III.C.2 Hydride Development for Hydrogen Storage

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Objectives

- Develop new complex hydride materials with greater than 6 weight percent system hydrogen capacity obtained below 100°C.
- Improve the kinetics of absorption and desorption and thermodynamic plateau pressures of alanate, new complex hydrides, and modified amides.
- Improve processing and catalytic doping techniques of these materials.
- Aid the engineering science for eventual development of hydrogen storage/delivery systems through analysis of materials engineering properties, durability, safety and compatibility of advanced materials.

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:

- A. Cost
- B. Weight and Volume
- C. Efficiency
- D. Durability
- E. Refueling Time
- F. Codes and Standards
- G. Life Cycle and Efficiency Analyses
- 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 synthesis and doping process to improve both rates and capacity.
- Experimentally characterize the materials properties using techniques such as X-ray and neutron diffraction, Raman, infrared (IR), nuclear magnetic resonance (NMR), low-energy electron microscopy

(LEEM), scanning tunneling microscopy (STM), scanning electron microscopy (SEM), low-energy ion scattering (LEIS), and electron spin resonance (ESR).

- Determine 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.
- Collaborate with Brookhaven National Laboratory on borohydrides and aluminum hydride.

Accomplishments

- Achieved 5 wt.% reversible hydrogen storage through the development of a destabilized Mg-modified Li-imide material.
- Using an oxide doping precursor and hydrogen-driven metallurgical reactions (HDMR), metallurgically stimulated thermal H₂ desorption from NaBH₄ was demonstrated.
- Using particle size control and metallurgical stimulation, experimentally demonstrated 7-8 wt.% H₂ desorption from AlH₃ at temperatures <200°C, i.e., demonstrated clear potential for meeting the DOE 2010 weight and volume system targets.
- Construction of a high-pressure synthesis station has been completed and validated by the synthesis of Mg₂FeH₆ from Mg and Fe metals.
- Li- and K-based complex hydrides have been produced by solution synthesis.
- Nano-crystalline and amorphous amides and imides have been produced using solution and gas reaction synthesis.
- First-principles calculations and experimental work are providing new insight into the role of titanium in the hydrogen sorption mechanisms of Ti-doped alanates.
- Materials engineering properties (thermal conductivity, lattice expansion forces, and electrical properties) of the alanates have been characterized in detail.
- Installation of experimental capabilities to determine durability, contamination effects, safety and special synthesis techniques is approaching completion.

Future Directions

- Metal Hydride Center of Excellence (MHCoE): Sandia National Laboratories (SNL) was selected through a competitive solicitation by the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program to participate in the Program's MHCoE, subject to congressional appropriations and direction. In this role, Sandia is tasked with achieving the Grand Challenge of developing hydrogen storage materials that meet or exceed the DOE FreedomCAR targets for an onboard hydrogen storage system. Sandia will meet this challenge through collaboration with its university, industrial and national research laboratory partners in the MHCoE and also by delivering cutting-edge results in its own research and development efforts.
- Development of reversible complex hydrides: Discover new complex hydrides and destabilize known hydrides to achieve high capacities and rapid kinetics.
- Modification of alanates: Achieve higher hydrogen storage capacities by modifying alanates.
- Development of low-temperature reversible amides: Develop advanced amides with lower operating temperatures and rapid kinetics through structural and compositional modifications.
- Development of reversible borohydrides: Extend the HDMR doping approach to maximize reversibility and substantially destabilize borohydride thermodynamics; move from NaBH₄ to LiBH₄.
- Aluminum hydride: Determine the optimum AlH₃ phase; perfect the metallurgical stimulation approach to achieve >8 wt.% H₂ desorption at <100°C; develop an off-board process to rehydride spent Al at a cost less than the 2010 DOE target.

- Structure properties and mechanisms of alanates and new materials: Understand transition metal doping effects that lead to enhanced kinetics, and investigate mechanisms for hydrogen uptake and release in newly developed materials.
- Materials synthesis development: Improve direct synthesis and nano-scale chemical processes for improved performance and scale-up of state-of-the-art materials.
- Effect of contaminants on hydrogen sorption properties: Determine the degree to which low-level contaminants in a hydrogen gas supply will impact the performance of hydrogen storage materials.
- Materials compatibility and safety studies: Develop science-based understanding of safety and materials compatibility issues of new hydrogen storage materials.
- Engineering materials properties characterization: Determine materials properties of advanced hydrides and amides to aid in the design of hydrogen storage systems.

