

## IV.1 Hydrogen Storage Sub-Program Overview

### Introduction

Hydrogen storage for on-board transportation applications continues to be a critical technology barrier to commercialization of hydrogen fuel cell vehicles. The Hydrogen Storage activity focuses primarily on the research and development of low-pressure, materials-based technologies to allow for a driving range of more than 300 miles while meeting packaging, cost, safety, and performance requirements to be competitive with current vehicles. Technologies developed under this effort may also be applicable to hydrogen delivery and off-board storage of hydrogen and will be closely coordinated with the Hydrogen Delivery program element.

Figure 1 shows the framework for DOE's National Hydrogen Project, which includes independent projects and Centers of Excellence (CoEs) in applied hydrogen storage R&D as well as basic science in hydrogen storage. The storage portfolio is comprised of approximately 40 universities, 15 companies and 10 federal laboratories, including 17 new basic science projects started in FY 2005.

The program fully recognizes the critical importance of hydrogen storage and agrees with the National Academies' recommendation that

"...DOE should continue to elicit new concepts and ideas, because success in overcoming the major stumbling block of on-board storage is critical for the future of transportation use of fuel cells" (Hydrogen Economy Report, National Academies).

The hydrogen storage effort will continue to increase longer-term, multidisciplinary exploratory research for breakthrough approaches to overcome the hydrogen storage technical barriers as recommended by the National Academies. Also in response to the National Academies, the sub-program will evaluate the CoE model before considering applying this approach to other parts of the program.

### Goal

Develop and demonstrate viable hydrogen storage technologies for transportation and stationary applications.

### Objectives

- By 2010, develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt%), 1.5 kWh/L (45 g H<sub>2</sub>/L), and \$4/kWh.
- By 2015, develop and verify on-board hydrogen storage systems achieving 3 kWh/kg (9 wt%), 2.7 kWh/L (81 g H<sub>2</sub>/L), and \$2/kWh.

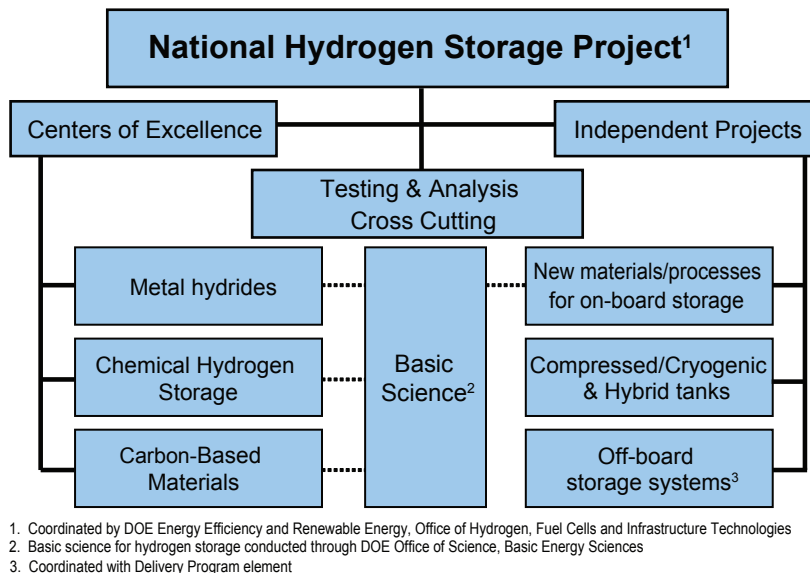
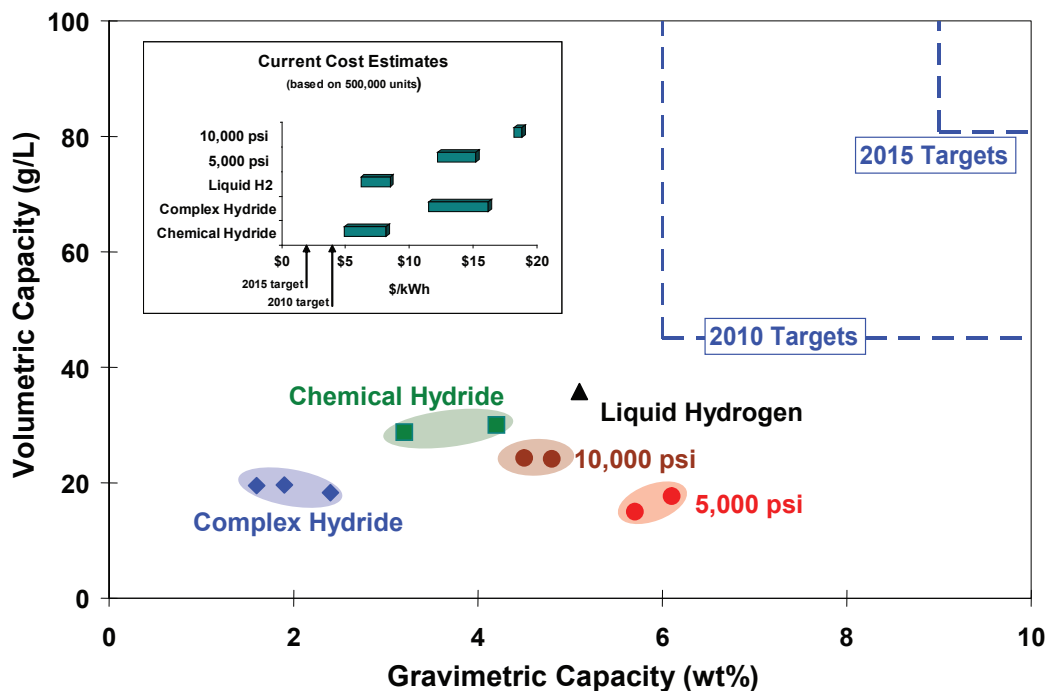


