

IV.C.1f Research and Coordination Activities within the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

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Start Date: FY 2005

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

Partner Approach

The NREL effort is based on coupling capacity, binding energy, material structure, and mechanistic measurements with novel synthetic techniques and advanced theoretical studies to rationally identify [1] and develop new materials that address the storage barriers delineated in DOE's Multi-Year RD&D Plan. The interplay between these efforts elucidate the physics and chemistry of uptake and enable the design of new materials with superior performance. During the past year, NREL has worked with a wide array of promising nanostructured materials, and developed new adaptable, 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 Center of Excellence (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. Advances are being disseminated to CoE partners and the larger hydrogen storage community and will help to establish standard test protocols for evaluating reversible hydrogen storage materials.

Partner FY 2006 Results

Rational Design of New Hydrogen Storage Materials

Theoretical studies were performed to develop a deeper understanding of experimental results that showed that transition metals in contact with sp^2 -bonded carbon atoms increased hydrogen uptake [2,3]. Going beyond simply explaining the already observed data, the computations also predict capacities and energetics for future hydrogen storage materials. The needed materials must be able to stabilize high capacities of hydrogen with a binding energy between ~10-50 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. Recently, NREL predicted the existence of a whole new class of organometallic systems [4] that can store hydrogen reversibly at near ambient conditions and room temperature. A completely independent theory group at NIST made a similar prediction, simultaneously. These theoretical breakthroughs provide new opportunities and prompt new questions. Answers to several of the key questions and new results are provided in the following.

- **Fe-Fullerene Synthesis Calculations** – As part of the initial effort to synthesize some of the new predicted organometallic materials, calculations were performed to identify potential synthesis pathways. For example, calculations determined thermodynamically acceptable processes involving ferrocene and other chemicals that could be used to form Fe-fullerene structures. The potential synthesis pathways identified were used to form the Fe-fullerene materials discussed in the following.
- **Metal Clustering on Fullerenes** – Recently, Sun *et al.* [5] suggested that Ti will preferentially cluster, rather than form the Ti-complexed C_{60} that could sorb substantial quantities of hydrogen [2]. Metal clustering will detrimentally affect hydrogen storage capacity. Subsequent calculations of the stability of Sc atoms on $C_{48}B_{12}$ determined that the Sc atoms prefer to bind with the fullerene cage rather than form Sc clusters, and that hydride species bound to the metals also stabilizes the dispersed arrangement. These results indicate that metal clustering is not expected generally, and that kinetic and stabilization considerations must be considered.
- **Metal Decorated Single-Wall Nanotubes (SWNTs)** – NREL also performed calculations for a Ti-coated

(5,5) SWNT. In general, the physical trends with the SWNTs are similar to the fullerene cases. However, because the SWNT is structurally more flexible in terms of deformation and distortion, and because the binding between metal and SWNT is generally weaker than that between metal and fullerene, metal clustering is more likely to be an issue. Additional calculations will be performed to identify possible synthesis routes for metal-SWNTs.

- **Alkali Metal Decorated Carbons** – As part of our overall investigation, NREL performed theoretical calculations to determine the H_2 storage capability of carbons decorated with lighter metallic elements (e.g. Na, K, Mg, and Ca) in both the atomic and intercalated phases. Preliminary results indicate that while most of the lighter elements do not hold a great deal of promise for hydrogen storage, there is a potential for substantial reversible hydrogen capacity in at least one identified system. Additional calculations and experimental validations are being performed to test the initial findings.
- **Hydrogen Interaction with Titanium-Carbide Nanoparticles** – The adsorptions of H_2 on metalcarbohedrene Ti_8C_{12} , and nanocrystal $Ti_{14}C_{15}$ were studied using first-principles calculations [6]. These studies predict that Ti atoms in these nanostructures can enable self-catalyzed dissociation of H_2 , to form hydrides, with barriers less than 25 kJ/mol. The Ti atoms are also capable of coordinating with multiple dihydrogen ligands. Overall hydrogen capacities of 6.1 wt% for Ti_8C_{12} and 7.7 wt% for $Ti_{14}C_{15}$ (Figure 1) are predicted. Among them, more than 80% are bound in the energy range between 0.17 and 0.89 eV/ H_2 , which

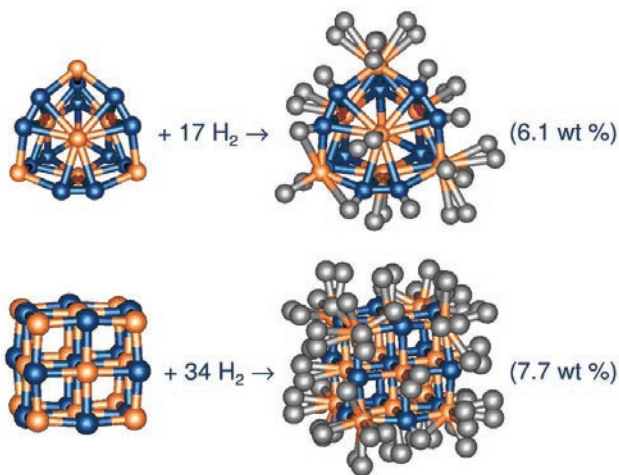


FIGURE 1. Schematic drawings of MetCar Structures that have the potential to meet DOE hydrogen storage system targets and that have demonstrated synthesis routes.

could be beneficial for reversible hydrogen storage at near ambient conditions.

- **Functionalization of Porous Carbon Materials with Transition Metals for Hydrogen Storage** – Highly porous carbon-based (HPC) materials now are available with uniform size distribution of nano-sized pores. However, experiments show only low capacity for hydrogen storage at near ambient conditions. NREL is considering several pathways to functionalize these types of materials with transition metal (TM) dopants. One possible route could directly implant a TM using ion beam methods. The implanted TM atoms might be sufficiently reactive to bind hydrogen, and the TM-hydrogen complex could modify the porosity further to enhance physisorption of additional hydrogen. A second possible approach could include directing a TM ion beam on the HPC through a hydrogen atmosphere. The generated TM-hydrogen clusters would be implanted into the HPC pores. Once the dihydrogen ligands are released from the HPC, the TM-hydride clusters will be trapped in the pores without coalescing into bulk materials, therefore without losing the ability to reversibly sorb dihydrogen.

B-doped SWNTs for Room Temperature Hydrogen Storage

Recent literature indicates that 3.8 to 6 wt% hydrogen can be stored on SWNT materials at 77 K and low pressures (a few bar). Specifically, Pradhan, et al., [9] reported over 6 wt% hydrogen sorption samples and Poirier et al. [10] reported 3.8 wt% H_2 sorption on SWNTs, both at 77 K. Recently, NREL applied new processing techniques to significantly improve reproducibility of hydrogen sorption capacities, but to achieve substantial storage at near room temperatures the intrinsic binding energy of the matrix material must also be significantly increased.

