

VI.C Carbon Materials

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

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Start Date: October 2004

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 H₂/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 H₂/m³ at room temperature and pressure.
- Performed calculations and preliminary experiments to determine hydrogen storage enhancement permitted by incorporating simple metals in sp²-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 H₂/D₂ 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⁻¹ 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 H₂ on SWNTs, the average adsorption energy per H₂, 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 m²/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.

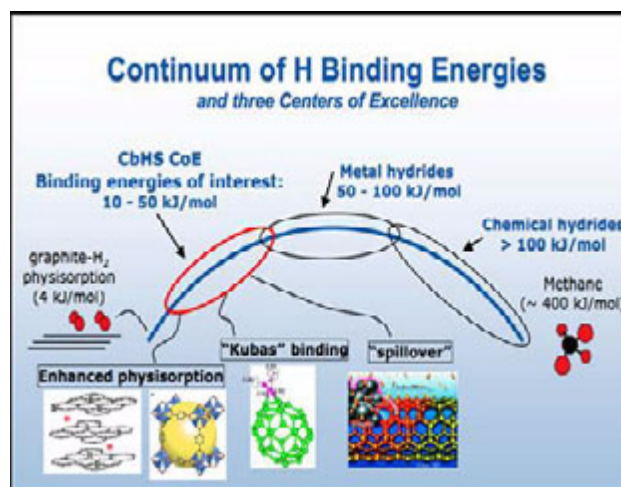


Figure 1. Depiction of the range of binding energies and several of the nanostructured materials of interest to the CbHS Center of Excellence.

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,

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 Rivieres) show 4 – 6 wt% under a few atmospheres of H₂ 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 H₂/m³). These results, along with recent theoretical calculations from NIST on Ti-doped nanotubes and from Steacie Institute for Molecular Sciences on H₂ 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.

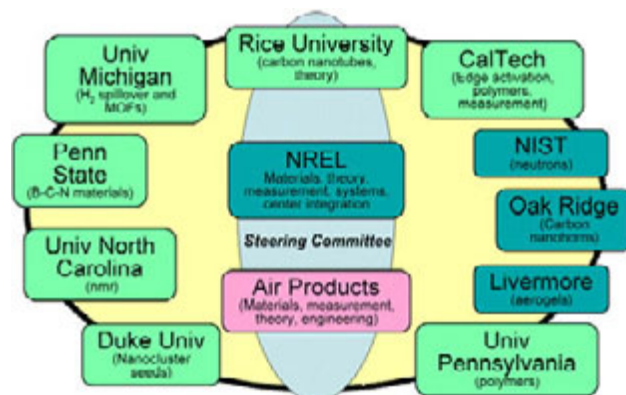


Figure 2. Diagram showing the organization of the Carbon-based Hydrogen Storage Center of Excellence, partner institutions, and primary responsibilities.

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% H₂ 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 sp²-hybridized carbon networks can bind dihydrogen via a Kubas-type interaction. For example, Figure 3 shows a boron-doped bucky ball (C₄₈B₁₂) 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