FIGURE 1. Framework for the U.S. National Hydrogen Storage Project

## FY 2006 Technology Status

On-board hydrogen storage approaches under investigation include advanced metal hydrides, carbon-based materials and other high surface area adsorbents, chemical hydrogen storage carriers, low-cost and conformable tanks, compressed/cryogenic hydrogen tanks, and new materials or processes, such as clathrates and conducting polymers. Compressed/cryogenic tanks, metal hydrides, high surface area adsorbents and carbon-based materials constitute on-board reversible hydrogen storage systems because hydrogen regeneration or hydrogen uptake can take place on-board the vehicle. For chemical hydrogen storage approaches as well as certain metal hydrides, material regeneration with hydrogen is not possible on-board the vehicle; thus, these systems must be regenerated off-board.

The current system status values, as shown below, are estimates provided by developers and by the R&D community and will be updated as information is available. Because it is often difficult to estimate system-level weight and volume when research is still at the stage of materials development, the current status data will be revisited periodically. However, it is clear that none of the current systems meets the combined gravimetric, volumetric, and system cost targets for either 2010 or 2015. It should also be reiterated that there are several other requirements such as hydrogen charging and discharging rates that are not illustrated in Figure 2.



Costs exclude regeneration/processing.  
Data based on R&D projections and independent analysis (FY05-FY06). To be periodically updated.

FIGURE 2. Current Status of Hydrogen Storage Systems versus Targets

## FY 2006 Accomplishments

FY 2006 was the first full year of funding for DOE's three Centers of Excellence (CoEs) in metal hydrides, carbon-based materials and chemical hydrogen storage with partial funding for several independent projects launched in FY 2005. In addition, the applied research program was more closely coordinated with basic science efforts, with both activities presented at the FY 2006 Annual Merit Review in May, 2006. A Theory Focus Session was also co-organized by the Office of Science

(Basic Energy Sciences) and Office of Energy Efficiency and Renewable Energy (Hydrogen, Fuel Cells and Infrastructure Technologies) with input from university, industry and national laboratory experts, including international experts in theory/modeling of hydrogen storage materials. Objectives and presentations are available at [http://www1.eere.energy.gov/hydrogenandfuelcells/wkshp\\_theory\\_focus.html](http://www1.eere.energy.gov/hydrogenandfuelcells/wkshp_theory_focus.html).

During FY 2006, a number of new materials were developed through the Centers of Excellence and independent projects initiated in FY 2005. Within several projects, down-selects were made that eliminated specific materials based on performance criteria and expanded work on more promising approaches. Table 1 shows gravimetric and volumetric material-based capacity data for materials under development in FY 2006. Note that these values do not include any balance-of-plant components needed to estimate system values. Although these promising results show potential materials-based capacities of over 5 to 9 wt% and over 45 g/L it must be reiterated that the targets of 6 wt% (and 45 g/L) by 2010 and 9 wt% (and 81 g/L) by 2015 are *system-level* capacities that include the storage media, tank and all balance-of-plant components needed for a vehicular system. Significant work is still needed to reduce operating temperatures and pressures to the required range.

