

## VI.C Carbon Materials

### VI.C.1 DOE Carbon-Based Hydrogen Storage Center of Excellence

*Michael J. Heben*

*National Renewable Energy Laboratory*

*1617 Cole Blvd.*

*Golden, CO 80401*

*Phone: (303) 384-6641; Fax: (303) 384-6655; E-mail: michael\_heben@nrel.gov*

#### *Partners:*

*Air Products and Chemicals Inc., Alan Cooper*

*California Institute of Technology, Channing Ahn*

*Duke University, Jie Liu*

*Lawrence Livermore National Laboratory (LLNL), Joe Satcher*

*National Institute of Standards and Technology (NIST), Dan Neumann*

*Oak Ridge National Laboratory (ORNL), Dave Geohegan*

*Pennsylvania State University, Peter C. Eklund*

*Rice University, Richard E. Smalley*

*Rice University, Boris Yakobson and Robert Hauge*

*University of Michigan, Omar M. Yaghi*

*University of Michigan, Ralph T. Yang*

*University of North Carolina (Chapel Hill), Yue Wu*

*University of Pennsylvania, Alan G. MacDiarmid*

*DOE Technology Development Manager: Sunita Satyapal*

*Phone: (202) 586-2336; Fax: (202) 586-9811; E-mail: Sunita.Satyapal@ee.doe.gov*

*DOE Project Officer: Jesse Adams*

*Phone: (303) 275-4954; Fax: (303) 275-4753; E-mail: Jesse.Adams@go.doe.gov*

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*Projected End Date: Project continuation and direction determined annually by DOE*

#### **Objectives of the Center**

- Advance the hydrogen storage performance of reversible high-surface-area sorbents and carbon-based materials to enable construction of vehicular systems in support of DOE's Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan.
- Create a collaborative teaming environment in which Center of Excellence partners can work synergistically to solve the Hydrogen Storage Grand Challenge.
- Determine the relationship between nanoscale structure and the energetics of hydrogen binding using a variety of experimental and theoretical tools.
- Develop material and system designs that can meet DOE's weight, volume, cost, and other system-level goals.
- Synthesize and test candidate materials and systems and provide a resource for assessment of new materials and approaches.

- Develop scalable synthesis, manufacturing and processing methods that will enable cost-effective use of candidate materials in on-vehicle hydrogen storage systems that meet DOE RD&D Plan goals.

### **Technical Barriers Addressed by the Center**

This project addresses the following technical barriers from the Hydrogen Storage section of DOE's HFCIT Program Multi-Year RD&D Plan:

#### General

- A. Cost
- B. Weight and Volume
- C. Efficiency
- D. Durability
- E. Refueling Time

#### 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
- Q. Thermal Management

#### Crosscutting Relevance

##### Compressed Gas Systems

- H. Sufficient Fuel Storage for Acceptable Vehicle Range
- I. Materials

##### Off-Board Hydrogen Storage Systems

- S. By-Product/Spent Material Removal
- T. Heat Removal

### **Technical Targets Addressed by the Center**

The Carbon-based Hydrogen Storage (CbHS) Center of Excellence (CoE) is developing novel carbon-based and high-surface-area materials and systems for on-board vehicle hydrogen storage. The Center was established during the past year and presently has fourteen active projects at twelve institutions. Center partners are conducting a wide range of research, development and engineering studies on currently available adsorbent materials and developing the design principals and synthetic methods for next-generation materials that will meet the following critical DOE 2010 hydrogen storage system targets:

- Specific Energy: 2 kWh/kg (6 wt%)
- Energy Density: 1.5 kWh/L (45 g H<sub>2</sub>/L)
- Storage System Cost: \$4/kWh

### **Overall Approach of Center**

- Design, synthesize and test a number of promising carbon-based and high-surface-area materials for reversible, on-vehicle hydrogen storage.
- Perform detailed experimental and computational investigations to determine the limits of performance of specific materials and extract general mechanistic information.

- Develop an in-depth understanding of the factors affecting adsorbent synthesis and stability to permit the fabrication of materials that are optimized for on-board vehicular hydrogen storage.
- Perform accurate measurements of hydrogen storage capacity as a function of pressure and temperature and characterize material properties and hydrogen storage behaviors.
- Develop methods to reproducibly activate and handle materials to permit scale-up and validation of hydrogen uptake/release.
- Create an environment that facilitates teaming, communication, discovery, and rapid advancement toward hydrogen storage objectives.
- Develop and test system configurations that can meet DOE RD&D Plan goals for on-vehicle reversible hydrogen storage.

### **FY 2005 Accomplishments of Center**

- Initiated Carbon-based Hydrogen Storage Center of Excellence with 14 collaborative efforts at 12 different institutions.
- Developed first computational model, based on Kubas-type binding of dihydrogen, for carbon-metal hybrid adsorbents capable of reversibly storing nearly 9 wt% hydrogen at more than 43 kg H<sub>2</sub>/m<sup>3</sup> at room temperature and pressure.
- Performed calculations and preliminary experiments to determine hydrogen storage enhancement permitted by incorporating simple metals in sp<sup>2</sup>-bonded carbon networks.
- Identified promising wet-chemical and gas-phase synthetic routes to synthesize predicted materials.
- Commercial samples of polyaniline emeraldine base and nanofibers were chemically treated and tested for hydrogen adsorption/desorption.
- Developed and applied nuclear magnetic resonance (NMR) and neutron scattering spectroscopy techniques to measure hydrogen in candidate materials.
- The locations of hydrogen adsorption sites in a metal organic framework (MOF-5) were determined using neutron powder diffraction.
- Synthesized and characterized boron-doped polymers, single-wall nanotubes (SWNTs), fibers and onions.
- Assessed H<sub>2</sub>/D<sub>2</sub> exchange on adsorbent materials to determine dissociative and non-dissociative hydrogen binding.
- Discovered that hydrogen storage capacities on hotwire chemical vapor deposition generated nano-crystalline graphite could be enhanced by the presence of iron nanoparticles.
- Observed hydrogen adsorbed in MOF-5 by Raman spectroscopy. Reversible physisorption occurred at all pressures employed, including 30 bar. At room temperature, a 10 cm<sup>-1</sup> decrease in the hydrogen stretching frequency was measured, indicating a fairly strong interaction.
- Developed a curvature-dependent force field and molecular dynamics model to calculate the optimal distribution of H<sub>2</sub> on SWNTs, the average adsorption energy per H<sub>2</sub>, and the electrostatic potential of SWNTs.
- Initiated collaboration in a modeling task to relate system-level performance to component and material capacities, with a focus on volumetric capacities.
- Performed measurements and collected volumetric sorption data from partners for two different carbons to ensure measurement uniformity with partner labs and Southwest Research Institute (SwRI).
- Synthesized and activated isorecticular metal organic framework (IRMOF) structures with surface areas up to 3080 m<sup>2</sup>/gm.
- Prepared series of metal-doped carbon aerogels (MDCAs) containing different metals (i.e., iron, nickel, cobalt) and completed structural characterization.

- Demonstrated processing to modify nanoporous carbons (NPC) with boron doping to increase hydrogen storage capacity.
- Developed methods to enhance collaboration between partners and facilitate information sharing through web-based interaction software, ftp file exchange, conference calls, and face-to-face meetings.

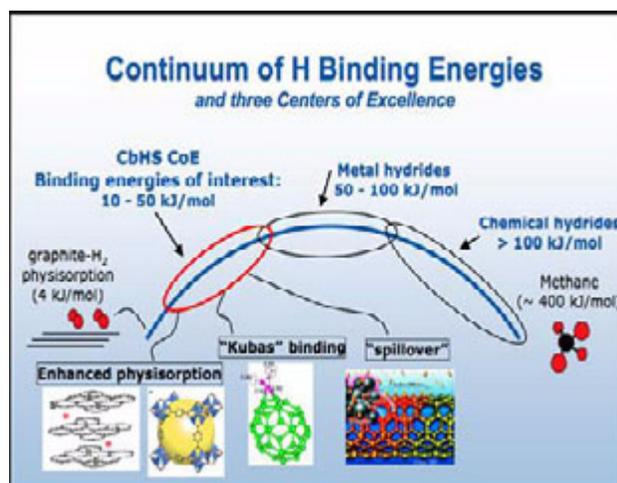
### Future Directions of Center for FY 2006

- Continue and enhance the collaboration and communication between Center members and other interested parties to effectively pursue the goals delineated in DOE's Multi-Year RD&D Plan.
- Develop advanced measurement and characterization techniques to enable a mechanistic understanding of hydrogen interaction with materials.
- Advance theoretical modeling of hydrogen interactions with materials for different sorption mechanisms to enhance understanding and provide guidance for materials development.
- Develop and implement synthesis/combinatorial approaches to rapidly identify and assess the hydrogen storage performance characteristics of promising materials.
- Develop cost-effective, high-volume fabrication and processing techniques for promising adsorbent materials to achieve reproducible storage capacities.
- Down-select materials and initiate system design and development.

### Introduction

Significant improvements over currently available hydrogen storage technologies are required if hydrogen is to become a viable energy carrier. The hydrogen storage targets presented in DOE's Multi-Year Research Development and Demonstration (RD&D) Plan for the Hydrogen, Fuel Cells, and Infrastructure Technologies (HFCIT) Program reflect the critical needs and goals (<http://www.eere.energy.gov/hydrogenandfuelcells/mypp/>). At this time, no storage system currently known can meet the mass, volume, cost, safety, and efficiency requirements for vehicular hydrogen storage systems. Consequently, DOE is investigating materials-based storage options such as metal hydrides, chemical hydrides, and carbon-based adsorbent materials. Nanostructured carbon and other high-surface-area materials containing carbon, metals, oxygen, and other elements show tremendous promise for breakthrough performance in vehicular hydrogen storage. However, the capabilities of these materials remain unclear due to a lack of understanding of both the factors governing their performance and the design principals for fabricating viable adsorbent systems.

The National Renewable Energy Laboratory (NREL) is leading the initiative to develop reversible carbon-based hydrogen storage materials within the U.S. DOE National Hydrogen Storage Project. A guiding principle in developing the required material is that a continuum of energies exists for hydrogen bound to substrates and molecules (Figure 1). On the weak side of the continuum is non-dissociative physisorption due purely to van der Waals (vdW) forces (4 kJ/mol). On the strong side is the full C-H chemical bond in methane with an energy of ~400 kJ/mol. Between these two limits, with binding energies between 10 and 50 kJ/mol,



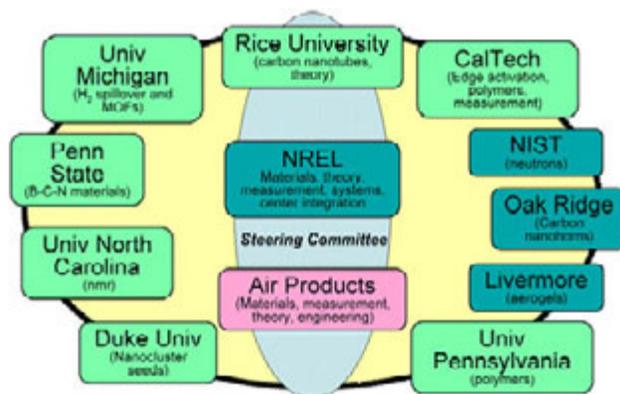
**Figure 1.** Depiction of the range of binding energies and several of the nanostructured materials of interest to the CbHS Center of Excellence.

are (i) stronger physisorption (due to modification of the key parameters affecting vdW forces); (ii) dihydrogen binding via the formation of complexes that exhibit Kubas-type interactions; and (iii) weak, reversible chemical bonding of mono-atomic hydrogen to strained C-C matrices (“spillover”). The DOE/HFCIT goals can be met with carbon-based materials if (i) the energy for hydrogen adsorption can be designed to be in an optimal range (4 – 40 kJ/mol) and (ii) efficient volumetric packing of a low-weight skeletal material can be achieved without compromising the density of adsorption sites. These goals are difficult to reach in conventional high-surface-area adsorbents that are limited by low physisorption binding energies, heterogeneity of the adsorbent surfaces and adsorption sites, excessive macroporosity and poor volumetric packing.

### Approach of the Center

The nanostructured carbon-based materials that are the focus of this effort offer tremendous potential for a breakthrough in hydrogen storage performance. For example, reliable data from NREL has shown that catalytic metals in intimate contact with cut nanotubes can activate room temperature and ambient pressure hydrogen storage, with up to 8 wt% hydrogen storage being demonstrated. Reproducible experimental results from Penn State and University of Quebec (Trois Rivières) show 4 – 6 wt% under a few atmospheres of H<sub>2</sub> pressure at 77 K. Furthermore, recent calculations from NREL predict that certain carbon-transition metal hybrid structures can achieve hydrogen storage densities near ~9 wt% with high volumetric storage densities (~43 kg H<sub>2</sub>/m<sup>3</sup>). These results, along with recent theoretical calculations from NIST on Ti-doped nanotubes and from Steacie Institute for Molecular Sciences on H<sub>2</sub> physisorption between pure graphene layers, provide a firm foundation for seeking to develop carbon-based materials to meet the DOE hydrogen storage system targets.

The main goal of the Carbon-based Hydrogen Storage Center of Excellence is to discover the limits of performance of high-surface-area adsorbents and to synthesize and test adsorbents that will meet the DOE system targets for reversible, on-vehicle hydrogen storage. This will involve the design and synthesis of materials that bind large amounts of hydrogen on both a per-weight and a per-volume basis as either (i) weakly and reversibly bound atoms or (ii) strongly bound molecules. An additional task will be the design and testing of appropriate containers for the selected adsorbents. For example, conformal tanks capable of lower temperature and moderate pressure (<100 bar) operation may be required. Initially, the CbHS CoE will focus on determining hydrogen binding mechanisms and energies, and the manner in which suitable sites may be organized in space to achieve a high volumetric density using low-weight frameworks. This will involve determining the effects of geometry, the introduction of defects, adventitious dopants, catalytic species, as well as elemental substitution. The CoE currently investigates a wide range of different light-weight carbon-based nanomaterials. These include pristine, metal-doped and metal-decorated graphitic materials, carbon aerogels, carbon nanohorns, graphite nanofibers, and conducting and boron doped polymers. Also included are metal organic frameworks, pure and defective SWNTs, and SWNT-metal and fullerene-metal hybrid materials. In addition to the current materials being studied, the Center will strive to be nimble in order to incorporate promising new ideas, materials, and concepts as they arise. Figure 2 shows the participants in the Center and highlights the primary research mission of each partner.