Introduction

The purpose of this project is to develop and demonstrate the next generation of practical metal hydride hydrogen storage materials. This work will focus on new materials including complex metal hydrides and modified amides with high reversible hydrogen storage capacities.

This project has grown from a foundation of achievements that Sandia made in developing advanced Ti-doped Na-alanates [1]. Those materials have nearly ideal equilibrium thermodynamics, high capacities, and moderate kinetics. However, while their hydrogen capacity is 2 to 3 times better than commercial low-temperature hydrides, they do not meet the DOE/FreedomCAR 2010 storage capacity targets. Thus, other higher-capacity reversible materials must be developed. At the same time, Naalanates continue to provide a good working model to better understand reversible hydrogen sorption in complex hydrides. Sandia's wide-ranging expertise in novel hydrides development, combined with strengths in modeling, synthesis, materials characterization and materials engineering science, is being employed to seek out and improve advanced materials that meet practical hydrogen storage performance requirements.

Promising cooperative work has begun with Brookhaven National Lab on the borohydrides and aluminum hydride.

Approach

• New complex hydrides will be discovered and tested through high-pressure synthesis.

- Known complex hydrides and amides/imides will be modified by substitution to improve capacity and thermodynamic stability.
- The borohydride family and solid AlH₃ will be metallurgically stimulated for improved H₂ desorption by adding dopants that would be expected to alloy with B and Al, respectively (hydrogen-driven metallurgical reactions, HDMR).
- Modeling and experimental validation will be applied to solve fundamental mechanism questions and guide research on advanced materials.
- Synthesis routes will be developed to enhance kinetics and cycle-life performance as well as aim at cost-effective bulk materials production.
- Materials and engineering science methods will be applied to characterize the practical storage aspects of new materials such as heat transfer, volume expansion, susceptibility to contamination and life-cycle degradation.

Results

New Complex Hydrides

A portable high-pressure test station was constructed for use in our remote operation test facility. The station can achieve hydrogen pressures up to 200 MPa and temperature control up to 973 K with continuous data recording. This facility allows us to produce unstable and kinetically hindered hydride materials in samples on the order of 20 grams. This has greatly enhanced our ability to develop new hydrogen storage materials. As a test case, we started with the known, but difficult to

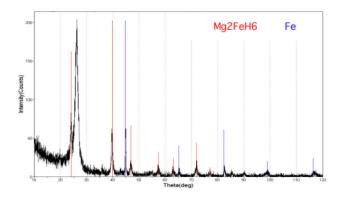


Figure 1. XRD Measurement of the High-Pressure Synthesis of Mg₂FeH₆. The broad peak at 298 K comes from the sample holder's Mylar cover.

synthesize, complex hydride Mg₂FeH₆. A test sample was prepared by milling Fe and Mg together under argon gas for 2 hours. After hydriding in the new station at 73 MPa and 573 K, we were able to achieve complete conversion of Mg and Fe to Mg₂FeH₆ (Figure 1). Noticeable changes in the sample included a color change from black to olive green and a near doubling of the volume of the powder sample. Besides validating the facilities capabilities, the synthesis of this compound is important for the development of new materials. This is because, as a non-alanate complex hydride, it will allow us to investigate whether or not the Ti-doping that is so important for reversibility in alanates can be applied to other materials. Our next task is to test this effect by doping the samples we have prepared of Mg₂FeH₆ with TiCl₃. Before we can do this, we must produce single-phase samples with no residual Fe. Synthesis will then focus on producing new complex hydrides with higher hydrogen capacities.

