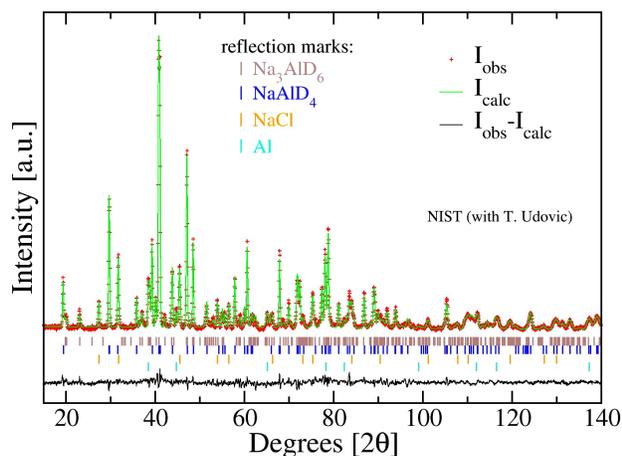
**Kinetics of Ti-doped alanates.** Hydrogen sorption rates of Ti-doped Na-alanate were measured at various temperatures, pressures, and hydrogen concentrations. Rate equations have been derived from this data to calculate the formation and decomposition kinetics of both  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$ . It was found that, in addition to temperature, the pressure differential (applied pressure vs. equilibrium pressure) and composition have a strong impact on the sorption rates. These equations provide important information that is needed for alanate performance modeling. Using these equations, the optimum temperature can be estimated for hydrogen absorption at a given applied pressure. For example, the best temperature for hydrogen absorption using 100 bar of hydrogen is 140°C, not 160°C (Figure 2). These equations can also be used to estimate the lowest temperature



**Figure 2.** Calculated Hydrogen Absorption Rates for  $\text{NaAlH}_4$  as a Function of Pressure at Different Temperatures

needed for desorption at a given rate and pressure. We intend to extend this approach to the kinetics of other hydrogen storage materials.

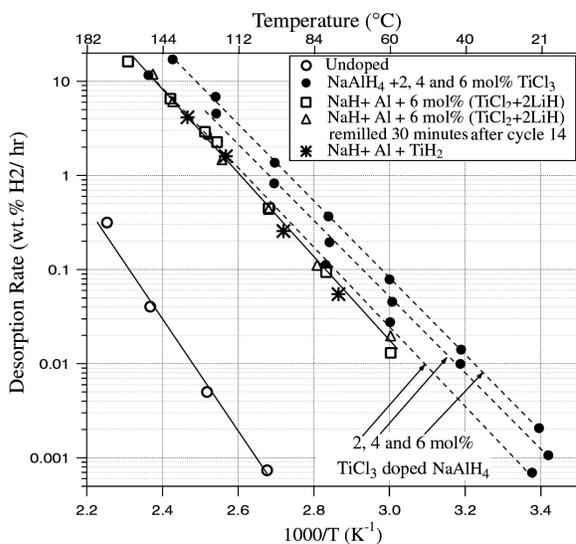
**Fundamental studies of Ti-doped alanates.** The structure of Ti-doped sodium aluminum deuteride has been determined using Rietveld refinement of X-ray and neutron powder diffraction data and compared to that of undoped  $\text{NaAlD}_4$  and  $\text{NaAlH}_4$ . Neutron powder diffraction data were taken at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) with T. Udovic (Figure 3). Refinement of the diffraction data for deuterium atom positions of  $\text{NaAlD}_4$  was complicated due to the four phases present in the sample: the tetra-deuteride  $\text{NaAlD}_4$ , the hexa-deuteride  $\text{Na}_3\text{AlD}_6$ ,  $\text{NaCl}$ , and  $\text{Al}$ . Due to the small level of Ti-doping (4 at.%), the presence of Ti-Al compounds could not be conclusively determined, and no attempt was made to include any Ti-Al phases in the refinements [6]. The refined lattice parameters for the tetragonal  $\text{NaAlD}_4$  structure are found to be  $a=5.010$  angstroms and  $c=11.323$  angstroms. Results of first-principles calculations of the lattice parameters are within a few percent of the Rietveld-refined values. The generalized gradient approximation (GGA) is found to produce significantly better agreement with the experimental data than the local-density approximation (LDA), which is attributed to a very inhomogeneous distribution of electronic density in the alanates. The Rietveld refinement, LDA, and GGA results for the