**TABLE 1.** Examples of Materials R&D in FY 2006

Metal Hydrides	Chemical H <sub>2</sub> Storage	Adsorbents
<p>Li Mg Amides ~5.5 wt%, ~80 g/L (&gt;200°C)</p> <p>Alane ~7-10 wt%, ~150 g/L (&lt;150°C)</p> <p>Li borohydrides &gt;9 wt%, ~100 g/L (~350°C)</p> <p>Destabilized Binary hydrides ~5-7 wt%, ~60-90 g/L (250°C)</p>	<p>4,7 Phenanthroline (organic liquids) ~7 wt%, ~65 g/L (&lt;225°C)</p> <p>Seeded Ammonia Borane &gt;9 wt%, &gt;90 g/L (&gt;120°C)</p> <p>Ammonia Borane/Li amide ~7 wt%, ~54 g/L (~85°C)</p>	<p>Metal/carbon hybrids, MetCars ~6-8 wt%*, ~39 g/L* (*theory)</p> <p>Bridged catalysts/IRMOF-8 ~1.8 wt%, ~10 g/L (room temperature)</p> <p>Metal-Organic Frameworks IRMOF-177 ~7 wt%, ~30 g/L (77K)</p>

Note: Material capacities only; not system values

## Selected Examples of FY 2006 Accomplishments

### Compressed and Cryogenic Tanks

- Completed fabrication of a cryo-compressed tank system and initiated testing on-board a vehicle modified to run on hydrogen; capacity projected to be ~5 wt% and 1.1 kWh/L. (S. Aceves, et al., Lawrence Livermore National Laboratory)

### Advanced Metal Hydrides

- Partial reversibility demonstrated for LiBH<sub>4</sub> destabilized with MgF<sub>2</sub>, MgS, and MgSe (gravimetric capacity: 5.5-7.6 wt%). Results show that destabilization by alloy formation is a promising approach for overcoming thermodynamic limitations. However, the experimental temperatures are much greater than predictions; this implies that the materials are kinetically limited. (J. Vajo and G. Olsen, HRL LLC, member of the Metal Hydride CoE)
- Significantly improved hydrogen sorption kinetics demonstrated for LiBH<sub>4</sub> incorporated into nanoporous carbon scaffolds. Dehydrogenation temperature was lowered by 100°C and cycling capacity (reversibility) improved compared to LiBH<sub>4</sub> in a non-porous carbon host. Results indicate that this is a promising approach for addressing the kinetics challenges in reversible light metal hydride systems. (J. Vajo and G. Olsen, HRL)
- Calculated reaction enthalpies and vapor pressures for a number of hydride reactions, including destabilized hydrides, demonstrating good correlation with experimental data. (K. Johnson, U. Pittsburgh and D. Sholl, Carnegie Mellon, members of the Metal Hydride CoE)

- First-principles based electronic-structure and thermodynamic calculations of the destabilized reaction  $\text{LiBH}_4 + \text{MgH}_2$  were completed. The work also showed the importance of rotational modes in these molecular solids. (D. Johnson, U. Illinois-Urbana Champaign, member of the Metal Hydride CoE)
- A Monte Carlo method was developed which allows crystal structures to be generated by minimizing the electrostatic energy of a combination of alkali or alkaline earth metals with negatively charged anions. The procedure is rapid, and yields results equivalent to, or better than, database structure searching. (E. Majzoub, Sandia National Laboratory, member of the Metal Hydride CoE)
- Anelastic spectroscopy was demonstrated to be a powerful tool for the detection of the hydrogen containing point defects whose generation is greatly promoted in Ti-doped  $\text{NaAlH}_4$ . (C. Jensen, U. Hawaii, member of the Metal Hydride CoE)
- Decomposition thermodynamics of  $\alpha$ ,  $\beta$  and  $\gamma$ - $\text{AlH}_3$  were measured and used to predict the  $\text{H}_2$  pressure required to re-hydride spent Al ( $P > 10^5$  bar). Based on these results a no-go decision was made on direct gas re-hydriding of spent Al. Three polymorphs of  $\text{AlH}_3$  ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) were prepared that meet a fuel flow rate of 1.0 g  $\text{H}_2$ /s (50 kW fuel cell) at a temperature of 112 °C. (J. Graetz, J. Riley and J. Wegrzyn, Brookhaven National Laboratory, member of the Metal Hydride CoE)