New and Modified Alanates

The objective of this task is to synthesize novel alanate phases and to test their hydrogen sorption/desorption characteristics. Alanates that we test will include Sc(AlH₆), Cr(AlH₆)₂, Co(AlH₆)₃, Ti(AlH₄)₄, Mg(AlH₄)₂, Fe(AlH₄)₂, and Sn(AlH₄)₄. The Ti and Mg phases are known to exist, but attempts at other laboratories to reversibly absorb and desorb hydrogen at lower pressure have not been successful. We will employ doping and subtitution to try to destabize these phases. This project is currently in

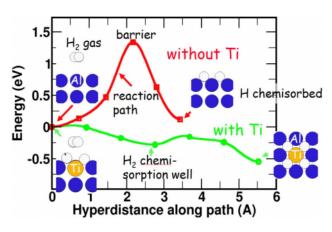


Figure 2. VASP Calculations of Interaction of H₂ with the Clean and Ti-covered Al(100) Surface

the setup phase. In parallel to the high-pressure facility above, we have refurbished a 2-furnace Leco Tem-Pres hydrothermal system that can simultaneously handle two reactor vessels at pressures up to 400 MPa. A custom 2-stage gas booster (172 MPa H₂) has been ordered and will be installed shortly. All process conditions have been evaluated for compatibility with our equipment design and materials handling. It is anticipated that sample synthesis will begin this next quarter in FY 2005.

Fundamental Studies of Advanced Hydrogen Storage Materials

The sorption rates of H₂ at metal surfaces and the effect of H on material transport at these surfaces is critical for complex hydride storage materials like Ti-doped NaAlH₄. Simple metals (e.g. Li, Mg, Al), while lightweight, do not readily react with H₂ by themselves. Transition metals (e.g. Ti, Ni, Pd) are known to catalyze H-chemistry, but how to incorporate this property into alloys and hydrides is not well understood. We have recently made progress in this area. Our first-principles calculations indicate that alloys of Al and Ti bind H differently than either metal alone. At exposed Ti in an Al matrix, we find very low barriers for H₂ dissociative adsorption and recombinative desorption (see Figure 2). These surface Ti atoms also stabilize a novel molecular chemisorption state that might be exploited in nano-structured hydrogen storage materials. A newly observed indirect effect of Ti is that Al surfaces with Ti atoms substitutionally

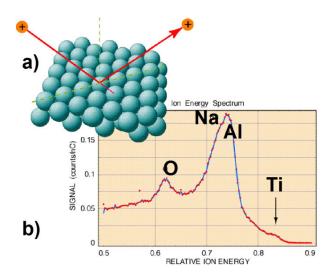


Figure 3. (a) Diagram of the Ion Surface Scattering
Process. The energy loss of scattered ions
indicates the mass of the exposed atoms.
(b) LEIS Data of a NaAlH₄ Surface, Showing
Oxygen Contamination and Traces of Ti at the
Surface of this Doped Sample

incorporated in the 2nd layer split H₂ more readily and bind H more strongly than pure Al surfaces.

Experimental work is being carried out in support of modeling efforts. STM, LEEM, and LEIS methods are being used to study surface structure and dynamics on hydrogen storage materials from atomic to macroscopic length scales. For example, LEIS, which provides information about surface atom identification and structure, was used to examine the surface of a Ti-doped NaAlH₄ sample, as shown in Figure 3. It was found that only a minor amount of Ti resides on the surface of the sample. Additional measurements are underway to determine if Ti populates subsurface sites and how the presence of H affects the segregation of bulk atoms to the surface.

Because of the potential influence of Ti compounds on sorption kinetics [2,3], the phase stability of Ti-compound formation was studied using x-ray diffraction (XRD) and NMR of 33 mol.% Ti-doped NaAlH₄ in milled and solution-doped samples. Both XRD and NMR indicate TiAl₃ formation (L12 structure) in mechanically milled samples [4]. XRD of solution-doped samples indicated very small coherence lengths, and NMR results point to possible nano-Ti-Al clusters

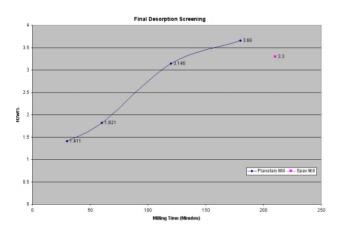


Figure 4. Measurements of the Final wt.% H₂ Desorbed from a High-Energy Shaker Milled Sample Compared with Planetary Milling for an Increasing Duration of Time

stabilized by Ti-tetrahydrofuran coordination [5]. Formation of Ti compounds is clearly dependent upon sample preparation techniques. Single crystals of pure and 'Ti-exposed' NaAlH₄ were gently crushed and studied for lattice parameter differences, which may indicate Ti substitution in the NaAlH₄ lattice. No differences were seen in Rietveld refinement lattice parameters. A full polarization analysis of single-crystal NaAlH₄ was performed and resulted in an unambiguous determination of every Raman active mode, which agreed with first-principles calculated phonon frequencies.