Recent theoretical studies suggest that boron-doped carbon fullerenes may show promise as hydrogen adsorbents [2]. These studies propose a three-center bond between boron dopants and hydrogen molecules with a binding energy of ~ 38 kJ/mol, a nearly ideal value for hydrogen storage. Essential to this binding is the localized empty p_z orbital of the boron dopant. Inspired by these findings, NREL explored the hydrogen storage properties of boron-doped carbon nanotubes (B-SWNTs) (Figure 2). Initial calculations indicate that B-SWNT structures like BC_3 are thermodynamically stable and can store more than 5 wt% hydrogen at room temperature.

Initial efforts to experimentally validate predictions suffered from the lack of highly pure samples having boron incorporated into an sp^2 lattice. While the

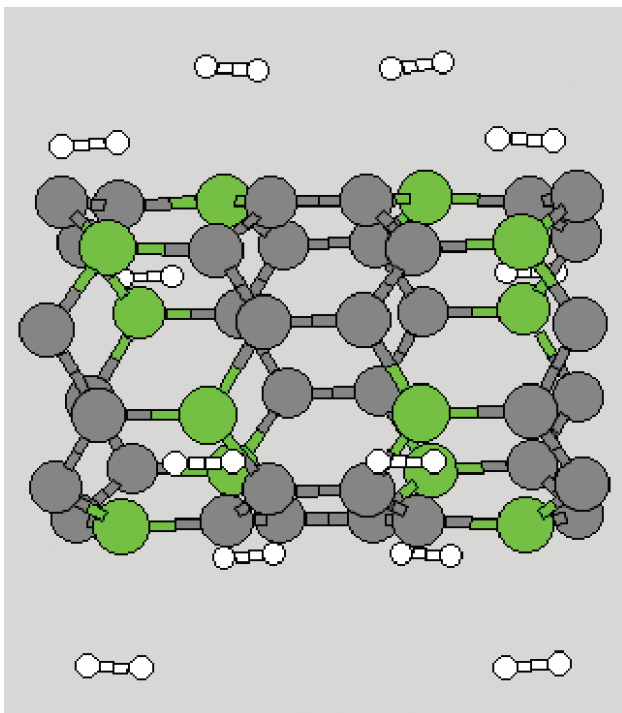


FIGURE 2. Schematic of a BC₃ SWNT structure predicted to have over 5 wt% hydrogen storage at room temperature and moderate pressure. The expected good performance is afforded by a 12 kJ/mol binding energy for H₂. Green spheres represent B, white dumbbells are H₂ molecules.

laser vaporization method is generally recognized to produce SWNTs of very high purity with low defect density, efforts to directly dope SWNTs with significant amounts of B using laser vaporization have been largely unsuccessful. To this end, NREL developed the first synthetic procedure for the high yield synthesis of B-SWNTs by pulsed laser vaporization [7]. NREL also applied the lessons learned to produce high purity B-SWNT using arc-synthesis.

To date, NREL has synthesized B-SWNTs with ~1.8 wt% B by laser vaporization and ~0.6 wt% B by arc-synthesis as measured by electron energy loss spectroscopy (EELS) and prompt gamma activation analysis (PGAA). Boron doping was verified by nano-probe EELS, Raman spectroscopy, and neutron scattering (PGAA). Thermogravimetric analysis (TGA) experiments indicate that B incorporation inhibits SWNT oxidation, increasing the combustion temperature by ~100°C. NREL also performed the first ¹³C nuclear magnetic resonance (NMR) analysis of substitutionally B-doped SWNTs. Removal of π electron density by the electron-deficient B dopants leads to a 2 ppm downfield shift in the ¹³C NMR resonance.

The B-SWNTs may be purified by a combination of acid reflux and oxidative treatments, allowing study of the hydrogen adsorption properties of highly pure

H₂ adsorbed on B doped SWNTs (NREL) H₂ pressure: 104 atm.

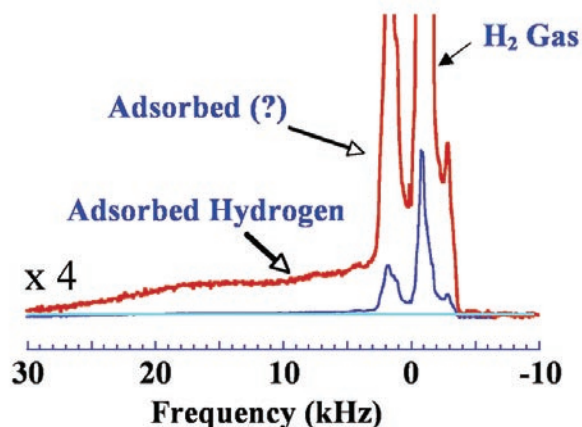


FIGURE 3. ¹H NMR spectrum of purified, B-SWNTs with 107 atm of H₂. The red spectrum is multiplied by four to more clearly show the broad peak associated with adsorbed hydrogen molecules. The data was collected by CbHS partners at UNC.

samples. Roughly 70 mg of purified B-SWNTs were sent to Yue Wu and Alfred Kleinhammes at the University of North Carolina, Chapel Hill for high-pressure ¹H NMR measurements. Initial results are shown in Figure 3. Previous work showed that when a pure carbon SWNT sample is charged with ~100 atm H₂, the NMR spectrum is dominated by one sharp gas phase hydrogen peak with a very small, broad peak underneath which corresponds to very weakly physisorbed H₂ molecules. The binding energy for the physisorbed H₂ molecules is very low, i.e. ≤4 kJ/mol. In contrast, when the B-SWNT sample is charged with ~100 atm of H₂, several new peaks are present in the ¹H NMR spectrum. While the largest peak, at ~-1 kHz corresponds to gas-phase H₂ in the sample space, peaks unique to the B-SWNTs occur: two fairly sharp correlated peaks at ~2 kHz and -3 kHz, and one very broad peak at ~15 kHz. The pressure dependence of these B-SWNT peaks was analyzed and demonstrated a Langmuir-like response, suggesting that they are associated with adsorbed hydrogen molecules. Approximate binding energies were extracted from a Langmuir fit to the pressure dependent data. The sharper peaks at ~2 kHz and -3 kHz correspond to molecules adsorbed with a binding energy of ~8.6 kJ/mol, while the very broad peak corresponds to a binding energy of ~12.6 kJ/mol. These values are significantly higher than that expected for physisorption on graphite, and demonstrates that enhanced binding is achieved for the boron-doped SWNTs. The enhanced binding energy with B is very important since ~12 kJ/mol may be sufficient to meet DOE hydrogen storage targets at room temperature and moderate pressures (~100 bar).

Interestingly, the hydrogen storage capacity of the arc generated B-SWNTs is ~10% *higher* than that of

the undoped arc-generated C-SWNTs. This has never been the case for laser-produced B-SWNTs, for which the capacity has always been lower than the undoped samples. Some possibilities for the enhanced adsorption of the arc-generated B-SWNTs include the previously discussed potential for higher defect density and boron incorporation, the smaller mean diameter, and the lack of multi-walled graphitic onions and cages that are prevalent in the laser synthesized materials.