#### Chemical Hydrogen Storage

- Demonstrated hydrogen storage capacity of  $>7$  wt% and  $>65$  g  $\text{H}_2$ /L with new organic liquid carrier containing heteroatoms. Also identified energetic conformers that significantly lower dehydrogenation temperatures. This strategy could be used for a large number of potential liquid carriers. Decreased dehydrogenation catalyst precious metal loading by a factor of 10 relative to commercial catalysts while showing superior activity relative to the commercial catalysts. (A. Cooper, et al., Air Products & Chemicals)
- Quantified and estimated gravimetric densities for 1<sup>st</sup> and 2<sup>nd</sup> equivalent hydrogen release for both neat and seeded solid ammonia borane (AB) to be 6.5 wt% and greater than 9 wt% respectively at 120°C. Determined that the hydrogen release rate from solid AB is governed and enhanced by a nucleation and growth mechanism. Preliminary results on higher loading scaffolds show that as the AB content is increased beyond a 1:1 ratio, kinetics, thermodynamics, and by-products begin to approach the neat material results. (T. Autrey et al., Pacific Northwest National Laboratory, member of the Chemical Hydrogen Storage CoE)
- Demonstrated that alternative reaction media such as ionic liquids can increase ammonia borane (AB) dehydrogenation rates and potentially open up new reaction pathways. Discovered that a system composed of a 90/10 mixture of AB/lithium-amide was found to liberate  $\sim 7$  wt%  $\text{H}_2$  after 6 h and  $\sim 9$  wt%  $\text{H}_2$  after 15 h at 85°C. (L. Sneddon, University of Pennsylvania, member of the Chemical Hydrogen Storage CoE)
- Discovered a number of catalysts for hydrogen release from ammonia borane (AB) in solution. Studies using acid catalysts in concentrated AB solutions demonstrated multiple dehydrogenation cycles at 60°C. Iridium catalysts with 'pincer' ligands, originally pioneered by C. Jensen et al. (U. Hawaii), were used to provide the fastest rate to date (complete in 14 minutes at 25°C with 1% catalyst) for release of one equivalent of hydrogen (rates up to  $2.77 \times 10^{-5}$  mole  $\text{H}_2$ /sec) from AB. (T. Baker et al., Los Alamos National Laboratory, and K. Goldberg and M. Heinekey, University of Washington, members of the Chemical Hydrogen Storage CoE).
- Demonstrated three key steps in the five-step AB regeneration process: 1) reduction of a B-X to B-H bond in a chloroboron catecholite compound with a regenerable, tin hydride as well as formation of the metal hydride from decarboxylation of a tin formate, 2) is proportionation of a hydridoboron catecholite to diethylaniline-borane, and 3) conversion of diethylaniline-borane to AB by reaction with ammonia. (D. Thorn et al., LANL, member of the Chemical Hydrogen Storage CoE)

- Used first principles computational chemistry approaches to obtain accurate thermodynamic data for hydrogen release from heteroatom-containing organics. Demonstrated hydrogen release in the laboratory for heteroatom-containing organics (1,1-elimination) with the potential for over 7 wt% storage in the material. (D. Dixon and A. Arduengo, University of Alabama, member of the Chemical Hydrogen Storage CoE)
- Developed on-board storage engineering assessment tools using on-board release models of sodium borohydride hydrolysis as a prototypical system. (Y. Wu, Millennium Cell, and D. Rector, PNNL; members of the Chemical Hydrogen Storage CoE)