**Figure 2.** Diagram showing the organization of the Carbon-based Hydrogen Storage Center of Excellence, partner institutions, and primary responsibilities.

## Results of the Center

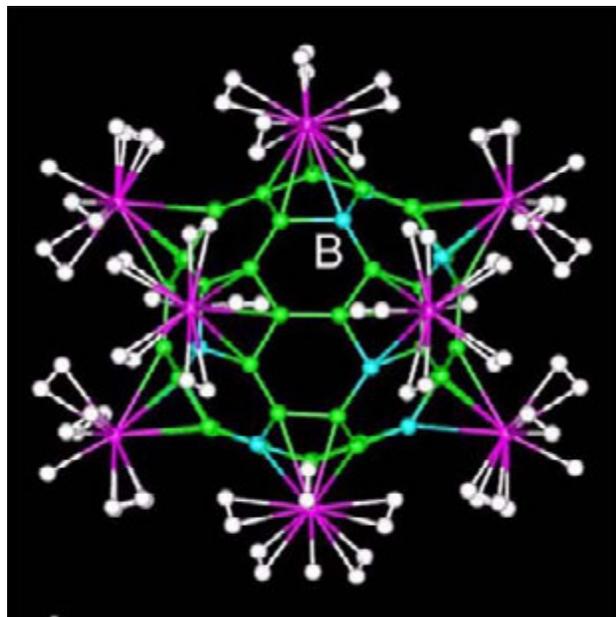
As previously indicated, the Center is interested in a wide array of materials, the study and development of the hydrogen storage capabilities of these materials, as well as the discovery and development of new, more promising materials. The Center effort is driven by a synergistic interaction between computational modeling, materials synthesis, hydrogen adsorption/desorption characterization, and systems-related engineering concerns. Numerous specific significant results from the FY 2005 Center activities were listed previously. These and others will be discussed in more detail in the Partner-specific portions of this report. Here we highlight three notable Center accomplishments.

### Development of a rational theoretical model for constructing materials capable of storing nearly 9 wt% H<sub>2</sub> at near ambient pressure and temperature.

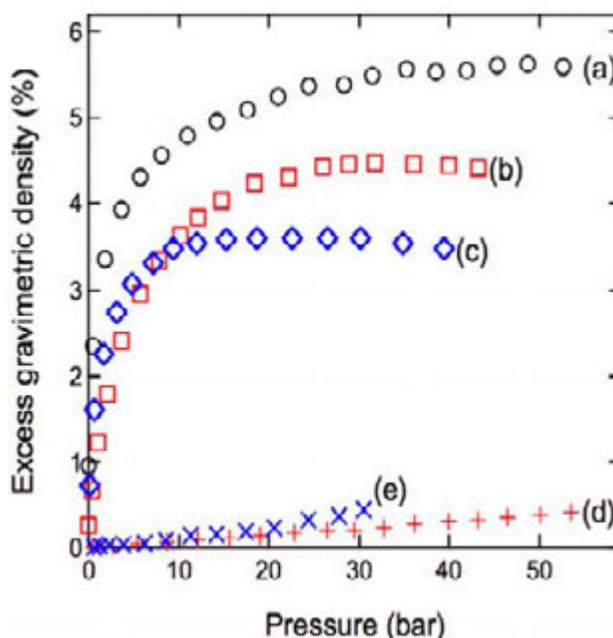
Theoretical studies performed at NREL have predicted the existence of carbon/metal hybrid materials that can stabilize copious amounts of hydrogen with binding energies that are optimized for room temperature, ambient pressure, on-vehicle hydrogen storage. These studies indicate that transition metal atoms coordinated to sp<sup>2</sup>-hybridized carbon networks can bind dihydrogen via a Kubas-type interaction. For example, Figure 3 shows a boron-doped bucky ball (C<sub>48</sub>B<sub>12</sub>) with twelve Sc atoms bound to the twelve five-atom rings of the fullerene. This structure stabilizes 8.8 wt% hydrogen reversibly as dihydrogen ligands. Future activities will focus on developing the synthetic procedures required to form such structures for testing and characterization.

### Evaluated hydrogen saturation in MOFs at 77 K; IRMOF-1 showed 4.5 wt% excess sorption at 30 bar and IRMOF-8 showed 3.6 wt% excess sorption at 15-20 bar.

Volumetric hydrogen adsorption studies performed at the California Institute of Technology on metal organic framework (MOF) materials demonstrated that pressures of 20 to 30 bar are required to fully saturate adsorption sites (Figure 4). Data taken at pressures up to 1 bar were consistent with earlier findings from the University of Michigan. Interestingly, the IRMOF-8 structure exhibited a higher sorption potential than did IRMOF-1 (6.1 kJ/mol vs. 4.1 kJ/mol), despite the fact



**Figure 3.** Boron-doped organometallic bucky ball of composition C<sub>48</sub>B<sub>12</sub>[ScH(H<sub>2</sub>)<sub>5</sub>]<sub>12</sub> which stores 8.8 wt% hydrogen reversibly. (Sc – purple, C – green, B – blue and hydrogen – white).

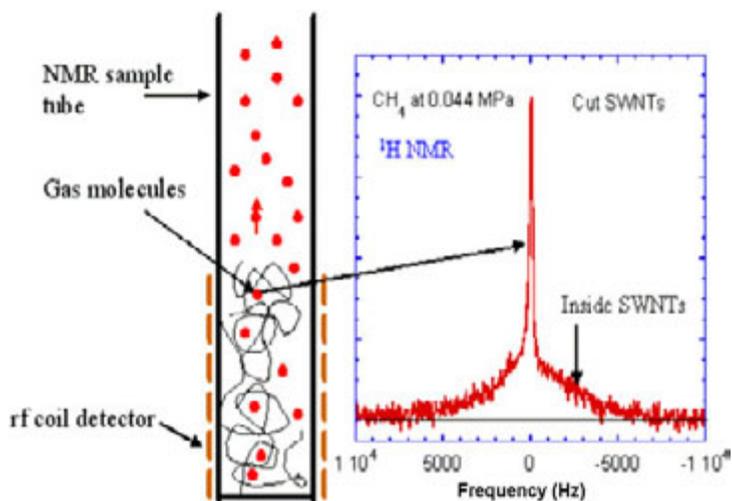


**Figure 4.** Excess adsorption at 77 K for (a) activated carbon with a mean pore size of 1.1 nm (●), (b) IRMOF-1 (■), (c) IRMOF-8 (◇), and at room temperature for (d) IRMOF-1 (+), and (e) IRMOF-8 (x).

that both materials exhibited a saturation density of 137 hydrogen molecules per unit cell. This result suggests that the active adsorption sites are associated with the zinc oxide corner units, but that the adsorption potential of the units can be modified by the characteristics of the organic linker.

### High-Pressure Cell Constructed and Tested for Nuclear Magnetic Resonance Studies of Hydrogen Adsorption up to 100 atm.

A significant component of the CbHS CoE effort is focused on developing an understanding of hydrogen interactions with high-surface-area materials. Specialized analytical techniques such as nuclear magnetic resonance (NMR) and neutron scattering are required to determine the atomic and molecular configurations of hydrogen adsorbed and bonded to solid-state materials. In addition to applying advanced neutron spectroscopy tools, discussed later in NIST's contribution to this report, efforts at the University of North Carolina (Chapel Hill) seek to establish NMR signatures for adsorbed hydrogen and to provide a quantitative, selective, and rapid method for measuring hydrogen adsorption capacities and identifying adsorption mechanisms. Towards this goal, a sapphire-based high-pressure cell was built and tested successfully up to 100 atm. The high-pressure cell is incorporated in an NMR probe for high-pressure NMR measurements. This capability is currently being employed to determine the structures and electronic states of hydrogen bound to several different adsorbent materials that have been provided by Center partners (Figure 5).



**Figure 5.** Proton NMR signal revealing both adsorbed (broad peak) and free gas (narrow peak) for methane molecules adsorbed in single-walled carbon nanotubes. The technique is currently being applied for the study of hydrogen adsorption.

## VI.C.1a Air Products and Chemicals, Inc.

*Guido Pez, Alan Cooper, and Hansong Cheng*

*Corporate Science and Technology Center*

*Air Products and Chemicals, Inc.*

*7201 Hamilton Boulevard*

*Allentown, PA 18195-1501*

*Phone: (610) 481-4271; Fax: (610) 481-7719; E-mail: PEZGP@apci.com*

*Contract Number: DE-FC36-05GO15074*

*Start Date: March 1, 2005*

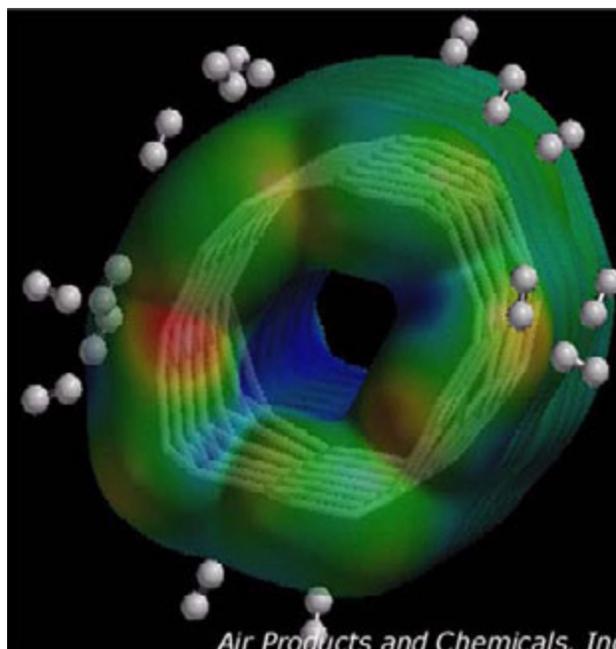
*Projected End Date: February 28, 2010*

### Partner Approach

This effort will develop and demonstrate reversible carbon-based hydrogen storage materials with at least 7 wt% materials-based gravimetric capacity and 50 g H<sub>2</sub>/L materials-based volumetric capacity, with potential to meet DOE 2010 system-level targets. This includes developing novel reversible H<sub>2</sub>-sorbent materials that are tailored for optimal binding energy, storage capacity and other parameters, such as charging rates and discharge kinetics. An integral component of the work is theoretical modeling, including an investigation of nanotube curvature chemistry and enhanced hydrogen physisorption. Air Products is collaborating with NREL and anticipates additional partner interactions for materials characterization and performance testing.

### Partner FY 2005 Results

- Developed conceptual system design using a system-engineering model of adsorption. In the model, the gravimetric hydrogen capacity is linked to the heat and the entropy of H<sub>2</sub> sorption, which determines the strength and extent of equilibrium binding to the sorbent, and to the volumetric space per unit mass of the sorbent that is accessible to hydrogen capture. Assumes reasonable values in the Langmuir isotherm model; the “tank” can deliver 7.56 wt% H<sub>2</sub>.
- Performed computational studies of hydrogen adsorption on carbon-based materials and developed new computational methods, including a curvature-dependent force field model. This constant, normal pressure and temperature (NPT) molecular dynamics model was implemented in an AIREBO simulation package to calculate the optimal distribution of H<sub>2</sub> and the average adsorption energy (kcal/mol) per H<sub>2</sub>. The uncertainty of the averaged adsorption energy is approximately ±0.5 kcal/mol. This model was then used to calculate the electrostatic potential of deformed single-walled nanotubes (SWNTs) (Figure 1).



**Figure 1.** Electrostatic potential mapped to the electron density of a deformed (5,5) single-walled carbon nanotube.

- Developed a differential pressure adsorption measurement technique that provides more accuracy than standard (absolute pressure) volumetric hydrogen adsorption measurements. The technique is equally accurate at low and high pressures (up to 120 bar), and high-temperature helium pycnometry enables accurate determination of hydrogen isotherms.
- Developing a novel, low-cost, high-throughput sorption measurement technique that directly measures the total amount of hydrogen (sorbed + gaseous) stored in a pressurized vessel containing a sorbent. The measurements can be performed at ambient to high temperatures and high hydrogen pressures, and the technique has the potential for high-throughput screening.
- Developed a non-destructive cutting procedure to “tailor” SWNTs for hydrogen storage.

### **Partner FY 2006 Plans**

Air Products will continue improving the curvature-dependent force field constant NPT molecular dynamics (MD) model through integration with Grand Canonical Monte Carlo (GCMC) simulations (in AIREBO) and density functional theory (DFT) with correct dispersion forces (implemented in SIESTA). Air Products will also begin several collaborative efforts to develop new materials and new modeling, including:

- Working with Rice University, Duke University and NREL to perform activation and adsorption characterization of carbon-based materials, especially on small-diameter SWNTs.
- Working with Penn State University to incorporate boron and nitrogen into carbon nanostructures.
- Working with California Institute of Technology on doping carbon nanotubes (CNTs) to enhance heat of adsorption of hydrogen as indicated by predictive computational modeling.
- Collaborating with Rice University and NREL to study (through experimentation and modeling, NPT-MD, GCMC) hydrogen storage capacities of carbon nanomaterials (nanotubes, nanohorns, nanofibers, etc.) at given pressures and temperatures and identify material properties key to adsorption.
- Working with Rice University, University of Michigan and NREL to evaluate (through experimentation and modeling, Monte Carlo, DFT, MD) the energetics for hydrogen spillover and identify chemisorption patterns and kinetics in carbon nanomaterials (nanofibers, nanotubes, etc.).

### **Air Products and Chemicals, Inc. FY 2005 Publications/Presentations**

H. Cheng, A.C. Cooper, G.P. Pez, M.K. Kostov, P. Piotrowski, S.J. Stuart, *J. Phys. Chem. B* 109, 3780 (2005).

## VI.C.1b California Institute of Technology

Channing Ahn, R. H. Grubbs and R. C. Bowman Jr.