Improvements in Materials Preparation and Synthesis

Improvements in hydrogen sorption rates from materials that involve phase separation reactions are likely to require the synthesis of nano-phase materials. Building on our previous direct synthesis of alanates work, we have characterized the effects of the use of planetary milling as the initial materials preparation step. A study was performed to evaluate samples prepared with milling times ranging from 30 minutes to 210 minutes. To our surprise, planetary milling not only produced a material with higher storage capacity than traditional high-energy shaker milling but also surpassed the typical storage capacities for the initial absorption of hydrogen (see Figure 4). The trend in the results indicates that higher capacities are possible. Current experiments

are in progress to determine if the theoretical limitation of 5% can be achieved.

We are also exploring novel chemical methods of synthesis to provide pure materials with controlled particle sizes and size distributions. The ultimate goal is to make dramatic improvements in hydrogen sorption rates and to provide economic routes for bulk production. We have successfully synthesized extremely pure Li₂NH, LiNH₂ [6], and Mg(NH₂)₂ powders using the following solution-based reactions:

$$\begin{split} \text{Li}^\circ + \text{NH}_3(\text{I}) &--> \text{Li}\text{NH}_2 + \text{Li}\text{OH} & \text{(crystalline)} \\ \text{Li}(\text{CH}_2\text{CH}_2\text{CH}_3) + \text{NH}_3(\text{g}) &--> \text{Li}\text{NH}_2 & \text{(crystalline)} \\ \text{Li}(\text{C}(\text{CH}_3)_3) + \text{NH}_3(\text{g}) &--> \text{Li}_2\text{NH} & \text{(crystalline)} \\ \text{Mg}(\text{CH}_2\text{CH}_2\text{CH}_3)_2 + \text{NH}_3(\text{g}) &--> \text{Mg}(\text{NH}_2)_2 & \text{(amorphous)} \end{split}$$

These samples show a high degree of phase purity and are now being tested for storage characteristics. A solution method for the synthesis of nano-XAIH₄ (X = Na, K, Li) has also been developed, and samples have been prepared to aid in the study of thermodynamic, capacity, and kinetics improvements through substitution.

Effects of Contamination on Hydrogen Storage Performance

Vibrational spectroscopy and mass spectrometry, coupled with temperature-programmed methods of adsorption/desorption and reaction, will be used to quantify the effects of contaminants (e.g. CO, O₂ and H₂O) on hydrogen uptake and release kinetics, as well as overall storage capacity of advanced materials. Testing of the viability of proposed spectroscopic techniques has been completed. Infrared transmittance of thin wafers of mixed NaAlH₄/KBr powders (5% to 100%) suggests that IR transmission will be problematic due to limited throughput and potential alanate/KBr interactions. Surface Raman spectra on pure and Ti-doped NaAlH₄ powders were obtained using the 532-nm line of a pulsed Nd:YAG laser. This technique proved fruitful only for the pure material. Based on these observations, an IR diffuse-reflectance method will be developed as the optical diagnostic. The design of a flow system with associated optical diagnostic and mass spectrometer has been completed and is under construction with the

anticipated completion date of August 1. The reaction cell is configured for diffuse-reflectance infrared Fourier Transform spectroscopy (DRIFTS) measurements and is capable of operating at pressures in excess of 5 MPa and up to 723 K. This will allow for in-situ probing of gas (vapor)-alanate interactions under realistic conditions.

Development of Low-Temperature Reversible Amides/Imides

This task's objectives were to validate the hydrogen storage properties of lithium imide reported by Chen [6] and to develop a less stable imide able to desorb 0.1 MPa of hydrogen at less than 473 K. Both objectives have been achieved. By partial substitution of Li by Mg in the nitride/ imide system, the plateau pressure was significantly increased to about 3 MPa at 473 K. The reversible capacity is 4.5 wt.%. This new material has the potential to deliver hydrogen at the useful pressure and temperature ranges to meet DOE targets for "on-board" applications. The van't Hoff diagram of Figure 5 shows a comparison of equilibrium pressure measurements of this new Mg-modified Li-imide with common hydrides. The results are very promising, as this 5 wt.% H₂ capacity storage material falls into the practical range of operating pressures for mid- to low-temperature hydrides.