NREL also sent B-SWNT samples to Carbon-based Hydrogen Storage (CbHS) partners at the National Institute of Standards (NIST) in Maryland for a series of neutron spectroscopy experiments. H_2 rotational spectra were obtained using a filter analyzer neutron spectroscopy (FANS) instrument that is used to measure the para-ortho transition spectra around 14.7 meV. Shifts and splittings imply a difference in orientational potential, and hence binding enthalpies. Hydrogen loading was performed such that only a specific number of hydrogen molecules were available per boron site. For example, at 1 H_2/B there is one hydrogen molecule for every boron atom in the sample. Figure 4 shows the neutron spectra for the laser and arc generated B-SWNTs. For both samples, the shape of the spectrum at low loading is quite different than that at high loading. At low loading, the ortho-para transition is split into two peaks, with a splitting of ~ 1.3 meV. This splitting implies a degeneracy lifting that is consistent with the binding of hydrogen in a more strongly bound site, i.e. the boron site.

The difference spectra (not shown) imply that the population of the binding sites change as a function of H_2 loading. The measured B/C ratio by PGAA is an upper limit of boron incorporated into nanotubes. The results indicate that H_2 binds first to the boron sites and does so preferentially up to 1 H_2 per boron. The shape of the difference spectrum between 2 H_2/B and 1 H_2/B is similar to that of the difference spectrum between full loading and 2 H_2/B , implying that the binding at coverages higher than 1 H_2/B is at the undoped carbon nanotube surfaces. These results are quite different than those obtained for all of the undoped C-SWNT samples that were previously studied. In those samples, only one peak was ever observed, no matter the H_2 loading level. Interestingly, the neutron spectra for the arc generated B-SWNTs are significantly broader than those for the laser generated B-SWNTs. It is possible that this difference arises from the smaller mean diameter of the arc tubes or the potentially higher defect density. The control experiments on undoped laser and arc generated C-SWNTs are in progress to confirm that the unique effects observed for the B-SWNTs are indeed a result of boron incorporation.

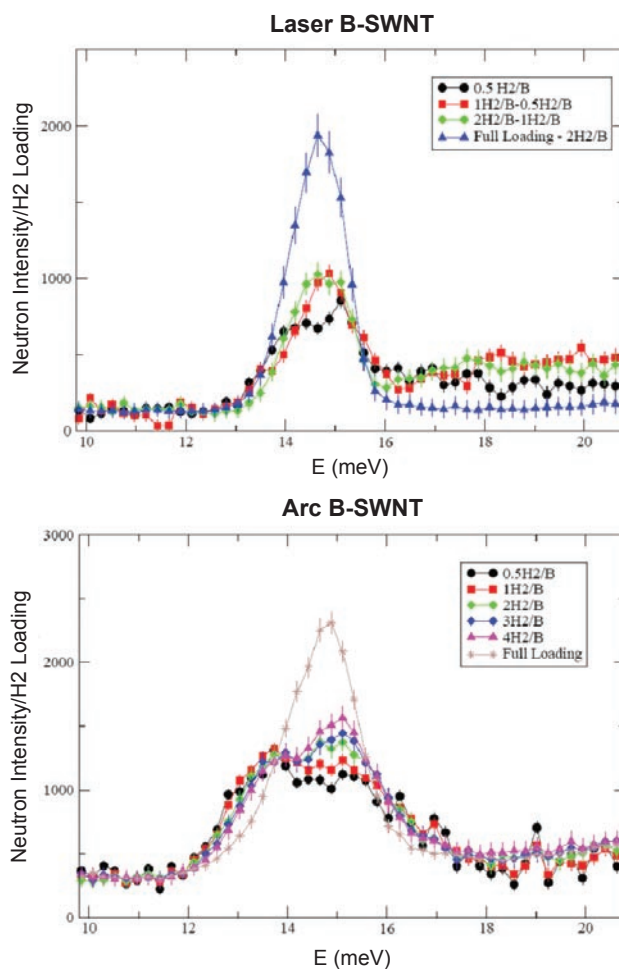


FIGURE 4. Neutron diffraction spectra for purified laser-produced B-SWNTs (top) and purified arc-produced B-SWNTs (bottom) taken at NIST.

Metallorganic Fullerenes and other Hybrid Materials for Room Temperature Hydrogen Storage

In FY 2005 NREL identified a novel class of theoretically predicted nanostructured materials that could revolutionize hydrogen storage materials [2]. The theoretical calculations showed that by complexing a graphene structure with transition metals (TMs), dihydrogen ligands may be bound with binding energies between ~ 30 - 40 kJ/mol. This energy is within the ideal range for onboard vehicular storage. However due to the metastable nature of many of these materials, synthesis is not straightforward and unique synthesis routes must be developed. Furthermore, in addition to the organometallic buckyballs, metal decoration of SWNTs and other structures may have enhanced hydrogen sorption properties. Thus, NREL has been developing several synthetic processes to create several of these different hybrid materials.