California Institute of Technology (Caltech)

1200 E. California Blvd.

MS 138-78 Pasadena, CA 91125

Phone: (626) 395-2174; Fax: (626) 795-6132; E-mail: cca@caltech.edu

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Start Date: February 1, 2005

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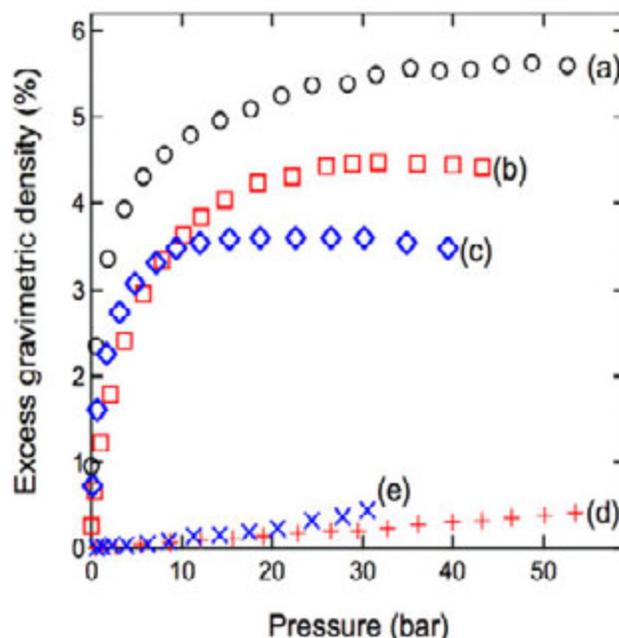
### Partner Approach

Establish the principle of enhanced dipole physisorption and evaluate the efficacy of carbon-based systems as commercially viable hydrogen storage sorbents. This is done by manipulating site potentials through the use of local charge states and pKa-adjusted edge sites to provide deeper insights into the hydrogen physisorption phenomenon and to enable design optimization for a material with characteristics that will address DOE storage targets. Specific activities include:

- Activation of mechanically-attrited carbons.
- Synthesis of intercalated nanotubes with local charge states that act as local high-potential surface sites.
- Synthesis of diacid-based and polymer structures that maximize edge geometries with well-controlled potentials.
- Characterization and evaluation of these materials for hydrogen sorption behavior with volumetric Sieverts apparatus.

### Partner FY 2005 Results

- Evaluated hydrogen saturation sorption behavior of isorecticular metal organic framework (IRMOF) structures showing 4.5 wt% excess sorption in IRMOF-1 at 77 K at 30 bar and 3.6 wt% excess sorption in IRMOF-8 at 77 K at 15-20 bar (Figure 1).
- Determined adsorption heats of 4.1 kJ/mole in IRMOF-1 and 6.1 kJ/mole in IRMOF-8.
- Sorption measurement of a wood-based activated carbon revealed 5.4 wt% excess sorption at 40 bar and 77 K, the highest value measured in a material of this type.



**Figure 1.** Excess adsorption at 77 K for (a) activated carbon with a mean pore size of 1.1 nm (●), (b) IRMOF-1 (■), (c) IRMOF-8 (◇), and at room temperature for (d) IRMOF-1 (+), and (e) IRMOF-8 (x).

## **Partner FY 2006 Plans**

Using synthesis techniques perfected in year one on systems of interest, work in FY 2006 will be performed on variants of known materials that have already been made at Caltech. These include diacid-modified framework structures that should have higher sorption potentials than those that were synthesized and tested in year one. Polymeric modifications should also enhance surface areas, a necessary attribute of the materials of interest, if high sorption capacities are to be attained.

Because of the high pressure/high temperature range capabilities of the Sieverts apparatus at Caltech and given the expertise developed with this type of measurement over the past 10 years, collaboration with Lawrence Livermore National Laboratory (LLNL – Ted Baumann) will continue to measure isotherms from LLNL carbon aerogels. LLNL has also begun examining some of the modified IRMOF materials from Caltech using nuclear magnetic resonance (Julie Herberg), and further collaboration is anticipated with Yue Wu (University of North Carolina) to perform additional NMR measurements. Collaboration with J. Karl Johnson of the University of Pittsburgh will continue, and collaboration with Dan Neumann and Craig Brown of the National Institute of Standards and Technology (NIST) is anticipated in FY 2006 to aid in the structural characterization of materials.

## **California Institute of Technology FY 2005 Publications/Presentations**

1. 2005 DOE Hydrogen Program Review, May 23-26, Crystal City.
2. 2005 Hydrogen in Metals Gordon Conference, July 11, Colby College.
3. "Saturation of Hydrogen Sorption in Zn Benzenedicarboxylate and Zn Naphthalenedicarboxylate," A. Dailly, J. J. Vajo and C. C. Ahn, submitted to *Angewandte Chemie*.

## VI.C.1c Duke University

*Jie Liu*

*Department of Chemistry*

*Duke University*

*Durham, NC 27708*

*Phone: (919) 660-1549; Fax: (919) 660-1605; E-mail: j.liu@duke.edu*

*Contract Number: DE-FC36-05GO15103*

*Start Date: February 1, 2005*

*Projected End Date: January 31, 2010*

### Partner Approach

This project is conducting fundamental studies of hydrogen storage in carbon nanotubes. The focus of the project is to understand the relationship between the diameter of single-walled carbon nanotubes and their hydrogen storage capacity and reversibility. To achieve this understanding, nanotube samples with controlled diameters will be prepared using different methods, and the samples will be shared with other members in the DOE Center of Excellence on Carbon-based Hydrogen Storage for the study of their storage properties. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials. Thus, several activities are being performed to:

- Study the effect of nanotube diameter on hydrogen storage properties.
- Develop methods to precisely control the diameter of the produced nanotubes.
- Produce large quantities of purified carbon nanotubes for hydrogen storage studies.

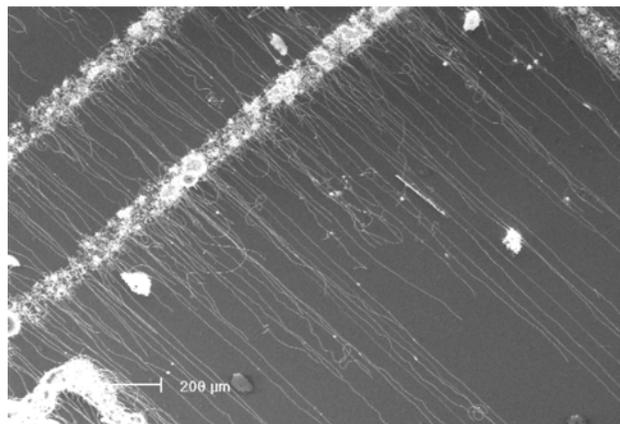
The diameter of single-walled carbon nanotubes is controlled by the size of the catalyst nanoparticle during the initiation stage of the growth. If the diameters of the catalysts can be controlled, the diameters of the nanotubes can be controlled. To control the diameter of produced carbon nanotubes, several approaches are being investigated. These include:

- Using Molecular Clusters as Catalysts - Molecular clusters are molecules with an identical number of metal atoms in each cluster, making them perfect catalysts for the growth of uniform nanotubes. The growth of uniform nanotubes was demonstrated before at Duke using one type of clusters. For this effort, several different types of nanocluster molecules with different sizes and chemical compositions will be explored. The goal is not only to prepare nanotubes with different sizes but also to understand the effect of different metals as catalysts for nanotube growth. The focus of the research will be on the production of small-diameter nanotubes that are believed to be better candidates for hydrogen storage based on theoretical calculations.
- Obtaining Nanotube Seeds for Nanotube “Cloning” - The underlying hypothesis assumes that if a catalyst nanoparticle is docked at the open end of an existing short nanotube, the new nanotube grown under appropriate conditions will adapt the same structure as the short nanotube used as seed. The seeds for the re-growth can be obtained in several ways. For this effort, methods will be developed to selectively dock nanoparticle catalysts to the open ends of short nanotube seeds.
- Using Inorganic Templates - Inorganic templates with uniform inner diameter channels can be used to control the diameters of prepared nanotubes. The types of templates that will be investigated include MCM-41 mesoporous materials and large-pore zeolites. By thermally decomposing carbon-containing precursors on the walls of the pores, the prepared nanotubes will be constrained physically. The research

activity includes the discovery of optimized reaction conditions for obtaining highly graphitized nanotubes and the synthesis of the right template systems with various pore diameters.

### Partner FY 2005 Results

- Raw HiPCO (high pressure carbon monoxide) nanotubes were identified as very good catalysts for the growth of long nanotubes, presumably due to the large amount of small Fe nanoparticles embedded in the raw sample.
- By patterning raw nanotubes on a Si wafer and performing chemical vapor deposition growth of nanotubes, a high density of long nanotubes was grown (Figure 1).
- Initially, when using raw HiPCO nanotubes as catalysts, the diameter distribution of the newly grown nanotubes is broad. The reason is the large number of Fe nanoparticles with different sizes that are attached to the walls of the HiPCO nanotubes. After treating the raw nanotubes with acid to remove these Fe nanoparticles used to grow new nanotubes, the diameter distribution is much narrower with a large amount of nanotubes with diameters smaller than 1 nm.



**Figure 1.** Scanning electron microscopy image of long nanotubes grown using raw HiPCo Nanotubes as catalysts.

### Partner FY 2006 Plans

In FY 2006, the research effort will focus on obtaining gram quantities of single-walled nanotubes with uniform diameters and providing them to other Center members to determine the relationship between the diameters of the nanotubes and the storage capacity of hydrogen. The diameter of one of the samples will be smaller than 1 nm. In addition, different factors that control the diameters of the produced nanotubes will be investigated to obtain a better understanding of the key factors. Specific research will include the growth of nanotubes using Fe/Mo clusters for nanotube growth and the use of zeolites as templates for nanotube growth.

Samples prepared at Duke will be sent to NREL, where small amounts of samples can be accurately characterized. Highly purified nanotubes will also be sent to the University of North Carolina (UNC) for NMR studies. Feedback from the NREL and UNC groups will provide direction for future synthesis efforts.

## VI.C.1d Lawrence Livermore National Laboratory

*Joe H. Satcher (Primary Contact), Theodore F. Baumann, Julie L. Herberg*

*Energy and Environment Directorate*

*Lawrence Livermore National Laboratory*

*7000 East Avenue*

*Livermore, CA 94550*

*Phone: (925) 422-7794; Fax: (925) 423-4897; E-mail: satcher1@llnl.gov*

*Start Date: FY 2005*

*Projected End Date: Project continuation and direction determined annually by DOE*

### Partner Approach

Metal-doped carbon aerogels (MDCAs) comprise a unique class of materials possessing a number of desirable properties for hydrogen storage, including tunable porosities, high specific surface areas (up to 1000 m<sup>2</sup>/g) and microstructures that consist of an intimate mix of metal nanoparticles and graphitic carbon. Our approach to optimizing the hydrogen storage properties of these materials is to utilize the flexibility associated with their preparation. The procedure used to synthesize MDCAs readily allows for modification of their structure, including the type and amount of incorporated metal species, degree of graphitization, surface area and bulk density. Hydrogen adsorption measurements will be used to down-select the number of MDCAs investigated, and the synthesis of the most promising candidates will be refined to further enhance their interaction with hydrogen. The synthesis and structural characterization of the MDCAs is performed at Lawrence Livermore National Laboratory (LLNL), while Center members at CalTech and Air Products will perform the hydrogen adsorption experiments on these materials. Advanced nuclear magnetic resonance (NMR) techniques will be used to unravel the mechanisms associated with hydrogen physisorption/chemisorption in these carbon-based materials. These experiments will be performed in conjunction with the NMR efforts at the University of North Carolina. Insights gained from these NMR studies will be essential in identifying the key structural features associated with hydrogen binding in these composite structures and, as a result, should be beneficial to the other Center efforts focused on the design of nanostructured carbon-based materials.

### Partner Results for FY 2005

- Prepared large quantities (multi-gram lots) of MDCAs containing different metals (i.e., iron, nickel, cobalt) and at different densities.
- Completed characterization of the microstructure of these different MDCAs using a variety of advanced techniques, including transmission electron microscopy, powder x-ray diffraction and x-ray photoelectron spectroscopy.
- Evaluating the hydrogen storage properties of these materials.

### Partner FY 2006 Plans

The major milestone for FY 2005 is the down-selection to two or three of the most promising MDCAs based on hydrogen adsorption measurements. Our plan for FY 2006 is to identify the key structural features in the most promising MDCAs (type/amount of metal, degree of graphitization, etc.) that correlate with favorable hydrogen uptake and then modify the materials synthesis with the goal of further improving the interaction of the MDCAs with hydrogen. Mechanistic studies will also continue using advanced NMR techniques to provide important insights regarding the nature of hydrogen binding in the MDCAs.

### Lawrence Livermore National Laboratory FY 2005 Publications/Presentations

1. Fu, R.; Baumann, T. F.; Cronin, S.; Dresselhaus, G.; Dresselhaus, M. S.; Satcher, J. H. "Formation of Graphitic Structures in Cobalt- and Nickel-doped Carbon Aerogels," *Langmuir*, **2005**, *21*, 2647.

## VI.C.1e National Institute of Standards and Technology

Dan Neumann (Primary Contact) and Craig Brown

NIST Center for Neutron Research

MS 8562

100 Bureau Dr.

Gaithersburg, MD 20899

Phone: (301) 975-5252; Fax: (301) 921-9847; E-mail: dan@nist.gov

Start Date: FY 2005

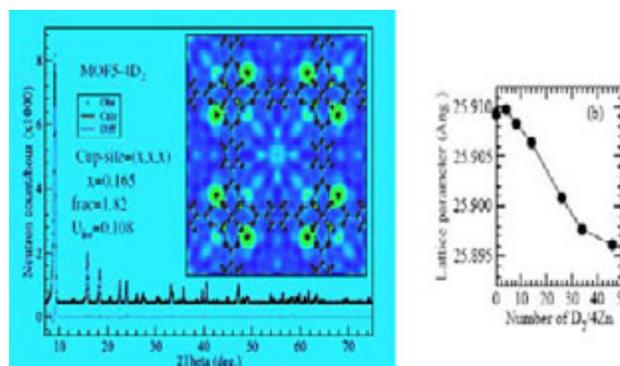
Projected End Date: Project continuation and direction determined annually by DOE

### Partner Approach

NIST will provide important materials characterization for Center partners using neutron-scattering measurements to probe the amount, location, bonding states, dynamics, and morphological aspects of hydrogen in carbon-based materials such as polymers, metal organic frameworks (MOFs), and carbonaceous materials such as carbon nanotubes. NIST will work directly with Center partners that produce novel hydrogen storage materials to analyze the most promising samples and to help determine the fundamental issues that need to be addressed.