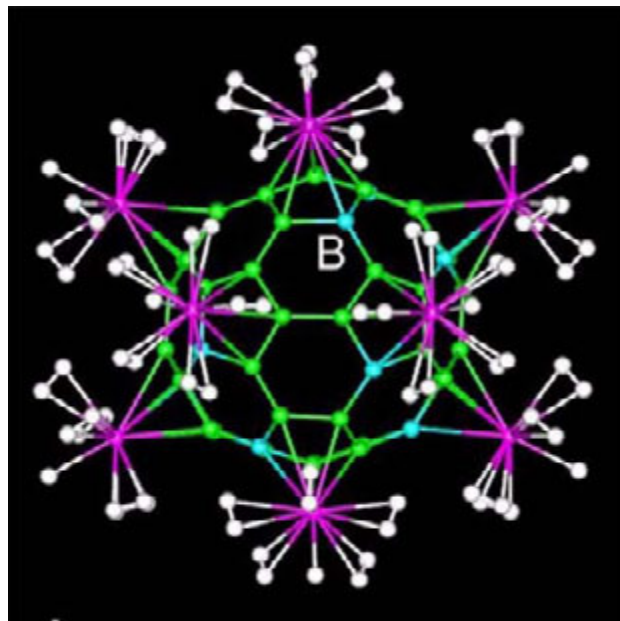


Figure 3. Boron-doped organometallic bucky ball of composition C₄₈B₁₂[ScH(H₂)₅]₁₂ which stores 8.8 wt% hydrogen reversibly. (Sc – purple, C – green, B – blue and hydrogen – white).

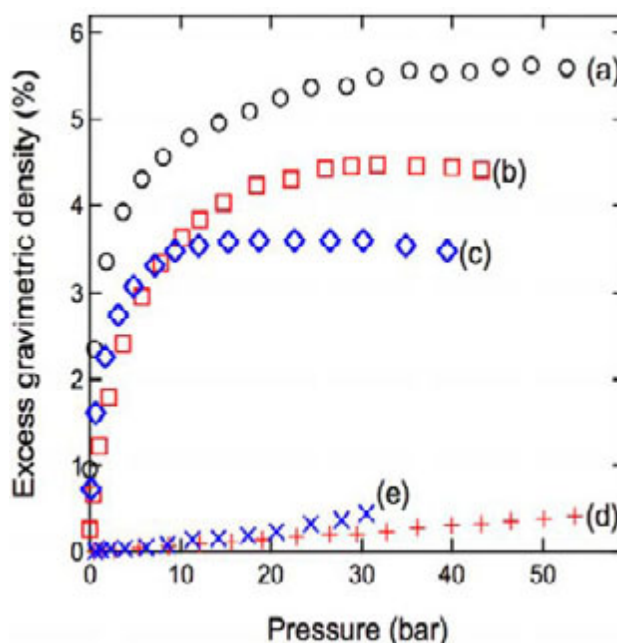


Figure 4. Excess adsorption at 77 K for (a) activated carbon with a mean pore size of 1.1 nm (●), (b) IRMOF-1 (■), (c) IRMOF-8 (◇), and at room temperature for (d) IRMOF-1 (+), and (e) IRMOF-8 (x).

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).

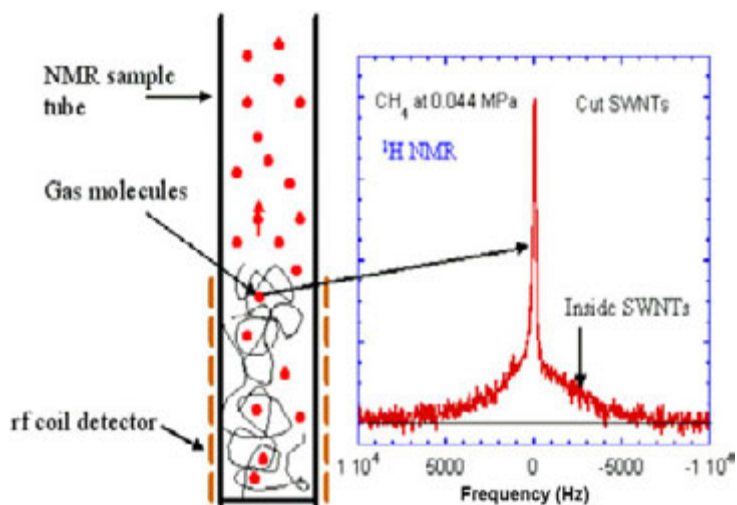


Figure 5. Proton NMR signal revealing both adsorbed (broad peak) and free gas (narrow peak) for methane molecules adsorbed in single-walled carbon nanotubes. The technique is currently being applied for the study of hydrogen adsorption.