- Organometallic Fullerenes** – In some of the predicted structures the TM shares charge with all of the carbon atoms in a fullerene pentagon through Dewar coordination. However, the chemistry of C_{60} is generally olefinic (i.e. the metal is coordinated to the fullerene through two carbon atoms contributing two electrons to the bonding). Thus, synthesis of fullerene-metal- H_2 complexes, where the metal is coordinating with five carbon atoms, is not expected to be straightforward. Rational synthetic methods to experimentally form five-fold coordination between a fullerene and a transition metal were demonstrated for the first time by NREL with ferrocene and fullerenes using solution-phase chemistry. Solid-state ^{13}C NMR spectroscopy measurements performed at NREL under fast magic angle spinning (MAS) identified precursor fulleride, K_6C_{60} , and suggested that $C_{60}-Fe-C_{60}$ was synthesized [8]. These syntheses and measurements were repeated several times to ensure reproducibility. Temperature programmed desorption spectroscopy measurements determined that the synthesized materials had enhanced hydrogen uptake with a binding energy of approximately 10 kJ/mol. This is explained by the fact that the Fe may not be fully coordinated with the fullerenes. These results may be consistent with the aforementioned theoretical calculations [2] and may indicate a weak Kubas complex. Future experiments will replace one of the C_{60} components with H to form the H-Fe- C_{60} complex that is expected to have significant room temperature hydrogen storage.
- Alkali Metal Decorated SWNTs** – In the course of our work to develop materials with a reversible hydrogen storage capacity, a novel set of alkali metal-decorated SWNT composites was synthesized that exhibit over 4 wt%, though mostly irreversible, hydrogen storage uptake at ambient temperature and pressure. These materials and results have been reproduced several times. Furthermore, the amount of Na and non-hydride forming transition metals in the samples are too small to account for the majority of the hydrogen sorption capacity. Thus, this intriguing discovery indicates that the bulk of the hydrogen must be adsorbed on the SWNTs. NREL is investigating the mechanism(s) associated with the unique irreversible hydrogen storage properties to determine if the uptake and release can be done reversibly. This will involve investigations with Li or other materials by conducting a series of experiments utilizing aprotic solvents and deuterated reagents.
- Transition Metal – SWNT Hybrid Materials** – In addition to increasing the surface areas/pore sites available, NREL also modified the surfaces of the nanotubes by attaching nanoparticle metals. The processes investigated for deposition of the metals included: spontaneous deposition; adsorption of metal ions followed by reduction with a chemical reducing agent; electrochemical deposition; and deposition of metals utilizing pre-reduced alkali metal-SWNT materials.
- Electrochemical deposition** – NREL investigated the use of electrochemical deposition with non-aqueous solvents like THF to deposit metal atoms or small clusters of Ti, Li, Mg, etc. on SWNTs. Removal of residual solvents and over deposits were the main issues that needed to be addressed. Hydrogen sorption/desorption measurements as well as the usual suite of characterization tests were performed to quantify hydrogen storage properties.
- Chemical deposition on SWNTs using Organic Solvents** – NREL has developed a unique methodology for creating reduced Na-SWNTs. When these materials are used in conjunction with metal salts (e.g. Ti(III)Cl₃·3THF complex) in non-aqueous solvents, the metal ions change to atoms (e.g. Ti(III) to Ti(0)) since the Na-SWNTs have a reduction potential of ~-3 V. The amount of metal deposited is adjusted by controlling the salt concentration. Initial results have demonstrated 1 to 2 wt% hydrogen storage.
- Chemical deposition on SWNTs using alcohol solvents** – NREL developed capabilities to deposit a number of metals (Cr, Sc, Ni, Co, Pd, etc.) on SWNTs using metal salts in alcohol solutions. In many of these systems, sodium borohydride was used to allow for facile reduction of the adsorbed metal species. Initial results are very promising. For example, with ~3 wt% Cr on SWNTs, temperature program desorption measurements showed near room temperature hydrogen release. In another sample, hydrogen desorption was observed at ~100 and 180°C with Pd deposited on SWNTs (Figure 5). Since Cr does not form a hydride and hydrogen desorption is not observed from Pd or SWNTs above room temperatures, the results from Cr-SWNTs and Pd-SWNTs may be evidence of a M-SWNT complex creating a predicted [2] Kubas type adsorption site.

Enhanced Hydrogen Storage Capacity Measurements

NREL is focused on optimizing adsorbents that store and release hydrogen with moderate temperatures and pressures for economic on-vehicle hydrogen storage. To aid development most effectively, measurement and characterization techniques must be developed/optimized that enable the use of the very small samples (a few milligrams) that are routinely produced/processed in the laboratory. NREL has developed unique temperature programmed desorption measurement

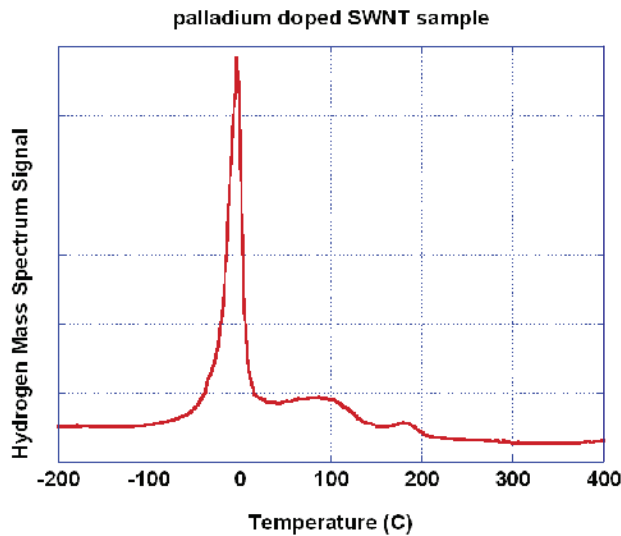


FIGURE 5. Temperature programmed desorption measurements of Pd-SWNT material suggest that new hydrogen binding may account for the higher temperature desorption peaks observed at ~ 100 and $\sim 180^\circ\text{C}$. The $\sim 0^\circ\text{C}$ is due to Pd-hydride.

techniques for these small samples in the past, and developed novel volumetric capacity capabilities that routinely provide accurate measurements at elevated pressures and lower temperatures on milligram size samples. Specific advances in FY 2006 include:

- To develop volumetric measurement capabilities that routinely measure ~ 0.1 wt% hydrogen uptake on milligram sized samples at temperatures as low as 77 K required NREL to develop and deploy temperature control strategies with the volumetric testing systems. Initially, these small sample measurement capabilities were implemented on an in-house volumetric system that enables single point measurements on ~ 5 samples per day. This system enables the rapid screening of laboratory-sized samples to accelerate hydrogen storage materials development. Once all the issues were resolved, the temperature control technology was transferred to a commercial PCTPro 2000 from Hy-Energy LLC to enable higher accuracy and smaller sample measurements at pressures >70 bar. While the temperature control technology was successfully transferred and is working properly, issues associated with the higher pressure measurements must still be fully resolved to achieve the desired accuracy with the PCTPro. However, the PCTPro system has been calibrated and demonstrates improved accuracy and stability with many samples including an activated carbon (TR-AC1) that has been used by DOE in a round-robin set of tests to determine lab-to-lab variability in hydrogen storage measurements. NREL's results were in excellent agreement (5-10%) with measurements performed

at other institutions. These unique capabilities are now being applied to validate the hydrogen storage spillover results on materials from the University of Michigan.

- Improved electronic control was implemented on a multi-port temperature programmed desorption system that now can process/measure up to four samples at the same time. This system provides valuable desorption information of samples heated under vacuum.

Accelerating Hydrogen Storage Materials Development through Collaborations and Leadership

NREL is leading the DOE CbHS CoE within the U.S. DOE National Hydrogen Storage Project. NREL is working closely with all the partners in the CoE (Figure 6) and also several groups outside the center to accelerate materials development. In addition to measuring and characterizing hydrogen storage materials, NREL also provides expertise to the community and is actively engaged in organizing technical sessions and meetings to foster additional technical exchange and collaborations (see "Special Recognitions" section).