### Partner FY 2005 Results

- The hydrogen adsorption sites in MOF-5 were determined using neutron powder diffraction (Figure 1). There is a slight lattice contraction upon increasing hydrogen loading (to a maximum of ~10 wt% H<sub>2</sub> at 3.5 K). The ZnO<sub>4</sub>-cluster is responsible for most of the adsorption, while the organic linker plays only a secondary role. The highest loadings can be described with hydrogen close contacts as short as 3.0 Å, as compared to 3.6 Å in solid H<sub>2</sub>. Density functional theory (DFT) calculations of hydrogen in the first adsorption sites leads us to expect significant splitting of the *ortho-para* rotational transitions for H<sub>2</sub> molecules that will require a proper treatment of translation-rotation coupling of the H<sub>2</sub> quantum dynamics to explain inelastic neutron data that we have also collected as a function of loading.
- Acquired and refurbished a laboratory dedicated to hydrogen storage efforts. This effort required fume hood adaptation, re-routing of electrical supplies and basic infrastructure work. Built a high-vacuum sample preparation and glass/quartz sample sealing station.



**Figure 1.** Neutron powder pattern and Rietveld structural refinement of deuterium-loaded MOF-5 containing 4 molecules of D<sub>2</sub> per 4 ZnO units. The insert shows a color Fourier difference map of the measured data and that from just the MOF-5 framework. The deuterium locations are clearly distinguishable from the extra scattering intensity in the (x, x, x) sites (with x=0.165) and are included in the refinement.

### Partner FY 2006 Plans

Continue isothermal gas loading, inelastic neutron scattering, neutron powder diffraction, and prompt gamma hydrogen content measurements on samples of interest to the Center. Samples will include at least four from the following: MOFs; aerogels; polymers; graphitic nanofibers; carbon nanotubes; hybrid B-N-C systems; and

doped carbon materials. Contacts have been made with Mike Heben at NREL, Peter Eklund at Penn State, Alan MacDiarmid at the University of Pennsylvania, and Channing Ahn at the California Institute of Technology. Further detailed neutron studies will be performed to evaluate the effects of controlled synthesis on materials such as MOFs and metal-decorated nanotubes.

**NIST FY 2005 Publications/Presentations**

1. Direct Observation of Hydrogen Adsorption Sites and Nano-Cage Formation in Metal-Organic Frameworks (MOF); T. Yildirim and M. R. Hartman submitted to Phys. Rev. Letts.

## VI.C.1f National Renewable Energy Laboratory

*M.J. Heben (Primary Contact)*

*Key Personnel: J.L. Alleman, J.L. Blackburn, C. Curtis, A.C. Dillon, T. Gennett, K.E.H. Gilbert, K.M. Jones, Y.-H. Kim, P.A. Parilla, L.J. Simpson, Y. Yan, S.B. Zhang, Y. Zhao*

*National Renewable Energy Laboratory*

*1617 Cole Blvd.*

*Golden, CO 80401*

*Phone: (303) 384-6641; Fax: (303) 384-6655; E-mail: michael\_heben@nrel.gov*

*Start Date: FY 2005*

*Projected End Date: Project continuation and direction determined annually by DOE*

### Partner Approach

The NREL effort addresses many of the technical barriers in Task 3 of DOE's HFCIT Program Multi-Year RD&D Plan. Theoretical modeling and experimental investigations are performed to discern mechanisms and provide guidance for materials development. These studies elucidate the physics and chemistry of adsorption and enable the design of new materials with superior performance. During the past year, NREL has broadened investigations beyond single-walled carbon nanotubes to include a wide array of promising nanostructured carbon-based materials, and developed new flexible, repeatable, and potentially scalable synthesis strategies. Hydrogen storage capacities of the nanostructured adsorbent materials of interest are accurately measured with custom-built temperature-programmed desorption and volumetric apparatuses. The capacity measurements support materials development work being done in-house and at CbHS CoE partners, and are also used to analyze promising samples prepared by researchers from other collaborating institutions. A thorough understanding of the sources of error in hydrogen storage measurements has permitted simplification of the measurement processes, allowing the development of high-throughput methods. These advances are being disseminated to CbHS CoE partners and the larger hydrogen storage community and will help to establish standard test protocols for evaluating reversible hydrogen storage materials.

### Partner FY 2005 Results

#### Route to 9 wt% Material Capacity for Carbon-based Hydrogen Storage

Theoretical studies were performed to develop a deeper understanding of experimental results [1] that showed enhanced hydrogen binding energies for transition metals in contact with  $sp^2$ -bonded carbon atoms. Going beyond explanation of the already observed data, the computations also predict the capacities and energetics for future hydrogen storage materials. Materials are required that can stabilize high capacities of hydrogen with a binding energy between  $\sim 4 - 40$  kJ/mol to allow for near-room-temperature operation at reasonable pressures. A moderate binding energy is also crucial for managing the heat load during refueling.

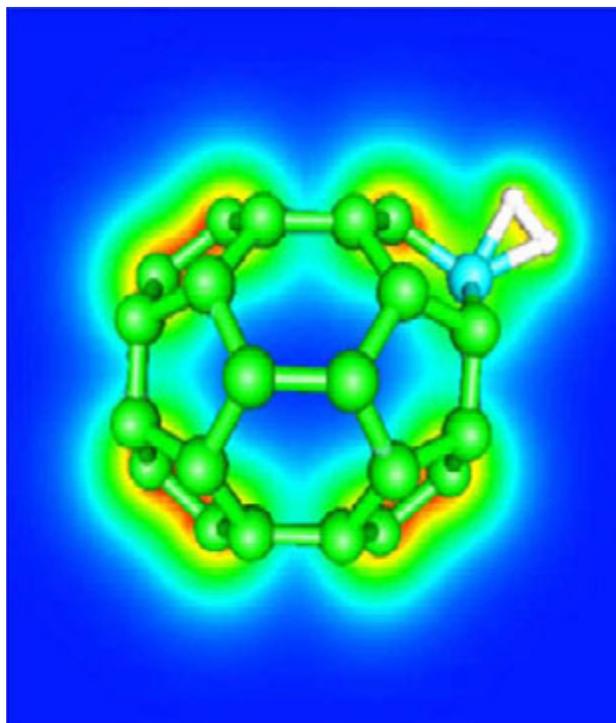
The energies with which hydrogen bonds to carbon range from quite weak to quite strong. Non-dissociative physisorption, due purely to van der Waals interactions, involves a binding energy of only  $\sim 4$  kJ/mol, whereas a C-H chemical bond can have an energy as large as 400 kJ/mol. Thus, the desired binding energy range for reversible vehicular storage dictates that hydrogen be stabilized in an atypical fashion. Extensive theoretical investigations were performed to discover new structures that could stabilize hydrogen at near ambient conditions. The results from these studies indicated that molecular hydrogen can be stabilized on  $sp^2$ -hybridized carbon networks that are either decorated or doped with a metal atom [2].

For example, Figure 1 shows the results from a calculation in which a boron atom is substituted into a  $C_{36}$  fullerene to form  $C_{35}B$ . The presence of the boron atom generates a hole in the electronic structure, and the localized positive charge stabilizes the hydrogen molecule with a binding energy of  $\sim 38$  kJ/mol. In a similar study where an iron dopant was employed to form  $C_{35}Fe$ , one of the carbon-iron bonds was broken upon exposure to hydrogen and dissociative adsorption was observed. Here the binding energy for the hydride formation was  $\sim 100$  kJ/mol, outside the desired binding energy range for vehicular storage applications. However, when an iron atom or another transition metal such as Sc, Ti, V, Cr, Mn, Fe, Co, or Ni is allowed to coordinate to a fullerene (Figure 2), it is possible to form an organometallic fullerene complex capable of stabilizing hydrogen and di-hydrogen ligands with the desired binding energies.

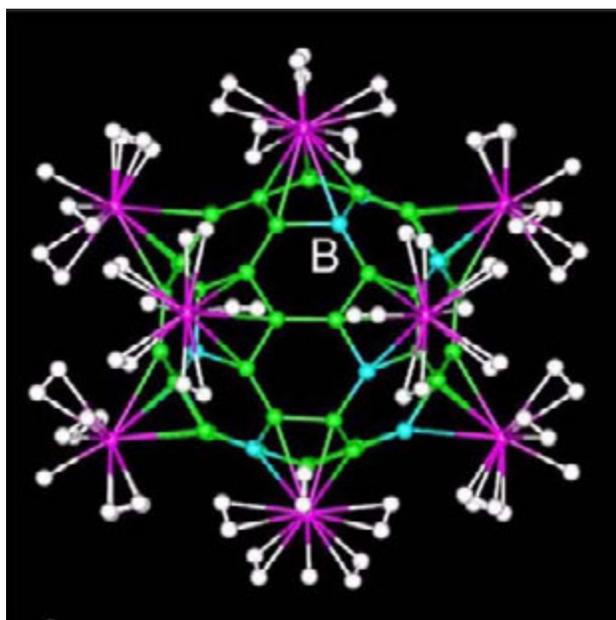
Combining both substitutional doping and metal decoration concepts permits construction of high-capacity adsorbents using fullerenes as a support. Such an organometallic fullerene complex utilizes both Dewar coordination of a transition metal to the twelve five-membered rings on  $C_{60}$  and the stabilization of multiple dihydrogen ligands through a Kubas interaction. Although each type of bonding is of historical importance in coordination chemistry, the combination of the two as a solution for hydrogen storage has not been considered previously. The interaction of hydrogen with these materials can result in both dissociative adsorption to form hydride species and non-dissociative adsorption to form bound dihydrogen molecules. A Sc-based organometallic fullerene complex capable of storing 8.8 wt% reversibly is depicted in Figure 2. It is important to note that the binding energy for the reversibly bound dihydrogen species is  $\sim 30$  kJ/mol, as required for use on-board vehicles.

#### High-Throughput Temperature-Programmed Desorption (TPD) Apparatus

As part of the collaboration activities within the CbHS CoE, NREL is providing high-quality hydrogen sorption and desorption measurements to partners to help characterize performance. To perform measurements more rapidly and to increase the number of samples that can be measured in a given amount of time, high-throughput measurement techniques are being developed. Temperature-programmed



**Figure 1.** Theoretical calculations showing a  $C_{35}B$  cluster with an  $H_2$  molecule (white) bonded to boron (blue) with a binding energy of  $\sim 38$  kJ/mol.



**Figure 2.** Boron-doped organometallic bucky ball of composition  $C_{48}B_{12}[ScH(H_2)_5]_{12}$  which stores 8.8 wt% hydrogen reversibly. (Sc – purple, C – green, B – blue and hydrogen – white).

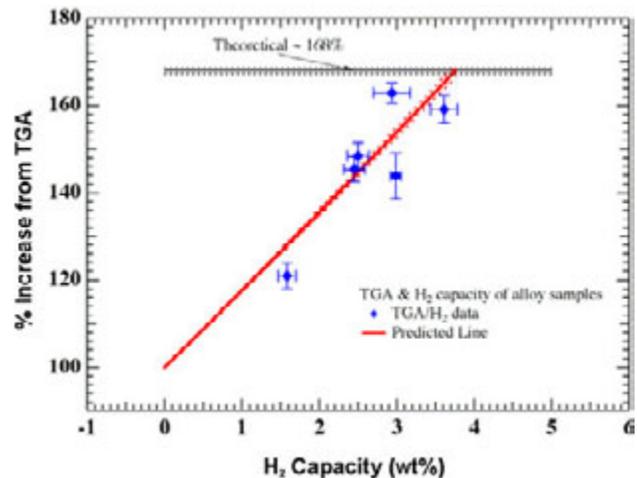
desorption (TPD) was down-selected over optical detection and volumetric measurement as the best choice for initial deployment in a multi-sample configuration. Previously, throughput was limited due to availability of a single piece of equipment that performs only one TPD measurement at a time. Thus, a multi-channel, high-throughput TPD apparatus was designed and constructed to measure at least six identical samples within 5% accuracy in a twenty-four hour period. The effort has created a resource for rapidly screening the hydrogen storage properties of multiple samples. Such a high-throughput measurement system enables expeditious support to the CbHS CoE and the wider community in general.

#### Hydrogen Storage Capacity of TiAlV Alloy

During the aggressive sonication used to generate single-walled nanotube (SWNT) samples that demonstrated up to 8 wt% hydrogen storage at room temperature and ambient pressure, [1] Ti-6Al-4V alloy particulates from the sonicator tip were produced and combined with the SWNTs to form a nanotube/alloy mixture. Previous control experiments determined the hydrogen capacity of the probe alloy particles that were produced in an identical manner but without nanotubes being present. These alloy samples consistently demonstrated ~2.5 wt% H<sub>2</sub> uptake during repeated measurements using both TPD and volumetric measurement techniques. Since the Ti metal fraction in the alloy should demonstrate ~3.6 wt% sorption by itself, these results suggest a shell/core structure for the particles (Ti-Al-V-O shell, Ti-Al-V core) due to the particles being oxidizing during sonication in nitric acid. This oxide layer on the surface is not expected to be an active hydride and can act as a diffusion barrier for hydrogen transfer. Both of these effects will reduce the amount of hydrogen stored by the samples. Thus, the measured 2.5 wt% value reflects the high reproducibility of forming the alloy particles with the same fraction of alloy/alloy-oxide composition, and is expected to represent the true hydrogen storage capacity of the alloy/alloy-oxide mixture even when the nanotubes are present. Even when generous estimates for hydrogen absorption by the alloy were used, data analysis consistently showed that hydrogen was being stored by the nanotubes.