Development of Reversible Borohydrides

This work was done in cooperation with Brookhaven National Laboratory (BNL) by Gary Sandrock (contractor to SNL) and James Reilly (BNL). The borohydrides contain very high inherent hydrogen contents (e.g., 10.7 wt.% H for NaBH₄ and 18.5 wt.% H for LiBH₄). Our aim is to determine how much H₂ can be thermally released from the borohydrides, the temperatures required, whether they can be improved by "doping" and if they can be made reversible. It has been shown by this work that the introduction of fine alloying "stimulants" by the decomposition of certain metal oxides via HDMR can significantly aid thermal decomposition of NaBH₄. For example, adding 5 mol.% Mo to NaBH₄ by the *in situ* ball-milling decomposition of the precursor MoO₃ increases the 25-400°C desorption of H₂ from <0.1 to 1.7 wt.%. Although much R&D work is yet needed to demonstrate practical

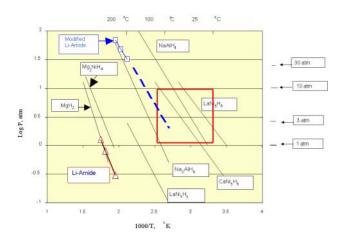


Figure 5. Van't Hoff Equilibrium Pressure Plot Comparing Common Hydrogen Storage Materials with Mg-modified Li-imide (blue)

borohydride reversibility and greatly decrease desorption temperatures, the potential of HDMR has been demonstrated. The borohydrides do not have much chance of meeting the 2010 DOE targets, but they should be considered serious contenders for meeting the 2015 targets.

Aluminum Hydride

This work was also done in cooperation with Brookhaven National Laboratory by Gary Sandrock (contractor to SNL) and James Reilly (BNL). AlH₃ contains 10.1 wt.% H, most of which can be liberated by simple thermal desorption, leaving only pure Al. Can this be accomplished at proton exchange membrane fuel cell waste heat temperatures (<100°C) and at rates fast enough to fuel a fuel cell automobile? Can it be stimulated by metallurgically active additions? Experimental results thus far suggest the answers to both questions will soon be YES. As shown by the temperature-programmed desorption (TPD) curves of Figure 6, simply ball milling to reduce particle size can lower desorption temperatures to the 100-175°C range. Adding certain metallurgical dopants (not disclosed for now) can further decrease the desorption temperature range. Although the quarter-century old α -AlH₃ we used is not at full theoretical capacity, it can be seen in Figure 6 that we have experimentally achieved 7-8 wt.% H₂ recovery by simple thermal desorption at <200°C, which is, as far as we know, a record range for the Hydrogen Program. The very low desorption

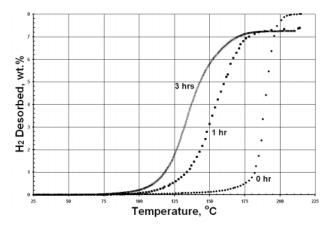


Figure 6. Effects of Ball Milling Time on TPD of H_2 from AlH₃. TPD scan rate = 2° C/min

enthalpy of AlH₃ (minimal heat exchange), longtime metastability in ambient air and very high crystal volumetric H density (0.148 kg H/L = 4.9kWh/L) suggest the 2010 weight, volume and cost system targets cited above can probably be met rather easily and perhaps well before 2010. But alas, the real problem is the fact that pure Al decomposition product cannot be easily rehydrided back to AlH₃. We know, for a priori thermodynamic reasons and from experimental attempts, that H-depleted Al powder can be rehydrided only at impractically extreme temperatures and pressures (e.g., 300°C and 28 kbar [400,000 psi] H₂ pressure) [7]. So, we are really looking at a hydrogen source that probably cannot be recharged onboard. A nonaqueous electrolytic technique might offer the best hope for achieving the very high hydrogen fugacities to accomplish the offboard Al \rightarrow AlH₃ recharging. In summary, if AlH₃ can be synthesized from Al within the DOE fuel cost target (1.50 \$/gal gasoline equivalent), then the main 2010 DOE goals will be met with this interesting and long overlooked elemental hydride.