6 wt% Hydrogen Storage with Carbon Nanotubes at Room Temperature

The DOE Hydrogen Program's Systems Integrator will perform a technical evaluation of the state, progress, and potential of research and development (R&D) to meet time-phased technical targets in the area of carbon nanotubes for hydrogen storage. This technical evaluation will be considered by DOE, along with other factors, in making a go/no-go decision in October 2006

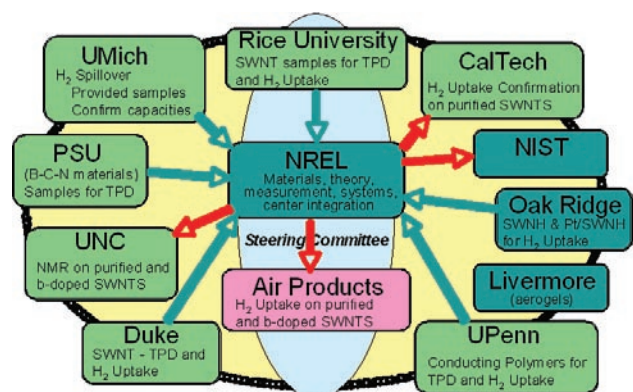


FIGURE 6. NREL developed technical interactions with nearly all CoE partners. The CoE interactions accelerates research and development efforts to meet DOE hydrogen storage system targets. The CoE is also working with SwRI, ATMI, U. Quebec, BES projects, and individuals outside of the CoE.

concerning the continuation of DOE-funded R&D on pure carbon nanotubes. NREL will assist in this technical evaluation by providing literature and technical results to the Systems Integrator. In addition to the go/no-go for pure carbon nanotubes at room temperature, the Systems Integrator will make recommendation regarding the use of carbon nanotube-based structures and hybrid systems to achieve the DOE 2007 and 2010 system targets at ambient and lower temperatures, with special consideration to the interplay between factors such as charge/discharge efficiency, thermodynamics and kinetics, and volumetric/gravimetric capacities.

Conclusions of Partner Effort for FY 2006

NREL continues to develop novel nanoengineered materials to meet the DOE's on-vehicle hydrogen storage goals. NREL demonstrated that doping sp^2 -hybridized structures such as carbon SWNTs with boron results in increased binding of dihydrogen. Furthermore, NREL demonstrated that decorating similar structures such as SWNTs or fullerenes with alkali, transition, or other metals also increases binding of dihydrogen. Both these results support NREL's previously published theoretical predictions. Experimental synthesis of boron-doped and metal decorated carbon nanostructures will be improved and purification processes optimized to enable the hydrogen storage capabilities of these materials to be fully realized. In addition, NREL has identified additional metal-carbon systems, such as MetCars, that may also meet DOE system targets and may be more easily synthesized. NREL will develop the synthesis and purification processes necessary to make and test the hydrogen storage properties of the new materials. In addition to materials development, NREL is also developing improved characterization methodologies and is leading the DOE CbHS CoE. In these efforts NREL seeks to fulfill a leadership an integration function for the DOE, CbHS partners, and the wider hydrogen storage community.

Partner Plans for FY 2007

- Provide technical direction to, and assist in, the integration of the CbHS CoE in support of DOE goals. Hold intensive workshops.
- Identify efficient, safe, cost-effective sorbent-based technologies that can meet the goals for on-vehicle hydrogen storage applications.
- Foster collaboration and communication between Center members, DOE and other interested parties as to Center activities and progress.
- Evaluate materials from Center members and others to identify future research directions.
- Continue to provide advanced hydrogen sorption measurements for in-house, CoE partner, and other external materials development efforts.

- Enhance measurement throughput and accuracy for samples produced in the CbHS CoE.
- Extend measurement techniques to enable smaller samples to be measured and to more accurately determine surface area and hydrogen uptake properties.
- 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.
- Optimize theoretical predictions involving the strength of non-dissociative dihydrogen binding on metal-nanostructured materials by varying the metal elements, adsorption sites coordination, and structure.
- Determine hydrogen sorption properties of MetCars, nanocrystals, etc.
- Advance the study of novel hydrogen storage materials recently cited in the literature with theoretical calculations and experimental syntheses.

NREL Special Recognitions & Awards/Patents Issued

1. Lead symposium organizer, A.C. Dillon, for a six-day symposium (including tutorial) entitled "The Hydrogen Cycle-Generation, Storage and Fuel Cells" Materials Research Society (MRS) Fall Meeting, Boston, Nov. 28–Dec. 2, 2005.
2. Co-organizer and session chair, A.C. Dillon, SPIE meeting on August 3, 2005.
3. Co-organizer, M.J. Heben, Symposium N and Editor of Proceedings Volume, "Hydrogen Storage Materials," at Fall meeting of the MRS, Boston, MA, Nov. 28–Dec. 2, 2005.
4. Editor, A.C. Dillon, The proceedings for the Symposium A entitled "The Hydrogen Cycle-Production, Storage and Fuel Cells" at the 2005 Fall Materials Research Society meeting. There were ~50 manuscripts reviewed and accepted for the proceedings. Approximately one-half of these papers were devoted to storage.
5. Co-editor, A.C. Dillon, of a special Focus Issue of the *Journal of Materials Research* entitled "Energy and the Environment" that was published with contributions from the 2005 Fall MRS Meeting. Four invited articles from Symposium A of the Fall 2005 MRS meeting, all pertaining to hydrogen storage, were included. Two of these articles highlight research in the DOE Carbon-based Hydrogen Storage Center.
6. Co-organizer, M.J. Heben, Symposium EE Editor of Proceedings Volume "Hydrogen Storage Materials" at Spring meeting of the MRS, San Francisco, CA, April 17-21, 2006.
7. Co-organizer, M.J. Heben, Symposium on Hydrogen Energy at the Spring meeting of the ECS, Denver, CO, May 8-12, 2006.

8. Co-organizer, M.J. Heben, 1st NIST NanoScience and Applications Conference, Boulder, CO, Oct. 17-19, 2005.
9. Instructor for tutorial, P.A. Parilla, "On-Board Hydrogen Storage—Breakthroughs and Barriers", Symposia 'A', Fall MRS Meeting, Boston, MA, November 27, 2005.
10. Symposium organizer, S. B. Zhang, "Simulating Hydrogen Storage: From Current Challenges to Future Promises", APS March Meeting, Baltimore, March 13, 2006.
11. Keynote lecture, advisory panel, A.C. Dillon, 2005 Taiwan Symposium on Hydrogen Storage in Carbon Nanomaterials, Oct. 18, 2005 Taipei, Taiwan.
12. Editor, L.J. Simpson and M.J. Heben, CbHS COE contribution to the DOE 2006 Annual Report.
13. Invited to co-organize, A.C. Dillon, a symposium entitled "Life Cycle Analysis," for the 2007 Fall MRS Meeting.
14. Invited to co-organize, M.J. Heben, Hydrogen Symposium of the Electrochemical Society, Chicago, 2007.
15. Nominated and accepted, A.C. Dillon, for the National Academy of Engineering Symposium on "Frontiers of Engineering," Dearborn, MI, September 21-23 (2006).
16. "Discovering the Mechanism of H₂ 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, *Mat. Res. Soc. Proc.* 837 (2005) 117-123. Received the ribbon award for the second best paper in the session.