However, to determine the maximum hydrogen storage potential of the TiAlV alloy particulates, a systematic set of procedures was performed to identify processing and test conditions that enabled a maximum hydrogen storage capacity. New procedures for generating the alloy were implemented to vary the oxide layer thickness. The new procedures included heat sinks to lower the temperature of the bath during sonication and adding a surfactant to aid in dispersal. Thermogravimetric analysis (TGA) and X-ray diffraction measurements on the alloy were used to quantify the amount of oxidation. As expected, the data indicated that the amount of oxidation is directly correlated to the hydrogen capacity (Figure 3) since oxidized metal no longer participates in hydrogen sorption. Furthermore, the results indicated that the room-temperature room-pressure hydrogen storage capacity of pure (unoxidized, commercially available pure material) Ti-6Al-4V alloy is 3.76 wt%. However, the highest measured value of any material made using the sonication process and extensive reduction was ~3.7 wt%.

While it may be possible that the presence of the nanotubes inhibits the oxide formation in some cases,



**Figure 3.** Percent mass increase due to oxidation in air versus H<sub>2</sub> capacity shows a correlation due to oxide coating on alloy particles. The red line shows the predicted correlation with no free parameters using the measured H<sub>2</sub> capacity for pure alloy obtained from Goodfellow. The black line shows the maximum theoretical TGA mass increase. Error bars are shown for both axes.

or that the carbon phase may act as a reductant during high-temperature degassing, it is unlikely that oxide formation was completely inhibited or that all the oxide could be removed. In any event, the fact that previous measurements [1] conclusively showed uptake on the carbon/alloy composite that was significantly above 3.7 wt% demonstrates that carbon nanotubes improve the hydrogen storage substantially beyond expectations based on adsorption in the alloy alone.

### H<sub>2</sub>/D<sub>2</sub> Exchange to Determine Dissociative and Non-dissociative Binding

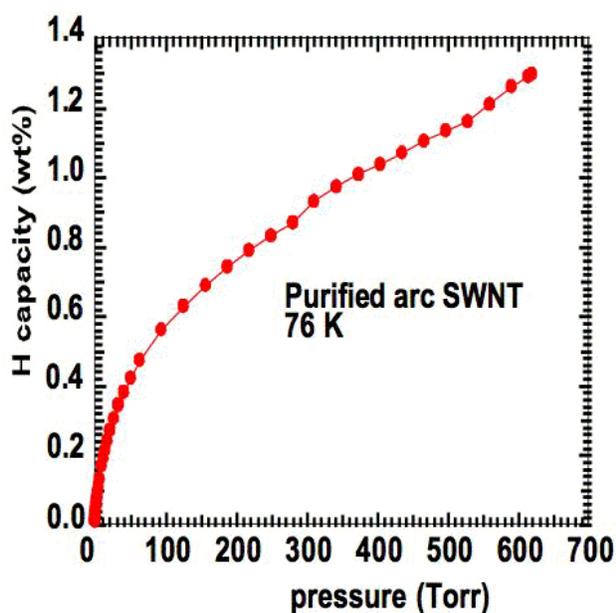
As part of the continuing effort to advance hydrogen storage materials performance, improved measurement and characterization techniques are required to provide insight into the actual mechanisms involved. While binding energies can be quantitatively measured, determining whether a hydrogen molecule is dissociated or not in a sorption process is not always straightforward. NREL has developed an analytical technique that unambiguously distinguishes when hydrogen is dissociated during a sorption process. The test uses hydrogen and deuterium molecules as probe sorbates. If the sorption is non-dissociative and both H<sub>2</sub> and D<sub>2</sub> species are sorbed, then only H<sub>2</sub> (molecular weight of 2) and D<sub>2</sub> (molecular weight of 4) species should be observed in the mass spectroscopy during desorption measurements. If, however, the sorption process is dissociative, as was observed for, e.g., cobalt/SWNT hybrid material, then mixed hydrogen-deuterium molecules (molecular weight three) are observed during desorption. While additional calibration activities will be performed to quantify the degree of dissociation, the technique has been demonstrated and will provide valuable mechanistic information for developing new hydrogen storage materials.

### Low-Temperature (77 K) and Low-Hydrogen-Pressure (1 atm) Sorption

Pure carbon nanotubes (CNTs) and other carbon materials have demonstrated significant hydrogen storage at moderately low temperatures (liquid nitrogen) and pressures. To fully understand and characterize all potential adsorption mechanisms that may be useful for on-vehicle storage, NREL has developed tests and procedures to quantify hydrogen storage performance at lower temperatures on relatively small samples. Figure 4 contains representative data demonstrating NREL's capabilities to perform high-quality measurements on milligram-sized samples at lower temperatures and pressures. The results with un-optimized SWNTs are encouraging and suggest a path to developing carbon-based materials for hydrogen storage. Also, these low-temperature measurement capabilities enable detailed characterization that will be required to engineer more advanced materials with improved performance.

### Hydrogen Storage Performance of Conducting Polymers

As discussed in the University of Pennsylvania work which follows, NREL collaborated with Dr. Alan MacDiarmid by performing TPD measurements on commercial polyaniline (PANI) treated with hydrochloric acid. The TPD measurements on these initial PANI samples provided a baseline for hydrogen storage performance that has led to other collaborative work involving conducting polymers.



**Figure 4.** Measured hydrogen capacity at liquid nitrogen temperatures as a function of hydrogen pressure for purified (no metals) SWNTs.

### Reproducible Processing of Hybrid CNTs that Demonstrate 4 wt% Hydrogen Storage

NREL is developing a number of complementary processes that improve the reproducible formation of hybrid CNTs. The goal is to use robust processing that reproducibly creates hybrid CNTs that demonstrate 4 wt% or greater reversible hydrogen storage. The materials' performance will be independently validated at Southwest Research Institute. Present efforts have developed reproducible processing that creates high-quality pure SWNTs. Furthermore, as discussed above, processing issues associated with alloy hydrogen storage performance have been defined, and advances in alloy/SWNT processing have been made. These improvements in component materials processing have resulted in the formation of hybrid materials that demonstrate more consistent hydrogen storage performance. In addition, Fe/multi-walled CNT materials have also been produced that demonstrate room-temperature and ambient-pressure hydrogen storage. These materials advancements have helped lead the way to a better understanding of the hydrogen adsorption mechanisms involved, which in turn will enable improved molecular engineering processes to be developed. All these developments are being integrated through systematic investigations to nano-engineer advanced hydrogen storage materials with over 4 wt% reversible hydrogen storage.

### **Conclusions of Partner Effort for FY 2005**

NREL continues to develop novel nano-engineered materials to meet the DOE's on-vehicle hydrogen storage goals. For example, NREL has demonstrated that doping  $sp^2$ -hybridized structures such as carbon SWNTs, fullerenes or other  $sp^2$ -hybridized nano-frameworks with boron may result in unanticipated hydrogen sorption properties. Experimental synthesis of boron-doped carbon nanostructures has been demonstrated, and optimization activities are in progress. Furthermore, NREL identified that decorating similar carbon nanostructures with transition metals, particularly Sc, Ti, V and Cr, may result in the formation of organometallic complexes that stabilize dihydrogen ligands with moderate binding energies. Both approaches and their combination will be actively investigated to engineer improved hydrogen storage materials. In addition to materials development, NREL is also developing improved characterization methodologies and is the lead organization for the DOE CbHS CoE, which is performing a diverse set of research and development activities.

### **Partner Plans for FY 2006**

- Provide technical direction to and assistance in the integration of the CbHS CoE in support of DOE, Office of Energy Efficiency and Renewable Energy (EERE), and HFCIT goals.
- Identify an efficient, safe, cost-effective carbon-based technology that can meet the goals for on-vehicle hydrogen storage applications.
- Foster collaboration and communication between Center members, DOE and other interested parties.
- Evaluate materials from Center members and others for future direction and hold intensive workshops.
- Continue to provide advanced hydrogen sorption measurements for in-house, CbHS CoE partner, and other external materials development efforts.
- Enhance measurement throughput and accuracy for the samples produced in the CbHS CoE.
- Extend measurement techniques to low temperature and moderate pressure conditions.
- Develop synthetic methods using gas-phase, solution-phase and other approaches where carbon, metal, and hydrogen (or other stabilizing ligands) may coalesce to form targeted C:M:H nanomaterials like the high hydrogen storage organometallic complexes that have been theoretically predicted.
- Optimize theoretical predictions of the strength of non-dissociative dihydrogen binding on metal-coated buckyballs and nanotubes by varying the metal elements, sorption sites coordination, and nanotube diameters and chirality.

- Determine non-dissociative dihydrogen binding mechanisms in metal carbides nanoclusters and nanocrystals.
- Advance the study of metal organic frameworks by investigating metal carbide nanocrystals and MetCars as replacements for the ZnO tetrahedrons to achieve higher reversible hydrogen storage capacities.

### NREL Special Recognitions & Awards/Patents Issued

1. A. Dillon, Organizer of symposium at the 2005 Fall Materials Research Society (MRS) Meeting entitled “The Hydrogen Cycle, Generation, Production and Storage”, and Editor of a special edition of Journal of Materials Research on the same topic.
2. M. Heben, Organizer of the International Partnership for the Hydrogen Economy meeting on Hydrogen Storage in Lucca, Italy, June, 2005.
3. M. Heben, Organizer of session on Hydrogen Storage Materials at the 2004 Fall MRS Meeting, Boston, MA, Dec. 2-4, 2004, and Editor of the Mat. Res. Soc. Proceedings Volume from the meeting session.
4. M. Heben, Organizer of session on Hydrogen Storage Materials to be held at the 2006 Spring Meeting of the MRS.
5. M. Heben, Organizer of session on Hydrogen Energy to be held at the 2006 National Meeting of the Electrochemical Society.
6. Best Poster Award, “Generalized Kubas Complexes as a Novel Means for Room Temperature Molecular Hydrogen Storage,” Y.-H. Kim, Y. Zhao, M.J. Heben, and S.B. Zhang, Poster at the 2004 Fall Meeting of the Materials Research Society.
7. Best Poster Award, “Interaction of Hydrogen with Carbon Based Molecules Through Transition Metal Atoms,” Y. Zhao, Y.-H. Kim, A.C. Dillon, M.J. Heben, and S.B. Zhang, 2004 Fall Meeting of the Materials Research Society.
8. Ribbon Award (second best paper), “Discovering the Mechanism of H<sub>2</sub> Adsorption on Aromatic Carbon Nanostructures to Develop Adsorbents for Vehicular Applications,” A.C. Dillon, J.L. Blackburn, P.A. Parilla, Y. Zhao, Y.-H. Kim, S.B. Zhang, A.H. Mahan, J.L. Alleman, K.M. Jones, K.E.H. Gilbert and M.J. Heben, 2004 Fall Meeting of the Materials Research Society.
9. NREL Nanotubes are the Purest: A sample provided by NREL to Robert Haddon’s research group was determined to be the purest sample they have ever evaluated. The sample was determined to have a purity value more than twice that of the previous best sample. The results were presented by Itkis/Haddon at a recent NIST workshop on nanotube purity.

### NREL FY 2005 Publications

1. Y. Zhao, Y.-H. Kim, A.C. Dillon, M.J. Heben, and S.B. Zhang, “Towards 9 wt%, Reversible, Room Temperature Hydrogen Adsorbents: Hydrogen Saturated Organometallic Bucky Balls,” *Phys. Rev. Lett.* 94(15), 155504 (2005).
2. L.M. Wagg, G.L. Hornyak<sup>1</sup>, L. Grigorian<sup>2</sup>, A.C. Dillon, K.M. Jones, J. Blackburn, P.A. Parilla and M.J. Heben, “Experimental Gibbs Free Energy Considerations in the Nucleation and Growth of Single-walled Carbon Nanotubes,” *J. Phys Chem. B.* 109, 10435-10440 (2005).
3. A.C. Dillon, J.L. Blackburn, P.A. Parilla, Y. Zhao, Y.-H. Kim, S.B. Zhang, A.H. Mahan, J.L. Alleman, K.M. Jones, K.E.H. Gilbert and M.J. Heben, “Discovering the Mechanism of H<sub>2</sub> Adsorption on Aromatic Carbon Nanostructures to Develop Adsorbents for Vehicular Applications,” *Mat. Res. Soc. Proc.* 837 (2005) 117-123.
4. Y. Zhao, Y.-H. Kim, A.C. Dillon, M.J. Heben and S.B. Zhang, “Interaction of Hydrogen with Carbon Based Molecules Through Transition Metal Atoms,” 2004 *Mat. Res. Soc. Proc.* (in press).
5. Y.-W. Lee, R. Deshpande, A.C. Dillon, M.J. Heben, H. Dai and B.M. Clemens, “The Role of Metal Catalyst in Near Ambient Hydrogen Adsorption on Multi-walled Nanotubes,” 2004 *Mat. Res. Soc. Proc.* (in press).
6. A.C. Dillon, A.H. Mahan, R. Deshpande, C. Engtrakul, J.L. Alleman, J.L. Blackburn, K.E.H. Gilbert, M.J. Heben, P.A. Parilla, K.M. Jones, R. To, S.-H. Lee and J.H. Lehman, “Hot-wire Chemical Vapor Synthesis for a Variety of Nanomaterials with Novel Applications,” *Thin Solid Films* (in press).
7. Y.-H. Kim, Y. Zhao, A. Williamson, M.J. Heben, and S. B. Zhang, “Non-dissociative Adsorption of H<sub>2</sub> Molecules in Light-element Doped Fullerenes,” submitted to *Physical Review Letters*.