#### Carbon-based Materials and Sorbents

- Demonstrated metal-organic framework (MOF) materials (MOF-177 and IRMOF-20) with hydrogen uptake of 6.7 to 7.5 wt% at 77K and pressure of 70 to 80 bar. IRMOF-20 and MOF-177 show the best uptake on a volumetric basis due to a combination of substantial H<sub>2</sub> uptake and moderate material densities. Volumetric capacities are 34 g/L for IRMOF-20 and 32 g/L for MOF-177 (both at 77K). (O. Yaghi, UCLA/University of Michigan)
- Demonstrated multiple routes to enhanced hydrogen storage via a hydrogen spillover mechanism. This included: 1.8 wt% H<sub>2</sub> at 298K and 10 MPa using AX-21 activated carbon and bridged Pd/carbon catalyst and IRMOF-8 and Pt/carbon catalyst. (R. Yang, University of Michigan, a member of the Carbon CoE)
- Performed detailed calculations to identify new hybrid materials (e.g. MetCars and dendrimers) with high hydrogen sorption capacities. In addition, advanced models were used to identify potential processing pathways to form these high performance metastable materials. (S. Zhang, et al., National Renewable Energy Laboratory, member of the Carbon CoE)
- Penn State developed arc-generated B-SWNTs (single walled carbon nanotubes) and B-doped carbons from polymer precursors. NREL has also developed arc- and laser-based processes to generate boron doped SWNTs. NIST confirmed the boron doping by prompt gamma activation analysis, and measured an enhanced binding energy ~12 kJ/mol for dihydrogen by neutron scattering. This binding energy may be sufficient to produce full saturation of the B sites at room temperature and moderate to high pressures. (P. Ecklund, M. Chung, Penn State University; D. Neumann, National Institute of Standards and Technology; and M. Heben, National Renewable Energy Laboratory; members of the Carbon CoE)
- The National Renewable Energy Laboratory demonstrated processing to decorate SWNTs and other porous carbon materials with metals such as Na, Cr, Rh, Pt, Sc, Pd, Ni, Co, or Ti. The Cr-SWNTs demonstrated near room temperature hydrogen sorption. The hydrogen uptake behavior of other metal-decorated SWNTs/carbons also demonstrated enhanced dihydrogen sorption characteristics. (M. Heben and A. Dillon, National Renewable Energy Laboratory)
- Rice University demonstrated regrowth of SWNTs from the end of dense, aligned SWNT fibers. Rice also developed processing to synthesize vertically aligned SWNT carpets. Routes to densified carpets and spun fibers were also demonstrated. These technical developments are required to construct functional SWNT-based sorbent materials for H<sub>2</sub> storage systems. (J. Tour, Rice, member of the Carbon CoE)

#### Testing and Analysis

- Completed validation of Southwest Research Institute test facility for adsorbent materials and measured MOF samples from UCLA, confirming over 7 wt% material capacity. (Miller and Page, Southwest Research Institute)
- Developed tool for chemical hydrogen storage regeneration efficiency analysis and metal hydride systems analysis. (R. Ahluwalia, et al., Argonne National Laboratory)
- Completed independent assessment of cryo-compressed tank technology, demonstrating potential to surpass 2007 gravimetric capacity (~4.7 wt% vs. 4.5 wt% target) and approach 2007 volumetric capacity. (~1 kWh/L vs. 1.2 kWh/L target, R. Ahluwalia, et al., Argonne National Laboratory)

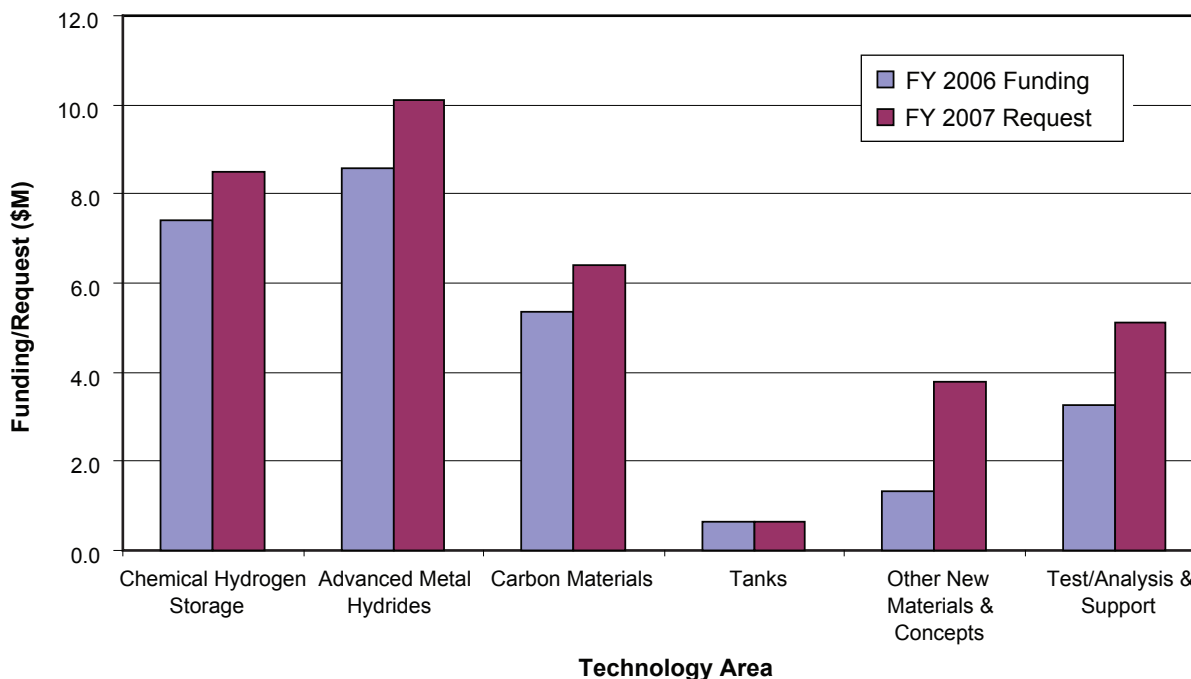
- Conducted independent sodium borohydride system cost analysis, cost analysis of cryo-compressed tank approach and sensitivity analysis on cost of compressed tanks and sodium alanate system. (S. Lasher, Y. Yang, J. Bowman, TIAX LLC)