NREL FY 2006 Publications

1. "Non-dissociative adsorption of H₂ molecules in light-element doped fullerenes", Y.-H. Kim, Y. Zhao, A. Williamson, M.J. Heben, and S. B. Zhang, *Physical Review Letters* **96**, 016102 (2006).
2. "Self-catalyzed Hydrogenation and Dihydrogen Adsorption on Metallo-Carbohedrenes and Related Nanocrystals" Yufeng Zhao, A.C. Dillon, Y.-H. Kim, M.J. Heben and S.B. Zhang, *Chemical Physics Letters*, in press.
3. "Synthesis and Characterization of Boron-doped Single-wall Carbon Nanotubes Produced by the Laser Vaporization Technique", Jeff L. Blackburn, Yanfa Yan, Chaiwat Engtrakul, Philip A. Parilla, Kim Jones, Thomas Gennett, Anne C. Dillon, Michael J. Heben. *Chemistry of Materials*, May 2006.
4. "Development and characterization of single wall carbon nanotube–Nafion composite actuators" B.J. Landi, R.P. Raffaele, M.J. Heben, J.L. Alleman, W. VanDerveer, T. Gennett, *Materials Science and Engineering B*, 116(3), 359-362, 2005.
5. "Systematic Inclusion of Defects in Pure Carbon Single-wall Nanotubes and Their Effect on the Raman D-band," A.C. Dillon, P.A. Parilla, J.L. Alleman, T. Gennett, K.M. Jones, and M.J. Heben, *Chem Phys Lett*, 401, 522-28, 2005.
6. "Generalized Kubas Complexes as a Novel Means for Room Temperature Molecular Hydrogen Storage," Y.-H. Kim, Y. Zhao, M.J. Heben & S.B. Zhang, *Materials for Hydrogen Storage-2004*, edited by M.J. Heben, I.M. Robertson, R. Stumpf & T. Vogt, 837, N3.21 (2005).
7. "The Role of Metal Catalyst in near Ambient Hydrogen Adsorption on Multi-Walled Carbon Nanotubes," Y.-W. Lee, R. Deshpande, A.C. Dillon, M.J. Heben, H. Dai & B.M. Clemens, *Materials for Hydrogen Storage-2004*, edited by M.J. Heben, I.M. Robertson, R. Stumpf & T. Vogt, *Mat. Res. Soc. Symp. Proc.* 837, N3.18 (2005).
8. "An Experimental Estimate of the Free Energy of Formation of Single Walled Carbon Nanotubes," L.M. Wagg, G.L. Hornyak, L. Grigorian, A.C. Dillon, K.M. Jones, J.L. Blackburn, P.A. Parilla & M.J. Heben, *Functional Carbon Nanotubes*, edited by D.L. Carroll, B. Weisman, S. Roth & A. Rubio, *Mater. Res. Soc. Symp. Proc.* 858E, HH2.7 (2005).
9. "Experimental Gibbs Free Energy Considerations in the Nucleation and Growth of Single-Walled Carbon Nanotubes," L.M. Wagg, G.L. Hornyak, L. Grigorian, A.C. Dillon, K.M. Jones, J. Blackburn, P.A. Parilla & M.J. Heben, *Journal of Physical Chemistry B* 109, 10435-10440 (2005).
10. "Hot-wire chemical vapor synthesis for a variety of nano-materials with novel applications," Dillon, A. C., Mahan, A. H., Deshpande, R., Alleman, J. L., Blackburn, J. L., Parilla, P. A., Heben, M. J., Engtrakul, C., Gilbert, K. E. H., Jones, K. M., To, R., Lee, S. H., and Lehman, J. H., *Thin Solid Films* 501 (1-2), 216-220, 2006.
11. "Importance of Turning to Renewable Energy Resources with Hydrogen as a Promising Candidate and on-board Storage a Critical Barrier" A.C. Dillon*, B. P. Nelson, Y. Zhao, Y.-H. Kim, C. E. Tracy and S. B. Zhang *Mat. Res. Soc. Proc.* Fall (2005), in press.
12. "High Yield Nanotube Synthesis in a Hot-zone Arc-discharge Apparatus", T. Gennett, C. Engtrakul, J. Blackburn, K. Franz, J. Alleman, K. Jones, A. Dillon, M. Heben, submitted.
13. "Rapid, Accurate, *In Situ*, Calibration of a Mass Spectrometer for Temperature Programmed Desorption Studies", K.E.H. Gilbert, P.A. Parilla, J.L. Blackburn, T. Gennett, A.C. Dillon, and M.J. Heben, manuscript in preparation.
14. "Competitive Adsorption between Carbon Dioxide and Methane on Carbon Nanotube Materials" K.E.H. Gilbert, P.A. Parilla, J.L. Blackburn, T. Gennett, A.C. Dillon, and M.J. Heben, manuscript in preparation
15. "Hydrogen Storage in Novel Carbon-based Nanostructured Materials" E. S. Whitney, C. Curtis, C. Engtrakul, M. Davis, T. Su, K. M. Jones, P.A. Parilla, L. J. Simpson, J.L. Blackburn, Y. Zhao, Y.-H. Kim, S. B. Zhang, M.J. Heben and A.C. Dillon *Mat. Res. Soc. Proc.* Spring (2006).

16. "Nano-octahedra of MoS₂ and MoSe₂: Global Topological Constraints on Bonding and Stoichiometry", Philip A. Parilla, Anne C. Dillon, Bruce A. Parkinson, Kim M. Jones, Jeff Alleman, David S. Ginley & Michael J. Heben, extended abstract for the ECS Meeting, Denver, CO, May 2006.
17. "Hydrogen Volumetric Sorption Measurements On Small Samples At Low Temperatures", P. A. Parilla, L.J Simpson, J.L. Blackburn, A.C. Dillon, T. Gennett, K.E.H. Gilbert, & M.J. Heben, manuscript in preparation.
18. "H₂ Sorption Volumetric Measurements of Single Wall Carbon Nanotubes", L.J. Simpson, P.A. Parilla, J.L. Blackburn, T. G. Gennett, K.E.H. Gilbert, C. Engtrakul, A.C. Dillon, and M.J. Heben. National Hydrogen Association Conference Proceedings, March 2006.
19. "Organometallic Complexes for Hydrogen Storage", Y. Zhao, A.C. Dillon, Y.-H. Kim, M.J. Heben, and S.B. Zhang, Preprints of Symposia, American Chemical Society 50(2) (2005) 452-456.
20. "Discovering the Mechanism of H₂ 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, Mat. Res. Soc. Proc. 837 (2005) 117-123. Received the ribbon award for the second best paper in the session.