8. B.J. Landi, R.P. Raffaele, M.J. Heben, J.L. Alleman, W. VanDerveer and T. Gennett, "Development and Characterization of Single Wall Carbon Nanotube Nafion Actuators," to appear in *Materials Science and Engineering B*.
9. K.E. H. Gilbert, "Purification and Gas Adsorption Studies of Single-walled Carbon Nanotubes," Doctoral Dissertation, Department of Chemical Engineering, Colorado School of Mines (2005).
10. A.C. Dillon, P.A. Parilla, T. Gennett, K.M. Jones and M.J. Heben, "Systematic Inclusion of Defects in Pure Carbon Single-wall Nanotubes and Their Effect on the Raman D-band," *Chem. Phys. Lett.* 401 (2005) 522.
11. A.C. Dillon, M. Yudasaka, and M.S. Dresselhaus, invited review article "Employing Raman to Qualitatively Evaluate the Purity of Carbon Single-Wall Nanotube Materials," *J. Nanosci. and Nanotech.*, 407 (2004) 691.
12. A.C. Dillon, P.A. Parilla, J.L. Alleman, A.H. Mahan, K.E.H. Gilbert, K.M. Jones, and M.J. Heben, "Enhancing Hydrogen Adsorption by Metal Incorporation in Carbon Multiwall Nanotubes Produced by Continuous Hot-Wire Chemical Vapor Deposition," *Mat. Res. Soc. Proc.* 801 (2004) 167.
13. P.A. Parilla, A.C. Dillon, B.A. Parkinson, K.M. Jones, J.L. Alleman, G. Riker, D.S. Ginley, and M.J. Heben, "Formation of Nanooctahedra in Molybdenum Disulfide and Molybdenum Diselenide Using Pulsed Laser Vaporization," *J. Phys. Chem. B* 108 (2004) 6197.
14. P. Lui, S-H. Lee, Y. Yan, T. Gennett, B.J. Landi, A.C. Dillon and M.J. Heben, "Electrochemical Transformation of SWNT/Nafion Composites," *Electrochem. Solid State Lett.* 7 (2004) A421.
15. Y.-H. Kim, Y. Zhao, M.J. Heben, and S.B. Zhang, "Generalized Kubas Complexes as a Novel Means for Room Temperature Molecular Hydrogen Storage," *Hydrogen Storage Materials (2004 Materials Research Society Symposium Proceedings)*.
16. Y-W. Lee, R. Deshpande, A.C. Dillon, M. Heben, H. Dai, B. Clemens, "Hydrogen Adsorption Mechanism in Carbon Nanotubes and the Role of the Metal Catalyst," *Hydrogen Storage Materials (2004 Materials Research Society Symposium Proceedings)*.

### **NREL FY 2005 Presentations**

1. "Conducting Polymers as New Materials for Hydrogen Storage," A.G. MacDiarmid, M.J. Heben, E.C. Venancio, S.K. Manohar, A.C. Dillon and K.E.H. Gilbert, IPHE International - Hydrogen Storage Technology Conference, June 19-22, 2005, Lucca, Italy.
2. "Novel Nanostructured Materials with a Variety of Applications" (invited talk / session chair), A.C. Dillon, SPIE - The International Society for Optical Engineering Nanotechnology Meeting, August, 2005.
3. "DOE Carbon-based Materials Center of Excellence: NREL Activities and Overview," M.J. Heben, 2005 DoE Hydrogen Program Review (oral).
4. "Overview of the DOE Carbon-based Hydrogen Storage Center of Excellence," L. Simpson, 2005 DoE Hydrogen Program Review (poster).
5. "NREL Research Activities within the DOE Carbon-based Hydrogen Storage Center of Excellence," P.A. Parilla, 2005 DoE Hydrogen Program Review (poster).
6. "Hydrogen Storage Materials" (invited talk), M.J. Heben, Nanoenergy Symposium, American Chemical Society in San Diego, CA, March 14, 2005.
7. "Carbon-based Nanostructured Materials for Hydrogen Storage" (invited talk), A.C. Dillon, American Physical Society Meeting, March, 2005.
8. "Discovering the Mechanism of H<sub>2</sub> Adsorption on Aromatic Carbon Nanostructures to Develop Adsorbents for Vehicular Applications," A.C. Dillon (invited talk), Materials Research Society Meeting, December, 2004.
9. "Hydrogen Energy and the Hydrogen Storage Grand Challenge," Invited Talk: M.J. Heben, The "Salute to Science" seminar series sponsored by Midwest Research Institute in Kansas City, MO, on December 8, 2004.
10. "Using Nanoscience to Design Hydrogen Storage Materials" (invited talk), M.J. Heben, 1<sup>st</sup> Symposium of the Global Climate and Energy Program (GCEP), Stanford University, June, 2005.
11. "Soft Interactions in Hydrogen Adsorption Materials and Nanoscale Self Assembly" (invited talk), M.J. Heben, Brown University, Providence, RI, March, 2005.

12. "Generalized Kubas Complexes as a Novel Means for Room Temperature Molecular Hydrogen Storage," Y.-H. Kim, Poster at the 2004 Fall Meeting of the Materials Research Society.
13. "Interaction of Hydrogen with Carbon Based Molecules Through Transition Metal Atoms," Y. Zhao, poster, 2004 Fall Meeting of the Materials Research Society.
14. "Hydrogen Adsorption Properties of Single Wall Carbon Nanotube-Organometallic Hybrid Materials," J.L. Blackburn, poster, 2004 Fall Meeting of the Materials Research Society.

## References

1. M.J. Heben, A.C. Dillon, T. Gennett, J.L. Alleman, P.A. Parilla, K.M. Jones, and G.L. Hornyak, "Rapid, Room Temperature, High-density Hydrogen Adsorption on Single-walled Carbon Nanotubes at Atmospheric Pressure Assisted by a Metal Alloy", *Mat. Res. Soc. Proc.* 663 (2001) A.9.1.; M.J. Heben, A.C. Dillon, Gilbert, K.E.H., P.A. Parilla, T. Gennett, J.L. Alleman, G.L. Hornyak and K.M. Jones, "Assessing the Hydrogen Adsorption Capacity of Single-Wall Carbon Nanotube/Metal Composites" in *Hydrogen in Materials and Vacuum Systems*, (A.I.P.) vol. 671 (2003) 77.
2. Y. Zhao, Y-H. Kim, A.C. Dillon, M.J. Heben and S.B. Zhang, "Hydrogen Storage in Novel Organometallic Buckeyballs", *PRL* 94 (2005) 155504/1-4.

## VI.C.1g Oak Ridge National Laboratory

*David B. Geohegan (Primary Contact), Alex A. Puretzky, Hui Hu, Hongtao Cui, Christopher M. Rouleau, Iliia N. Ivanov, and Bin Zhao*

*Oak Ridge National Laboratory*

*2360 Cherahala Blvd.*

*Knoxville, TN 37932*

*Phone: (865) 576-5097; Fax: (865) 576-3676; E-mail: geohegandb@ornl.gov*

*Subcontractor:*

*Oak Ridge Institute for Science and Education, Oak Ridge, Tennessee*

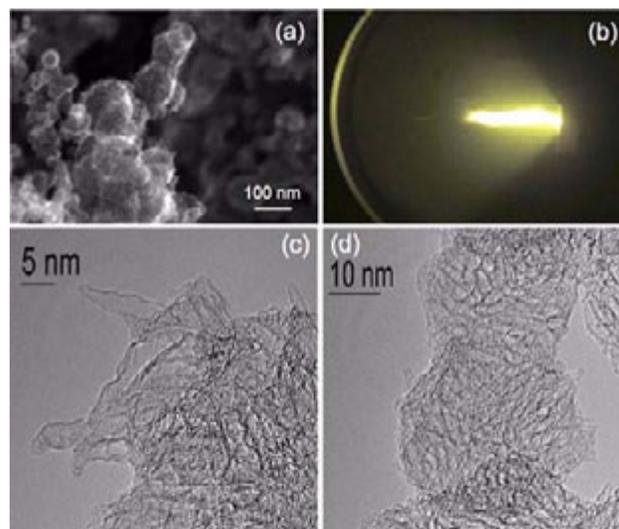
*Start Date: FY 2005*

*Projected End Date: Project continuation and direction determined annually by DOE*

### Partner Approach

The purpose of this work is to synthesize and process single-walled carbon nanohorns (SWNHs) for evaluation as pure carbon hydrogen storage materials and as metal cluster catalyst supports for catalyst-assisted hydrogen storage (e.g., “spillover”). As shown in Figure 1, SWNHs are similar to single-walled carbon nanotubes (SWNTs), except that they are shorter, closed structures containing numerous defect sites and different interstitial pore sizes within their flower-shaped aggregates which provide a rich variety of possible preferred adsorption sites for hydrogen storage and proven success in stabilizing small metal nanoparticles against aggregation. A rich variety of nanohorn aggregates can be synthesized using different parameters, providing a multitude of opportunities for varying the number and type of hydrogen storage sites and increasing the need to understand and control the synthesis conditions for reproducible, understandable hydrogen uptake measurements. In comparison, SWNHs have been shown to support very small metal nanoparticles. Ideally, for optimal volumetric and gravimetric hydrogen storage densities, metal clusters consisting of a few atoms would be supported on partially graphitized, close-packed carbon structures. The research in this project is designed to explore methods to achieve and test these designed material types.

This project will controllably synthesize and characterize single-walled carbon nanohorns as a hydrogen storage media and metal catalyst support. Once nanohorns are produced, methods will be developed and optimized for decorating nanohorns with small metal catalyst clusters. Nanohorn samples will be provided to different CbHS CoE partners to perform characterization and hydrogen storage performance measurements.



**Figure 1.** SWNHs formed by high-power laser vaporization at ORNL. (a) Scanning electron micrograph of SWNH aggregates of up to 100 nm diameters. (b) Laser vaporization plasma used to synthesize SWNHs in atmospheric-pressure, room-temperature argon gas. (c) High-resolution transmission electron micrograph (HRTEM) of individual SWNHs protruding from the edge of a SWNH aggregate particle. (d) HRTEM image of a SWNH aggregate particle composed of many SWNHs.

**Partner FY 2005 Results**

- Implemented a nanohorn production facility utilizing a robotically-controlled, 600-W industrial laser that for the first time permits the synthesis and rapid sampling of SWNHs and SWNTs at high temperatures.

**Partner FY 2006 Plans**

SWNHs can be synthesized relatively inexpensively by arc or high-power laser vaporization of pure graphite into different buffer gases. However, their synthesis mechanism is unknown. Since their nanoscopic structure (and therefore their ability to stably support metal catalysts) is sensitive to and dependent on the processing environment, a special flowing chamber and collection apparatus will be designed and tested to synthesize and collect SWNHs with controllable yield, purity, and aggregate morphology. In situ diagnostics of the process will be implemented to understand how the size, shape, defect level, and aggregate morphology of the SWNHs are determined by the vaporization rate of the graphite, the thermalization of the laser ablation plume in different inert background gases, and as-yet undetermined processes. Methods of capturing the nanoparticles using filtration, electrostatic precipitation, and thermophoresis will be tested in this phase. The size, morphology, and defect structure of the SWNHs and their aggregates will be characterized through high-resolution electron microscopy and correlated with the synthesis conditions. Specifically, FY 2006 research will include:

- Laser synthesis to controllably and directly synthesize (a) pure SWNHs and SWNH/SWNTs with well-characterized graphitic structure and “catalyst sites” to support metal nanoparticles, and (b) metal-loaded SWNHs and SWNH/SWNTs.
- Post-processing of SWNHs and SWNHs/SWNTs to vary the graphitic structure and the metal catalyst loading.

Materials generated will be supplied to partners for Bruner, Emmett and Teller (BET) analysis, hydrogen adsorption, and other measurements.

## VI.C.1h Pennsylvania State University

*T. C. Mike Chung, Henry C. Foley and Peter C. Eklund (Primary Contact)*

*Eberly College of Science*

*104 Davey Laboratory*

*University Park, PA 16802*

*Phone: (814) 865-5233; Fax: 814-863-3297; E-mail: pce3@psu.edu*

*Contract Number: DE-FC36-05GO15077*

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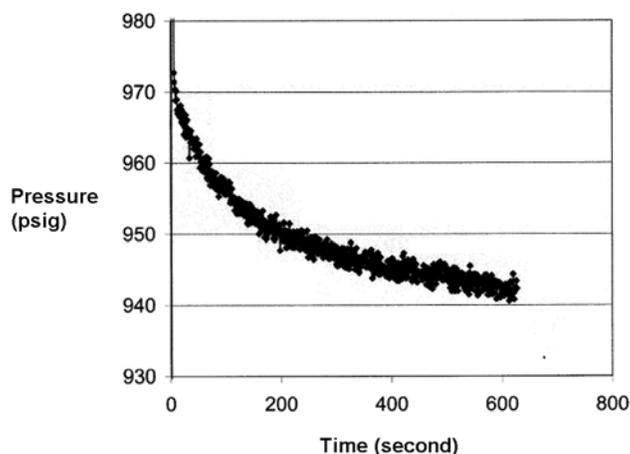
*Projected End Date: January 31, 2010*

### Partner Approach

This effort explores the development of new hydrogen storage materials that can form intermediate strength bonds with molecular hydrogen. Ternary high-surface-area materials are emphasized that are constructed from boron-doped carbon and light element metals. These may be synthesized by pyrolysis, high-temperature chemical processing, and high-temperature vapor phase approaches. The effort elucidates the relationships between physical properties, hydrogen storage performance, pore size distribution and metallic character of the materials. Measured properties are then correlated with the local atomic chemistry and the pore structure of various materials.

### Partner FY 2005 Results

- Modified activated nanoporous carbon (NPC) with tetraethyl ammonium borohydride (TEAB) and studied the resulting B/NPC structure, observing hydrogen storage capacity.
- Developing chemistry to prepare a series of B/C precursors that have the composition of  $BR_xCl_{3-x}$  (R: phenylacetylene). Upon pyrolysis at 600-1200°C, the precursors were transformed into B/C materials with B content ~1.5%, low degree of graphitization, and large d-spacing.
- Examining the resulting B/C materials in hydrogen absorption at ambient temperature. The preliminary results showed that some B/C materials exhibited significantly higher hydrogen storage capacity (>0.5 wt%) than the corresponding C materials, despite their dense structure (Figure 1).
- Designed and constructed computer-controlled high sample throughput differential volumetric hydrogen storage (DVHS) apparatus. Tests run at 77 K and at temperatures in the range  $0 < T < 400^\circ\text{C}$  and pressures  $0.01 < P < 100$  atm.
- Investigated size effect in the H-storage of carbon-nPd material, where nPd means 2-3 nm crystalline core covered with a nanoporous carbon shell (~10 nm thick).
- Finished investigation of the microscopic properties of  $H_2$  in high-surface-area activated carbon by neutron scattering.