### FY 2007 Plans and Budget

The funding portfolio for hydrogen storage addresses primarily long-term materials R&D to meet 2010 and 2015 targets for on-board applications. The requested EERE FY 2007 funding profile (subject to congressional appropriations), which includes the CoEs and independent projects, continues to address the National Academies' recommendations to "shift...away from some development areas towards more exploratory work" and that "the probability of success is greatly increased by partnering with a broader range of academic and industrial organizations..." Continued support, at a low level, for compressed hydrogen/cryogenic tanks emphasizes cost reduction and novel conformable designs. In addition, it is recognized that materials-based solutions will require low-cost, conformable tanks and would benefit from current R&D in this area.

Key milestones for FY 2007 will be (1) a system that meets the targets of 1.5 kWh/kg and 1.2 kWh/L and (2) a go/no-go decision on sodium borohydride-based systems. Subject to congressional appropriations, the storage program will also have approximately three to six new awards from the FY 2006 solicitation that will start in FY 2007. The chart below illustrates the funding in FY 2006 for each major activity along with planned funding in FY 2007 based on the Program's budget request. In addition, as a result of DOE's go/no-go decision on pure single walled carbon nanotubes planned for the end of FY 2006, adjustments to the portfolio may be made.

The R&D planned on advanced metal hydrides will continue to focus on the design and discovery of high capacity materials using theory and combinatorial/high throughput methods to increase the efficiency of materials identification and screening. Research is broadening to address methods to improve kinetics including catalysis/doping, size effects and incorporating materials into high-surface area structures. Engineering science research and analysis efforts will increase to address system design, thermal management and hydrogen re-fill issues.



The R&D planned on chemical hydrogen storage will focus on optimizing hydrogen storage and release and the related kinetics and energetics for materials such as organic compounds and ammonia borane as well as investigating new chemistry concepts for materials with greater storage capacities. Significant efforts will also be placed on demonstrating efficient regeneration reactions for materials currently under investigation including  $\text{NaBH}_4$  where the outcome will contribute to the go/no-go decision for  $\text{NaBH}_4$ . Engineering assessments for complete chemical hydride systems will also be initiated.

In the area of carbon-based/adsorbent materials, the planned R&D will focus on breakthrough concepts for optimizing binding energies and storing hydrogen at room temperature such as hybrid metal/carbon nanotubes and metal/fullerene hybrids, aerogels, nanofibers, metal-organic frameworks and conducting polymers. The level of theoretical modeling and structure prediction has increased leading to possible material candidates. Efforts will increase to demonstrate the theoretically predicted structures by stressing synthesis and hydrogen uptake/discharge performance experimentally.

Finally, the robust effort in systems analysis, including life-cycle cost, energy and environmental impact analyses, will be continued to aid in the down-selection of various options. The coordination with basic science, including theory, characterization and novel concepts will continue to be expanded in FY 2007.



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