**Figure 3.** Rietveld Refinement of Powder Neutron Diffraction Data of a Ti-doped Alanate Sample

Al-H bond length in  $\text{NaAlD}_4$  are 1.626, 1.634, and 1.631 angstroms, respectively. Refined values of the Al-H bond lengths in  $\text{Na}_3\text{AlD}_6$  are in agreement within 2% of earlier work on undoped  $\text{Na}_3\text{AlD}_6$  [5].

**Improvements in materials synthesis.** Our previous work raised questions about the importance of the Ti halide to Na halide decomposition reaction on the overall Ti-induced enhanced kinetics. It is this reaction that is responsible for most of the hydrogen capacity loss on Ti-doping the alanates. For this reason, an indirect doping process was tested. A sample was prepared in which  $\text{TiCl}_2$  was pre-reacted with LiH by mechanical milling. The resulting powder was then milled in a 6 mol.% ratio with NaH and Al to form a pre-alanate mixture in which the Ti-halide had not been directly reacted with NaH. From a mechanistic point of view, this method should indicate whether or not the Ti halide and Na reaction is necessary for Ti-enhanced kinetics. From a practical perspective, this method may also provide an incremental improvement in capacity at higher doping levels due to the formation of the lighter LiCl byproduct rather than NaCl. The mixture was subjected to a series of hydriding / dehydriding cycles. The measurements showed an activation process that is much more profound than in the direct Ti halide doped materials. An Arrhenius plot (Figure 4) of desorption rates vs. temperature indicates



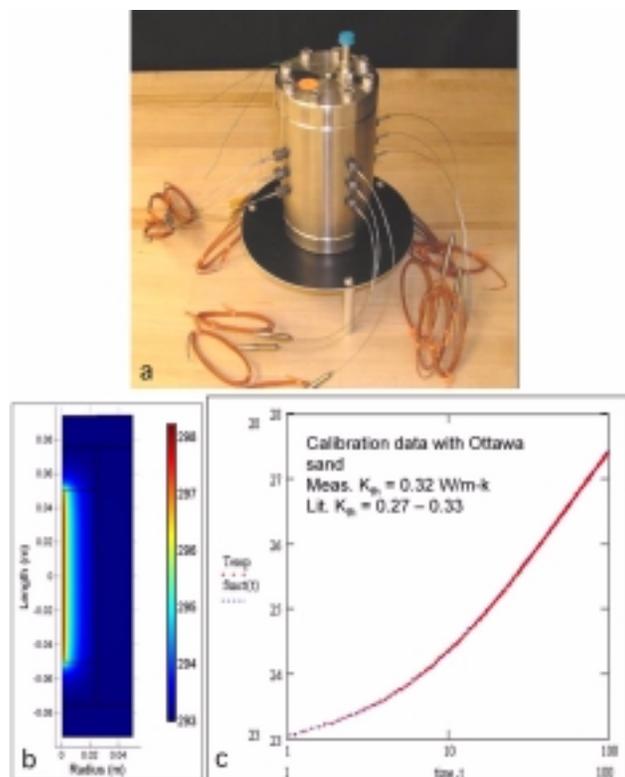
**Figure 4.** Arrhenius Plot Comparing  $\text{NaAlH}_4$  Desorption Rates of Generation II, III-D, and III-E Alanates (rates: II on a total weight basis, III-D and III-E on a NaH + Al weight basis)

similar activation energies for both the direct and the indirect doping methods. Thus, directly reacting Ti halides with sodium (hydride or metal) is beneficial for initially rapid kinetics, but not necessary for long cycle-life materials.