**Figure 1.** Hydrogen absorption of a dense B/C material at ambient temperature. (The hydrogen absorption capacity is ~0.7 wt% in 10 minutes. The same measurement for a porous activated C material (Aldrich) reveals <0.2 wt%.)

- Developed simple protocol for the production of a mechanically strong, low-resistivity carbon-based electrode for arc synthesis.
- Converted arc discharge machine to a computer-controlled fully automated apparatus for the production of high-surface-area carbons to operate in H<sub>2</sub>/He mixtures.
- Produced high-surface-area B-doped carbons incorporating catalysts (Fe, Mo, Ni, Co, Y) in the material.

### **Partner FY 2006 Plans**

- Optimize NPC activation conditions to increase microporosity and enhance hydrogen sorption capability.
- Study B/NPC structure and the relationship among microporosity, B doping concentration and H<sub>2</sub> sorption amount.
- Evaluate the H-storage capacity of arc discharge produced high-surface-area carbons.
- Prepare porous B/C materials to increase surface areas and enhance hydrogen absorption capability.
- Study structure-property relationship of hydrogen absorption on B/C surfaces.
- Develop new precursors to increase B content in B/C material.
- Directly measure spectroscopic evidence of hydrogen absorption on B/C surface, and quantify hydrogen absorption capacity under various conditions (pressure and temperature).
- Prepare B/C samples for Dr. Wu (University of North Carolina) to examine the hydrogen absorption by nuclear magnetic resonance technique.

### **Pennsylvania State University FY 2005 Publications/Presentations**

1. "X-ray Diffraction and Hydrogen Uptake of Carbon-Coated Ultra Small Pd Particles, ACS Preprint", D.G. Narehood, P.E. Sokol, S. Kishore, J.A. Adair, J. Nelson, H. Goto, and P.C. Eklund et al., ACS Meeting, August 28, 2005.
2. "Inelastic Neutron Scattering of H<sub>2</sub> Adsorbed on Activated Carbon", D.G. Narehood, P.E. Sokol, P.C. Eklund, ACS Preprint, ACS Meeting, August 28, 2005.

## VI.C.1i Rice University

*Richard E. Smalley*

*Rice University*

*Carbon Nanotechnology Laboratory*

*MS100*

*6100 Main Street*

*Houston, Texas 77005*

*Phone: (713) 348-4658; E-mail: smalley@rice.edu*

*Contract Number: DE-FC36-05GO15073*

*Start Date: February 1, 2005*

*Projected End Date: January 31, 2010*

### Partner Approach

To meet DOE hydrogen storage targets, the key objective is the development of scalable processes that can cost-effectively produce carbon-based materials on a commercial scale. Thus, Rice University will focus on developing technology to reduce the cost of single-walled nanotubes (SWNTs) and to produce SWNTs of specific types that are best suited for hydrogen storage. Extensive experience will be used to develop and optimize novel techniques to prepare carbon nanotubes as well as to cut, dope, and grow seeds on supports and to attach catalysts to cut tubes. The main effort is developing scalable processing for producing type-selected SWNTs through either direct specific growth or sorting methodologies.

### Partner FY 2005 Results

- Three SWNT cutting procedures are being developed: a) fluorine at  $\sim 150^\circ\text{C}$  followed by hydrazine and a strong oxidizing agent reproducibly breaks bonds to cut the SWNTs; b) ozonation in a fluorocarbon solvent at room temperature creates a large degree of epoxy coverage of the surface, enabling cutting as a function of the degree of ozonation; c) high energy electron irradiation (3 MeV) of fluoro and ozonated SWNTs enables controlled cutting with exposure times.
- Length sorting of cut tubes was achieved as follows: a) phenylate the sidewalls; b) sulfonate the phenyl groups (making them strongly acidic and negatively charged in water); c) the negatively charged tubes are selectively extracted from the water with positively charged organic group through complexing. By controlling the amount of organic positive ion, the shorter SWNTs are the first to be extracted. This was demonstrated with an increasing amount of the organic group TOAB (tetraoctyl ammonium bromide) being added to a two-phase water and toluene system. Figure 1 illustrates



**Figure 1.** The effect of TOAB concentration on the extraction of SWNTs into an ethyl acetate phase. The solutions (a) before and (b) after extraction. The TOAB:SO<sub>3</sub><sup>-</sup> ratios for vials 1 – 9 are 0, 0.15, 0.3, 0.45, 0.6, 0.75, 0.9, 1.0, and 2.0, respectively.

how SWNTs move from the water phase to the organic phase as the concentration of TOAB is increased. This is expected to be a scalable length separation method.

### **Partner FY 2006 Plans**

FY 2006 activities will continue development efforts underway, including:

- *Preparation of cut tubes and metal catalyst precursor for docking* – Attachment of catalyst to tube ends is facilitated by creating open-ended tubes with chemical groups that readily form adducts to metal species. The open ends normally contain carboxyl groups that are adequate for bonding to catalyst particles. A number of approaches for generation of 1-3 nm metal oxide particles (initially iron oxide particles) will be investigated.
- *Attachment of catalysts to cut tubes* – For a SWNT with attached catalyst to grow, the catalyst must be perfectly bonded to the end of the SWNT. Since the catalyst is initially attached through intermediate carbonyl groups, the SWNT must be processed in an environment that causes the metal to bond directly to the tube ends. Procedures that lead to catalyzed etch of the ends in oxidizing and hydrogen gas environments will be developed.
- *Growth of seeds on supports* – Atomic force microscopy studies of individual SWNTs on highly oriented pyrolytic graphite have shown growth of SWNTs with attached catalyst. Studies will continue to determine the parameters most important to obtaining high growth rates and yields.

In addition, new activities involving the growth of seeds by injection into a gas environment and the evaluation of scaled-up processing that can be commercialized at a scale and price relevant to the DOE Hydrogen Storage task will be performed.

## VI.C.1j Rice University

*Boris I. Yakobson (Primary Contact) and Robert Hauge*

*Rice University*

*Mechanical Engr & Materials Sci MS321*

*6100 Main Street*

*Houston, Texas 77005*

*Phone: (713) 348-3572; E-mail: biy@rice.edu*

*Contract Number: DE-FC36-05GO15080*

*Start Date: February 1, 2005*

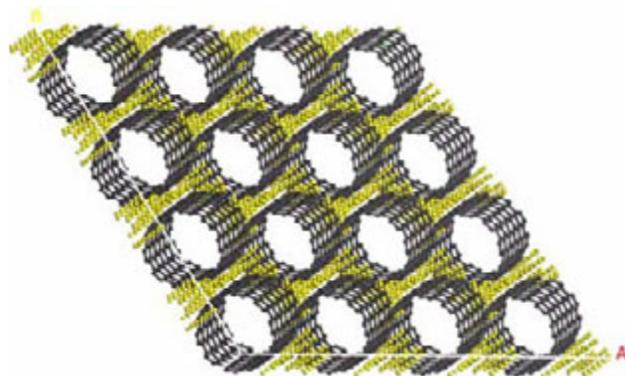
*Projected End Date: January 31, 2010*

### Partner Approach

This project focuses on single-walled nanotube (SWNT) synthesis approaches for low-cost, high-volume manufacturing. The objective is to take advantage of the tunability of the high-pressure carbon monoxide (HiPco™) synthesis process to produce SWNTs optimized for hydrogen sorption. Structure-capacity correlations will be theoretically derived to guide the experimental HiPco™ effort. The role of catalyst concentration, ability to control produced SWNT type (diameter, chirality, metal-enhancement), and metal-SWNT complexes stability will be investigated for better H-adsorption.

### Partner FY 2005 Results

- The HiPco reactor was extensively redesigned to improve carbon monoxide preheating and long-term operation. A continuous run of 1.5 months with an average production rate of 30 grams/day was demonstrated.
- The effects of metal catalyst concentration on SWNT length, diameter and fullerene content were investigated. Analysis of the raw HiPco material indicated that as the catalyst concentration was decreased, the SWNT lengths and diameters increased, the residual iron particle size increased, and the large fullerene content decreased.
- Investigation has been initiated of bistability-bifurcation on the energy surfaces of  $C(sp^2)+H_2 \ll C(sp^3)+2CH$ . This included classical-potential simulations of the  $H_2$  molecules as they entered the inter-SWNT area. Simulations performed with DL\_POLY allow the position of  $H_2$  to be approximated to facilitate further quantum mechanical calculations (Figure 1).
- Electronic structure calculations (PM3 semi-empirical method) of SWNT- $H_n$  ( $n = 1,2,4$ ) cluster models of various lengths have been performed to evaluate the influence of cluster approximation. To quantify the influence of geometrical structure on binding strength, systematic SWNT- $H_2$  calculations have been initiated for various *chiralities and diameters* interacting with one molecule of hydrogen.
- A charged SWNT/ $H_2$  model was developed using density functional theory (DFT)-based computations of chemical binding in complexes of metals with conjugate aromatic systems. Relaxed structures show a



**Figure 1.** Classical Molecular Dynamics Calculations of  $H_2$  Positions

Sc-C distance of 2.22Å, evidence of good binding. The metal binding to multinuclear aromatic systems was also shown to depend on distortion of the benzene ring; in the absence of such distortion, the binding is much weaker. It follows that the bonding strength of the ligand with nanotubes depends on diameter and chirality. Further calculations should establish the kind of these dependencies.

### **Partner FY 2006 Plans**

- The dependence of the SWNT length, diameter and chirality distributions on reaction parameters will be measured. Material will be provided to Center partners for measurement of surface area and adsorption capacity.
- SWNT-membrane feasibility investigation is planned after installation of carbon-metal empirical (Muruyama) potential.

### **Rice University FY 2005 Publications/Presentations**

1. Nano Letters, 5, p. 163, 2005.
2. May 22-25, 2005, R. Hauge, DOE Hydrogen Program Review.
3. June 19-22,2005, B. Yakobson, IPHE International Hydrogen Storage Conference.

## VI.C.1k University of Michigan

*Omar M. Yaghi and Adam J. Matzger (Primary Contact)*

*Department of Chemistry*

*2815 Chemistry Building*

*910 N. University*

*Ann Arbor, Michigan 48109-2136*

*Phone: (734) 615-6627; Fax: (734) 615-8553; E-mail: matzger@umich.edu*

*Contract Number: DE-FC36-05GO15076*

*Start Date: February 1, 2005*

*Projected End Date: January 31, 2010*

### Partner Approach

Metal organic frameworks (MOFs) are synthetic nanoporous crystalline materials composed of inorganic and organic building blocks. This project investigates the hydrogen affinity of MOFs and optimizes hydrogen storage performance by testing and evaluating various structures, synthetic methods, and activation procedures. Partners will help in two major ways. Several techniques, such as nuclear magnetic resonance (NMR) spectroscopy, will be used to provide additional insights into the mechanism of hydrogen uptake in MOFs. In addition, accurately determining the level of hydrogen uptake in MOFs is a critical issue, and several partners and the Southwest Research Institute testing facility will help to conduct these measurements.

### Partner FY 2005 Results

- Observed hydrogen adsorbed in MOF-5 by Raman spectroscopy. Reversible physisorption occurred at all pressures employed, including 30 bar. At room temperature, a 10 wavenumber decrease in the hydrogen stretching frequency was measured, signaling a reasonably strong interaction.
- A high-pressure volumetric sorption analyzer was procured that can measure uptake to nearly 100 bar.

### Partner FY 2006 Plans

- Continue optimizing MOFs for hydrogen sorption.
- Measure temperature and pressure dependence of H<sub>2</sub> uptake in 4 existing MOFs.
- Conduct Raman measurements on hydrogen uptake in several more MOFs.
- Determine binding energy of hydrogen in MOFs.
- Execute materials transfer agreements with NREL and other partner laboratories to implement testing and characterization of MOFs.

### University of Michigan FY 2005 Publications/Presentations with Partial DOE Support

1. Centrone, A.; Siberio-Pérez, D. Y.; Millward, A. R.; Yaghi, O. M.; Matzger, A. J.; Zerbi, G.; "Raman Spectra of Hydrogen and Deuterium Adsorbed on a Metal-Organic Framework," *Chem. Phys. Lett.* 2005, In Press.
2. Rowsell, J. L. C.; Yaghi, O. M.; "Strategies for Hydrogen Storage in Metal-Organic Frameworks," *Angew. Chem. Int. Ed.* 2005, In Press (cover feature).
3. Presentation by O. M. Yaghi: CSIRO, Hierarchical Materials: New Porous Materials, Melbourne, Australia (March 2005); CNSI lecture, University of California, Los Angeles (May 2005); BASF, Ludwigshafen, Germany (February 2005); Conference on MOFs as New Materials, Germany (February 2005); ExxonMobil, Global Research, Annandale, New Jersey (February 2005); Nano 05 3rd Annual Meeting, Aarhus, Denmark (January 2005); Gordon Research Conference on Hydrocarbon Resources, Ventura, California (January 2005).

## VI.C.11 University of Michigan

*Ralph T. Yang (Primary Contact), Anthony J. Lachawiec, Jr., Gongshin Qi*

*Department of Chemical Engineering*

*University of Michigan*

*910 N. University*

*Ann Arbor, Michigan 48109-2136*

*Phone: (734) 936-0771; Fax: (734) 764-7453; Email: yang@umich.edu.*

*Contract Number: DE FC36 05 GO15078*

*Start Date: February 1, 2005*

*Projected End Date: January 31, 2010*

### Partner Approach

Graphite nanofibers (GNFs) can be synthesized using metallic catalysts and have exhibited the ability to store hydrogen. The focus of this effort is on characterizing and enhancing hydrogen spillover using graphite nanofibers and other solid carbonaceous substrates to develop a viable storage system. A key objective of this work is to develop a better understanding of the spillover mechanism to enhance hydrogen storage capacities. In this work, optimal catalyst compositions will be identified that yield the GNF with consistently the highest hydrogen storage capacity. Inherent in this is the identification of optimal methods to add the catalyst to the GNF that yield the best sorbent for hydrogen storage. Furthermore, the specific mechanisms of hydrogen spillover (from metals) and surface diffusion of the spilt over hydrogen will be studied.