NREL FY 2006 Presentations

Invited Presentations

1. "Using Nanoscience to Design Hydrogen Adsorbents", M.J. Heben, A.C. Dillon, Y. Zhao, J.L. Blackburn, P.A. Parilla, Y.-H. Kim, T. Gennett, C. Curtis, K.E.H. Gilbert, J.L. Alleman, K.M. Jones, S.B. Zhang, and L.J. Simpson, (invited talk), First Conference of Stanford's Global Climate and Energy Program, Stanford, CA, June 13-14, 2005.
2. "Using Nanoscience to Design Hydrogen Adsorbents", M.J. Heben, 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, (invited talk), TMS Symposium in Honor of Gary Sandrock, Louis Schlapbach, and Seijirau Suda, March 13-16, San Antonio, TX, 2006.
3. "DOE Carbon-based Hydrogen Storage (CbHS) Center of Excellence", M.J. Heben, J.L. Blackburn, C. Curtis, A.C. Dillon, T. Gennett, M.J. Heben, K.M. Jones, Y.-H. Kim, P.A. Parilla, L.J. Simpson, Y. Yan, S.B. Zhang, Y. Zhao, (invited talk), The FreedomCAR & Fuel Partnership Tech Team Meeting, Washington, D.C., March 23, 2006.
4. "Hydrogen Storage in Novel Carbon-based Nanostructured Materials" A.C. Dillon, (invited talk / session chair), Materials Research Society Meeting, April 30, 2006, San Francisco, CA.
5. "Grand Challenge of Vehicular Hydrogen Storage: Developing an Appropriate Adsorption System" A.C. Dillon, (invited talk/ session chair), Materials Research Society Meeting, November 30, 2005, Boston, MA.
6. "The Grand Challenge of the Hydrogen Cycle-Production, Storage and Fuel Cells" A.C. Dillon, (invited key note lecture / advisory panel / session chair), 2005 Taiwan Symposium on Hydrogen Storage in Carbon Nanomaterials, Oct. 18, 2005, Taipei, Taiwan.
7. "Novel Nanostructured Materials with a Variety of Applications" A.C. Dillon, (invited talk / session chair), SPIE-The International Society for Optical Engineering Nanotechnology Meeting, August 3, 2005, San Diego, CA.
8. "Organometallic Methods for Hydrogen Storage: Functionalization of Porous Materials" Yufeng Zhao, Y.-H. Kim, A. C. Dillon, M.J. Heben, and S. B. Zhang, (invited seminar), Dept. of Chemistry, University of Michigan, Nov. 7, 2005.
9. "Theory of Hydrogen Storage: a New Strategy within Organometallic Chemistry" Yufeng Zhao, Y.-H. Kim, A. C. Dillon, M.J. Heben, and S. B. Zhang, (invited colloquium talk), Dept. of Mechanical Engineering and Material Science, Rice University, Sept. 28, 2005.
10. "Theory of Hydrogen Storage: a New Strategy within Organometallic Chemistry" Yufeng Zhao, A. C. Dillon, Y.-H. Kim, M.J. Heben, and S. B. Zhang, (invited talk), APS March Meeting, Baltimore, March 13, 2006.
11. "Towards high wt%, room temperature reversible, carbon-based hydrogen adsorbents", S. B. Zhang (invited talk), IPHE Hydrogen Storage Technology Conference, Lucca, Italy, June 21, 2005.
12. "Activities in the DOE center of excellence for carbon-based hydrogen storage materials", S. B. Zhang, Y. Zhao, Y.-H. Kim, A. C. Dillon, M. J. Heben, (invited talk), Materials Science & Technology 2005 Conference (MS&T'05), Pittsburgh, PA, September 26, 2005.
13. "Prediction of Novel Organometallic Nanomaterials for High Weight Percent Reversible Hydrogen Storage", S. B. Zhang, (invited talk), Materials Research Society Fall Meeting, Symposium A, Boston, November 30, 2005.
14. "Novel Organometallic Nanomaterials for Room-Temperature Reversible Hydrogen Storage: A First-Principles Prediction", S. B. Zhang, (invited talk), TMS 135th Annual Meeting & Exhibition, San Antonio, TX, March 15, 2006.
15. "Fullerenes and Nanostructured Materials for Room-Temperature Reversible Hydrogen Storage: A First-Principles Study", S. B. Zhang, (invited talk), The 61st Annual Meeting of the Physical Society of Japan, Matsuyama, Japan, March 27, 2006.
16. "Fullerenes and Nanostructured Materials for Room-Temperature Reversible Hydrogen Storage: A First-Principles Study", S. B. Zhang, Y. Zhao, Y.-H. Kim, A. Williamson, A. C. Dillon, M. J. Heben, (invited talk), The 209th Electrochemical Society (ECS) Meeting, Denver, CO, May 7, 2006.

17. "Update on Activities for the Storage Systems Analysis Working Group", P.A. Parilla, (invited talk), Fuel Cell Seminar, Palm Springs, CA, November 2005.
18. "Determining Purity and Quality of Carbon Single-Wall Nanotubes: Importance of Raman Scattering", Philip Parilla, Anne Dillon, Jeff Alleman, Tom Gennett, Kim Jones, Jeff Blackburn, Katie Gilbert, Mike Heben, (invited talk), 1st NanoScience & Applications Conference, NIST, Boulder, CO, October 17-19, 2005.
19. "On-Board Hydrogen Storage—Breakthroughs and Barriers", Instructors: Tom Autrey, Weifeng Luo & Philip Parilla, Symposia 'A' (Tutorial), Fall MRS Meeting, Boston, MA, November 27, 2005.
20. "Carbon-Based Nanostructures for Hydrogen Storage" Thomas Gennett, Anne C. Dillon, Phillip Parilla, Jeffrey Blackburn, Sheng Bai Zhang, Michael J. Heben, (invited speaker) The 25th Annual Esther and Bingham J. Humphrey Memorial Symposium in Chemistry Saturday, September 30, 2006, University of Vermont.
21. "Department of Energy Carbon-based Materials Center of Excellence", Lin Simpson, (invited talk), Hydrogen Storage Workgroup Meeting, Clean Energy Research Center, University of South Florida, November 2005.
22. "Hydrogen Storage in Carbon-Based Materials: Increasing Hydrogen Sorption", Yufeng Zhao, CbHS CoE technical exchange meeting, Boston, MA, 11/29/05.
23. M.J. Heben, Presentation at University of Colorado (Boulder) series on renewable energy science and technology.
24. M.J. Heben, presentation to Dr. Ray Orbach, DOE's Director of the Office of Science, December 16, 2005.
25. "New Structures for Hydrogen Storage: the Organometallic Frameworks" Yufeng Zhao, CbHS Center of Excellence Tech Team Meeting, Washington, D.C. and Gaithersburg, March. 23-24, 2006.
26. "Novel Organometallic Nanomaterials for Room-Temperature Reversible Hydrogen Storage: A First-Principles Prediction", S. B. Zhang, TMS 135th Annual Meeting & Exhibition, San Antonio, TX, March 15, 2006.
27. "Fullerenes and Nanostructured Materials for Room-Temperature Reversible Hydrogen Storage: A First-Principles Study", S. B. Zhang, The 61th Annual Meeting of the Physical Society of Japan, Matsuyama, Japan, March 27, 2006.
28. "Synthesis and Characterization of Carbon Nanotube Based Structures for Hydrogen Storage" Jeff Blackburn, Chemical Sciences Seminar Series, National Renewable Energy Laboratory, March 14, 2006.
29. "Novel Nanostructured Materials for a Variety of Renewable Energy Applications" A.C. Dillon, International Conference on Composites and Nano-engineering, July 7, 2006 Boulder, CO.
30. "Hydrogen Storage in Novel Carbon-based Nanostructured Materials," E. Whitney, ACS sponsored Green Chemistry Workshop in Washington, D.C., June 22-24, 2006.