Extending the above notion that Ti-diffusion/substitution may be possible without using a Ti halide or organic precursor, a sample was tested using only  $\text{TiH}_2$ . Once again, the desorption rates are nearly identical to those of the indirect doped material and the 2 mol.%  $\text{TiCl}_3$ -doped alanates. From an applications perspective,  $\text{TiH}_2$  as a dopant precursor should overcome the problem of capacity loss associated with the formation to Na halides when using Ti halide precursors.

**New complex hydrides.** We have been investigating other complex hydrides besides the Na alanates. These include Li alanates and Mg alanates. So far, neither system could be made to reversibly absorb hydrogen under moderate conditions (100 bar and up to  $300^\circ\text{C}$ ). We have also investigated the Mg-Fe-H system through our International Energy Agency task 17 collaboration with the University of Geneva, Switzerland. Using our direct synthesis approach, we started with  $\text{MgH}_2$  and Fe powders, which were mechanically milled together. The second absorption cycle showed activity beyond the formation of  $\text{MgH}_2$ . X-ray diffraction measurements showed both  $\text{MgH}_2$  (about 41 wt%) and  $\text{Mg}_2\text{FeH}_6$  (about 15 wt%) along with Fe (about 44 wt%) (Figure 5). We also tested the material prepared in the same manner but doped during the milling process with 4 mol.%  $\text{TiCl}_3$ . This preparation appears to have an effect on the rehydriding kinetics. Notably, there is rapid hydrogen absorption associated with the formation of  $\text{MgH}_2$  even below  $100^\circ\text{C}$ . The study of the Mg-Fe-H system is important because it is an analog to the Na alanate system. Demonstration of doping-enhanced reversibility in the Mg-Fe-H system will provide more clues as to the role of Ti and other transition metal dopants. In addition, it will demonstrate the possibility that a wider class of complex hydrides can be modified through doping. Detailed measurements are being performed at this time.

**Engineering material properties.** Engineering material properties investigations of Ti-doped sodium alanates is currently underway. The selection of the properties and the associated parameter space



**Figure 4.** X-ray Diffraction Patterns of  $\text{MgH}_2 + \text{Fe}$  Before and After Hydriding Showing Presence of  $\text{Mg}_2\text{FeH}_6$

focuses on hydrogen-storage application needs. For example, the characterization of the thermal conductivity of complex hydrides is critical for advanced design and modeling of hydride-based hydrogen storage systems. The thermal conductivity test hardware has been built and calibrated. A finite element model was used to determine optimum instrument design geometry as well as to validate the experimental method used to determine thermal conductivity. The model helped to minimize the mass of sodium alanate necessary to achieve accurate and measurable results. Testing on various calibration materials has provided consistent and repeatable results. Thermal properties testing of sodium-alanate as a function of phase composition and hydrogen gas pressure is in progress. In addition, a test cell has been constructed that can measure the pressure exerted on a wall by constraining the sodium aluminum hydride, and an electrical-properties cell has been built for measuring DC and AC response of the alanate material. All instrumentation has been designed to be used in the

future to characterize new hydrogen storage materials as they are developed.

## Conclusions

The results presented above demonstrate that solid progress is being made on the development of light-weight complex hydrides for hydrogen storage applications.

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4. "Titanium-Halide Catalyst-Precursors in Sodium Aluminum Hydrides," E. Majzoub, K.J. Gross, presented at the International Conference on Metal Hydride Systems, Annecy France, 2002
5. "Sodium Alanates: From Principle to Practice," K.J. Gross, E. Majzoub, presented at the International Conference on Metal Hydride Systems, Annecy France, 2002
6. "New Reversible Complex Hydrides for Practical Hydrogen Storage", K.J. Gross, E. Majzoub, World Hydrogen Energy Conference, 2002, Montréal, Canada

### **Special Recognitions & Awards/Patents Issued**

1. Sandia National Laboratories internal funding through Laboratory Directed Research and Development grants: 1) Alanate-hydride fuel cell demonstration project (Gross), 2) Transition metal catalyzed sodium aluminum hydrides (Majzoub)

### **FY 2003 Publications**

1. "The Reversible Hydrides Solution for Hydrogen Storage", K.J. Gross, presented at the G-CEP Hydrogen workshop, Stanford University, Palo Alto, CA, 2003