### Partner FY 2005 Results

- Developed an efficient bridge-building technique for hydrogen spillover that enhanced storage capacity by a factor of 2.9 at ambient temperature and 10 MPa.
- Constructed a specially designed Sievert's apparatus that measures adsorption amount and rate at pressures from 0.1 MPa to 10 MPa. The apparatus was calibrated at 298 K using LaNi<sub>5</sub> powder (Cerac, Inc.).
- Demonstrated that by mixing a hydrogen dissociating catalyst with carbon receptors, the storage capacity of the receptor can be significantly increased. This enhancement is caused by the spillover of hydrogen atoms from the catalyst (shown in Figure 1). The material was a "super" activated carbon, AX-21, with a BET (Bruner, Emmett and Teller) surface area of 2600 m<sup>2</sup>/g, and the catalyst was a commercial hydrogenation catalyst, 5% Pd doped on activated carbon (Pd-C).
- Discovered a method with which to build carbon bridges between the catalyst and the receptor, and the enhancement factor can be further increased significantly. Here, bridge building is accomplished by mixing with a powder of glucose followed by a heating protocol to carbonize the glucose.
- At 298 K and 10 MPa, the hydrogen storage capacity of the receptor alone is 0.5 wt%. By physically mixing the receptor with the catalyst (at 9:1 ratio), the storage capacity was increased to 0.8 wt%. By using our bridge-building technique, the storage capacity was increased to 1.8 wt%. The storage was totally reversible.

### Partner FY 2006 Plans

- Further develop the bridge-building technique using various carbon bridge precursors.
- Study various carbons as the receptor for spillover hydrogen.

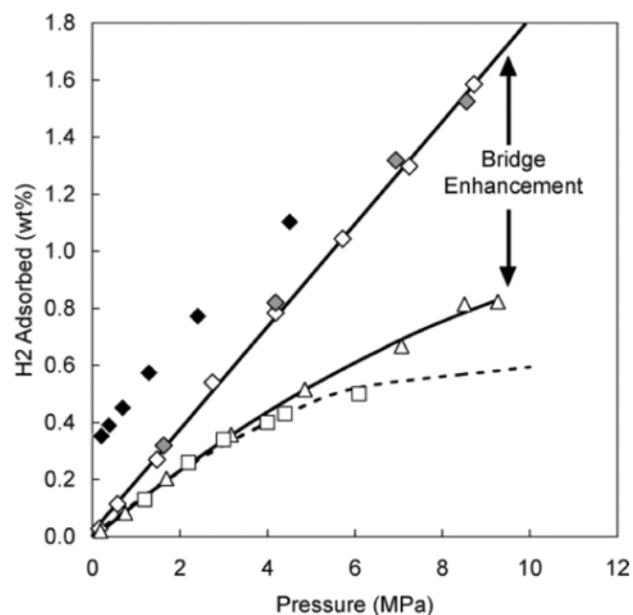
- Develop the most efficient spillover technique/system for storage.
- Find a carbon/catalyst system that meets the storage target at room temperature.
- Develop basic understanding of the hydrogen dissociation-spillover phenomenon.
- Collaborate with NIST on neutron scattering experiments to obtain an understanding of the spilt over hydrogen.
- Collaborate with NREL to confirm the storage amount and bond energies

### University of Michigan Special Recognitions & Awards/Patents Issued

1. UDCT Golden Jubilee Award, University of Mumbai, UDCT, India.
2. Elected to the National Academy of Engineering as a member.

### University of Michigan FY 2005 Publications/Presentations

1. J. Lachamiec, G. Qi and R. T. Yang, "Hydrogen Storage in Nanostructured Carbons by Spillover: Bridge Building Enhancement," *Langmuir*, submitted.



**Figure 1.** High-pressure hydrogen isotherms at 298 K for AX-21 receptor. AX-21/Pd-C/carbon bridge (8:1:1) first adsorption; AX-21/Pd-C/carbon bridge (8:1:1) desorption; AX-21/Pd-C/carbon bridge (8:1:1) second adsorption; AX-21/Pd-C physical mixture (9:1); AX-21.

## VI.C.1m University of North Carolina (Chapel Hill)

Yue Wu

University of North Carolina-Chapel Hill

Cameron Avenue

Chapel Hill, NC 27599-3255

Phone: (919) 962-0307; Fax: (919) 962-0480; E-mail: yuewu@physics.unc.edu

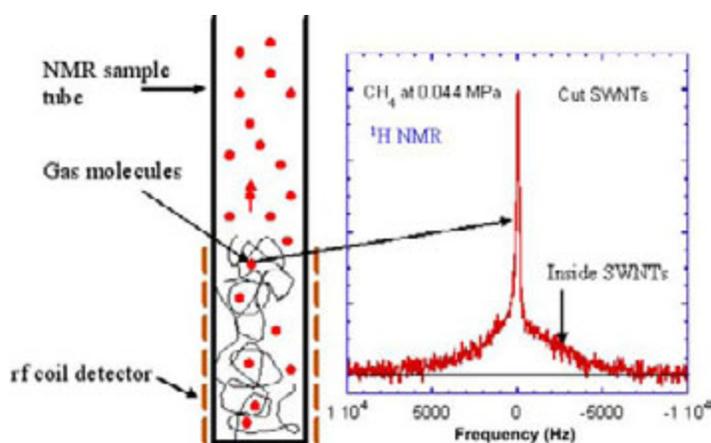
Contract Number: DE-FC36-05GO15081

Start Date: February 1, 2005

Projected End Date: January 31, 2010

### Partner Approach

The primary goal of the investigation is to identify adsorption mechanisms in carbon-based materials that will lead to desirable adsorption isotherms under the operating conditions of future fuel cells for vehicles. At present, the adsorption enthalpy of hydrogen in carbon-based materials is too low, and the CbHS CoE is working toward enhancing the adsorption enthalpy. One of the approaches is boron doping of various carbon-based materials, e.g., B-doped carbon nanotubes by the NREL group and B-doped graphite by the Penn State group. Nuclear magnetic resonance (NMR) techniques will be used to measure the hydrogen adsorption isotherms and study the structures of such B-doped systems using  $^{13}\text{C}$  and  $^{11}\text{B}$  NMR. The NMR characteristics of pure carbon nanotubes and other carbon systems have been established at the University of North Carolina (UNC). This allows the studies to be extended systematically to B-doped systems. The UNC will also work closely with the Duke and Rice groups to investigate effects of other modifications for carbon nanotubes such as diameter and catalytic effects. Initial NMR adsorption studies have been performed on conducting polymers developed by the University of Pennsylvania group. Such studies will continue and will be extended to lower temperature. Finally, transition metal-carbon material interactions will be investigated by NMR. The mechanism (i.e., the nature of the adsorbed hydrogen) of the spillover effect will be investigated by NMR. Such studies will also be very valuable for future studies of new transition metal-carbon hybrid systems.



**Figure 1.** Proton NMR signal revealing both adsorbed (broad peak) and free gas (narrow peak) for methane molecules adsorbed in single-walled carbon nanotubes. The technique is currently being applied for the study of hydrogen adsorption.

### Partner FY 2005 Results

- Adsorption was observed by NMR, though less than 1 wt%, in some carbon nanotubes with a few wt% of catalytic metal particles. This indicates that some transition metal-carbon hybrid systems show promising adsorption potentials.
- Completed the construction and testing of the room-temperature, high-pressure NMR system. In-situ NMR measurements of samples under exposure of at least 100 atm hydrogen gas are being conducted (Figure 1).

- Measured adsorption isotherms by NMR of purified-and-cut carbon nanotubes as well as conducting polymer samples at room temperature and up to 100 atm.
- Room-temperature hydrogen adsorption in highly purified carbon nanotubes is very small, and cutting of nanotubes does not lead to enhancement of adsorption.
- Established a procedure to measure quantitatively the adsorbed hydrogen in these samples.

### **Partner FY 2006 Plans**

UNC will conduct NMR investigations of B-doped carbon nanotubes (NREL) and graphite (Penn State), conducting polymers (University of Pennsylvania), and spillover effects of engineered carbon fibers (University of Michigan). Effects of carbon nanotube diameters and catalytic particle effects (NREL, Duke, Rice) will also be investigated by NMR. Experimentally, UNC will also extend the temperature range of the high-pressure hydrogen NMR setup to 77 K.

### **University of North Carolina (Chapel Hill) FY 2005 Publications/Presentations**

1. Poster presentation at the May 23-26, 2005, DOE Review Meeting in Crystal City, Virginia.
2. Poster presentation at the June 19-22, 2005, IPHE Hydrogen Storage Technology Conference in Lucca, Italy.

## VI.C.1n University of Pennsylvania

*Alan G. MacDiarmid*

*Blanchard Professor of Chemistry*

*Department of Chemistry*

*231 South 34th Street*

*Philadelphia, PA 19104*

*Phone: (215) 898-8307; Fax: (215) 898-8378; E-mail: macdiarm@sas.upenn.edu*

*Contract Number: DE-FC36-05GO15075*

*Start Date: February 1, 2005*

*Projected End Date: January 31, 2010*

### Partner Approach

Recently, Cho et al. [1] reported approximately 8 wt% (reversible) hydrogen gas storage in doped (metallic) forms of organic conducting polymers (“synthetic metals”), polyaniline and polypyrrole. Polyaniline is a unique type of conducting polymer in which the charge delocalization can, in principle, offer multiples sites on the polymer backbone for the adsorption and desorption of hydrogen, involving weakening of the H-H bond followed by “spillover” adsorption of this hydrogen onto the adjacent nano-fibrous network. Thus, the University of Pennsylvania (UPenn) group will investigate the use of polyaniline in its different oxidation states (doped and non-doped forms) and other conducting polymers (especially polypyrrole) for optimization of hydrogen storage applications. Specific activities to understand the fundamental mechanisms involved and to determine the hydrogen sorption performance include:

- Using nanofibers of polyaniline that can be easily prepared in large quantities.
- Using different treatments (e.g., concentration of HCl, etc.) of commercial polyaniline and nanofibers of polyaniline.
- Determining optimum polymer preparative methods, chemical compositions and polymer crystallinity and morphology to give quantitative optimum conditions of hydrogen gas adsorption and desorption.
- Measuring H lability in polyaniline by exposure to a D<sub>2</sub> atmosphere and evaluating H-D formed mass spectrometrically.

### Partner FY 2005 Results

- Temperature-programmed desorption (TPD) studies were performed in collaboration with NREL on samples of polyaniline (PANI).
- Commercial samples of polyaniline were treated using excess of concentrated hydrochloric acid using a procedure similar to Cho’s procedure. Preliminary results showed that these samples did not demonstrate 6 wt% hydrogen storage. However, we know that “there are as many different types of polyaniline as there are people who make it!” [3]. Therefore, further studies on different types of polymers of aniline will be performed.
- Polyaniline nanofibers doped with camphorsulfonic acid in the presence of a non-ionic surfactant [Triton X100 – 4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol] have shown an extremely broad desorption peak (~ -165 to -25°C) with a shoulder at ~ -60°C. This could indicate the presence of a variety of different binding sites, and though this system is not at room temperature, the temperature is easily accessible through standard cooling methods. In such systems, the potential roles of the surfactant and dopant are considered to be of very great importance for further study.

- The Penn group has developed a potentially new useful electrochemical method for determining H<sub>2</sub> uptake by "polyaniline" and "polypyrrole".
- Penn studies to date have lead to the conclusion that no definite statement can be made at the present time concerning the ability of "polyaniline" or "polypyrrole" to ad- or de- sorb H<sub>2</sub> because of the ill-defined composition of the polymers used in the sorbtion studies performed by all research groups [1,4,5].

### **Partner FY 2006 Plans**

Specific activities for FY 2006 include:

- Synthesize different types of polymers of aniline [2] and polypyrrole, i.e., different oxidation states, morphology and materials.
- Continue on-going TPD studies on conducting polymer samples in collaboration with Center members at NREL to characterize hydrogen sorption properties.
- Continue on-going NMR studies on conducting polymer samples in collaboration with Center members.
- Perform neutron scattering measurements on conducting polymer samples in collaboration with NIST to obtain direct atomic and nanoscale information related to hydrogen adsorption sites and diffusion mechanisms.
- Examine the surface area and microporosity by standard gas adsorption studies of the nanofibers of an electronic polymer in collaboration with CbHS CoE partners.

### **University of Pennsylvania Special Recognitions & Awards/Patents Issued**

1. IP Disclosure (submitted to CTT/Univ. Pennsylvania on April 15, 2005): *Morphology Manipulation of Polymerized Aniline Synthesized in an Aqueous Medium*.

### **University of Pennsylvania FY 2005 Publications/Presentations**

1. E.C. Venancio, P.C. Wang and A.G. MacDiarmid, "*The Azanes: A Class of Material Incorporating Nano/Micro Self-Assembled Spheres Obtained by Aqueous Oxidative Polymerization of Aniline*", *Synth. Met.*, accepted for publication (April 2005).
2. A.G. MacDiarmid, M.J. Heben, E.C. Venancio, S.K. Manohar, A.C. Dillon and K.E.H. Gilbert, "*Conducting Polymers as New Materials for Hydrogen Storage*", IPHE International - Hydrogen Storage Technology Conference, 19-22 June 2005, Lucca, Italy.

### **References**

1. Cho et al., *Fuel Chem. Div., 224th Nat. Mtg. Am. Chem. Soc.* 47 (2002) 790.
2. E.C. Venancio, P.C. Wang and A.G. MacDiarmid, accepted for publication, *Synth. Met.* (April 2005).
3. A.G. MacDiarmid et al., *Synth. Met.*, 119 (2001) 27.
4. (a) A.G. MacDiarmid, "Conducting Polymers as New Materials For hydrogen Storage", DOE Annual Report, July 12, 2005; (b) A.G. MacDiarmid, "Conducting Polymers as New Materials For hydrogen Storage", DOE Review Meeting, STP-42, May 23-26, 2005.
5. Roth et al., *Synth. Met.*, 151 (2005) 208.