Engineering Materials Properties

Understanding the engineering materials properties of these new classes of hydrogen storage materials is critical for their ultimate vehicular use. Using hardware that was specially designed and built for this project, the dependence of thermal conductivity of sodium alanates on composition, temperature, gas species, and gas pressure was

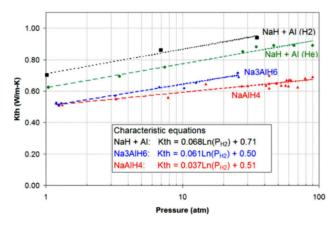


Figure 7. Thermal Conductivity of Sodium Alanate as a Function of Composition and Gas Pressure.

characterized. The thermal conductivity was determined and found to vary by greater than 90% as a function of the parameters (Figure 7). In addition, thermal wall resistance was accurately measured using an optimized bed and numerical modeling methods.

Alanates experience lattice volume expansions on the order of 50% upon hydriding. Thus, characterization of the resulting expansion forces exerted by this effect is vital for proper structural design of storage vessels. The material expansion pressure was quantified as a function of initial packing density (0.7, 0.9, 1.2 g/cc). In general, only modest pressures are experienced for packing densities below 1.0 g/cc, while much larger pressures are experienced up to full density. Moreover, highly compacted materials (1.2 g/cc) showed 67% lower reversible hydrogen capacities than unconstrained samples. Below 1.0 g/cc this limitation was not observed. These experimental capabilities are now being used to evaluate new storage materials. including the modified amides.

IEA and Other DOE Activities – Gary Sandrock

The U.S. DOE is a charter member and 1977 signatory to the International Energy Agency (IEA) Hydrogen Implementing Agreement (HIA). Sandia/DOE contractor Sandrock was appointed in 1996 to serve as DOE's official Operating Agent for the hydride-carbon hydrogen storage annexes within IEA HIA: Annex 12, Metal Hydrides and Carbon for Hydrogen Storage (1995-2000), and Annex 17, Solid

and Liquid State Hydrogen Storage Materials (2001-2006). Presently active Annex 17 comprises experts from about 35 universities, national laboratories and industrial R&D laboratories in 12 countries (Canada, European Commission, Finland, Italy, Japan, Lithuania, Norway, Spain, Sweden, Switzerland, United Kingdom and United States). With 33 active projects at this moment, it is fair to say that Annex 17 is the largest international collaboration on hydrogen storage materials ever established. As part of DOE's contribution to IEA HIA. Sandrock has created a comprehensive series of hydride databases that serve the world's hydride R&D and applications community [8]. The databases include ones on hydride materials, properties, applications, references, organizations and meetings, as well as a profile of IEA Task 17, its publications and presentations and its 2003 Project Reports.

This activity addresses the following philosophy stated in the Program Management section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

"The Secretary's call for an International Partnership will build on the efforts of the last several years in which DOE has coordinated activities involving the European Union and the International Energy Agency (including Japan, Europe, and Canada) to advance hydrogen and fuel cell technologies. The Program is taking leadership in the International Energy Agency Hydrogen Implementing Agreement and Advanced Fuel Cell Implementing Agreement (AFCIA)."

The following FY 2004 accomplishments can be cited for the Task 17 Operating Agent:

- Fulfilled all the requirements of IEA, including two Semiannual Reports, two Executive Committee Presentations, an Annual Report and two Semiannual Experts' Workshops
- Successfully led Task 17 to a formal 2-year extension (to 2006)
- Started a tentative collaboration between IEA HIA Task 17 and IEA AFCIA Task XX
- Five presentations and publications in addition to those required by IEA

 Served on the Organizing Committee of the 2005 DOE/EC/IPHE/IEA International Hydrogen Storage Conference

Conclusions

The results presented above demonstrate that solid progress is being made on the development of advanced lightweight materials for hydrogen storage applications.

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Special Recognitions & Awards/Patents Issued

1. Patent applications submitted: new hydrogen storage materials and methods of synthesis.