Contributed Presentations

1. "Hydrogen Storage in Titanium-Carbide Nanoparticles" Yufeng Zhao, A. C. Dillon, Y.-H. Kim, M.J. Heben, and S. B. Zhang, (contributed talk), MRS Fall Meeting, Boston, Dec. 2005.
2. "Novel Organometallic Functionalization of Fullerenes for Hydrogen Storage Applications" A.C. Dillon, (contributed talk), Spring Electrochemical Society Meeting, May 10, 2006.
3. "New Structures for Hydrogen Storage: the Organometallic Frameworks" Yufeng Zhao, (contributed talk), CbHS Center of Excellence Tech Team Meeting, Washington, D.C. and Gaithersburg, MD, March 23-24, 2006.
4. "Quantum Monte Carlo studies of the non-dissociative absorption of hydrogen to doped fullerenes" A. Williamson, Y.-H. Kim, and S. B. Zhang, (contributed talk), APS March Meeting, Baltimore, March 14, 2006.
5. "Hydrogen Storage in Metallo-carbohedrenes," Yufeng Zhao, A. C. Dillon, Y.-H. Kim, M.J. Heben, and S. B. Zhang, (contributed talk), 230th ACS Meeting, Washington, D.C., Aug. 28, 2005.
6. "Hydrogen Volumetric Sorption Measurements On Small Samples At Low Temperatures", P. A. Parilla, L.J Simpson, J.L. Blackburn, A.C. Dillon, T. Gennett, K.E.H. Gilbert, & M.J. Heben, (contributed talk), Spring MRS Meeting, San Francisco, CA, April 2006.
7. "Nano-octahedra of MoS₂ and MoSe₂: Global Topological Constraints on Bonding and Stoichiometry", Philip A. Parilla, Anne C. Dillon, Bruce A. Parkinson, Kim M. Jones, Jeff Alleman, David S. Ginley & Michael J. Heben, (contributed talk), ECS Meeting, Denver, CO, May 2006.
8. "Modified Arc Discharge Chamber for the Improved Synthesis of Single Wall Carbon Nanotube Materials" T. Gennett, C. Engtrakul, K. J. Franz, J. A. Alleman, P. A. Parilla, K. M. Jones, J. Blackburn, K.E.H. Gilbert, A. C. Dillon, M. J. Heben, (poster), MRS Meeting Boston, MA December 2005.
9. "Carbon-Based Nanostructures for Hydrogen Storage" Thomas Gennett, Anne C. Dillon, Phillip Parilla, Jeffrey Blackburn, Sheng Bai Zhang, Michael J. Heben, (invited talk) College of Science Colloquium Speaker, Rochester Institute of Technology, Rochester, NY, Oct. 2005.
10. "Hydrogen Storage Properties of Boron-doped Carbon Nanotubes." Jeff Blackburn, Anne Dillon, Thomas Gennett, Phil Parilla, Katie Gilbert, Yong-Hyun Kum, Y. Zhaou, S.B. Zhang, Yanfa Yan, Kim Jones, Michael Heben. (contributed talk), Materials Research Society Meeting, Fall 2005, Boston, MA.
11. "Hydrogen Storage Properties of Laser-generated Boron-doped Carbon Nanotubes." Jeff Blackburn, Anne Dillon, Thomas Gennett, Phil Parilla, Lin Simpson, Katie Gilbert, Yong-Hyun Kim, Yufeng Zhao, Shangbai Zhang, Yanfa Yan, Kim Jones, Michael Heben, (contributed talk), Electrochemical Society Meeting, Spring 2006, Denver, CO.

12. "H₂ Sorption Volumetric Measurements of Single Wall Carbon Nanotubes", L.J. Simpson, P.A. Parilla, J.L. Blackburn, T. G. Gennett, K.E.H. Gilbert, C. Engtrakul, A.C. Dillon, and M.J. Heben. (contributed talk) National Hydrogen Association Conference, March 2006.

13. "Hydrogen Storage using Carbon Nanomaterials", L.J. Simpson, P.A. Parilla, J.L. Blackburn, T. G. Gennett, C. Engtrakul, A.C. Dillon, and M.J. Heben. (contributed talk) Electrochemical Society Meeting, May 2006

References

1. "Assessing The Hydrogen Adsorption Capacity Of Single-Wall Carbon Nanotube / Metal Composites," Michael J. Heben, et al., in *Hydrogen in Materials and Vacuum Systems*, edited by G.R. Myneni, and S. Chattopadhyay, American Institute of Physics Conference Proceedings no. 671: 77-89, (2003).
2. "Rapid, Room Temperature, High-density Hydrogen Adsorption on Single-walled Carbon Nanotubes at Atmospheric Pressure Assisted by a Metal Alloy," M.J. Heben, A.C. Dillon, T. Gennett, J.L. Alleman, P.A. Parilla, K.M. Jones, and G.L. Hornyak, *Mat. Res. Soc. Proc.* 663 (2001) A.9.1.
3. Yildirim et al., *PRL* 94, 175501 (2005).
4. "Hydrogen Storage in Novel Organometallic Buckeyballs," Y. Zhao, Y-H. Kim, A.C. Dillon, M.J. Heben and S.B. Zhang, *PRL* 94 (2005) 155504/1-4. "Non-dissociative adsorption of H₂ molecules in light-element doped fullerenes," Yong-Hyun Kim, Yufeng Zhao, Andrew Williamson, Michael J. Heben, and S. B. Zhang, *Phys. Rev. Lett.* **96**, 016102 (2006).
5. "Clustering of Ti on a C60 Surface and Its Effect on Hydrogen Storage," Q. Sun, Q. Wang, P. Jena, and Y. Kawazoe, *JACS* **127**, 14582 (2005).
6. "Self-catalyzed Hydrogenation and Dihydrogen Adsorption on Metallo-Carbohedrenes and Related Nanocrystals" Yufeng Zhao, A.C Dillon, Y.-H. Kim, M.J. Heben and S.B. Zhang, *Chemical Physics Letters*, in press.
7. "Synthesis and Characterization of Boron-doped Single-wall Carbon Nanotubes Produced by the Laser Vaporization Technique", Jeff L. Blackburn, Yanfa Yan, Chaiwat Engtrakul, Philip A. Parilla, Kim Jones, Thomas Gennett, Anne C. Dillon, Michael J. Heben. *Chemistry of Materials*, May 2006.
8. "Hydrogen Storage in Novel Carbon-based Nanostructured Materials" E. S. Whitney, C. Curtis, C. Engtrakul, M. Davis, T. Su, K. M. Jones, P.A. Parilla, L. J. Simpson, J.L. Blackburn, Y. Zhao, Y-H. Kim, S. B. Zhang, M.J. Heben and A.C. Dillon *Mat. Res. Soc. Proc.* Spring (2006).
9. Pradhan, et al., *J. Mater. Res.* 17, 2209 (2002).
10. Poirier et al. *App. Phys. A* 78, 961 (2004).