

III.D Carbon Materials

III.D.1 Hydrogen Storage in Carbon-Based Materials

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Objectives

- Advance performance of on-board adsorbents in support of DOE Multi-Year Research, Development and Demonstration Plan.
- Demonstrate accuracy of hydrogen measurements on adsorbent materials.
- Develop methods to reproducibly activate and handle materials to permit scale-up and validation of hydrogen uptake.
- Widen scope and throughput to develop scientific and technical basis for adsorbent use in hydrogen storage.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- General:
 - A. Cost
 - B. Weight and Volume
 - C. Durability
 - D. Refueling Time
- Reversible Solid-State Material Storage Systems:
 - M. Hydrogen Capacity and Reversibility
 - N. Lack of Understanding of Physisorption and Chemisorption
 - O. Test Protocols and Evaluation Facilities
- Crosscutting Relevance:
 - H. Sufficient Fuel Storage for Acceptable Vehicle Range
 - S. Cost
 - T. Efficiency

Approach

- Develop carbon-based materials for high volumetric and gravimetric hydrogen storage.
- Improve reproducibility.
 - Conduct in-house review of measurement techniques.
 - Develop repeatable methods to prepare high-capacity samples.
 - Validate results in external lab.
- Understand physics/chemistry of adsorption.
 - Discern mechanisms with computational methods.
 - Experimentally probe mechanisms.
 - Broaden investigation beyond carbon nanotubes.
- Engineer and fabricate best hydrogen adsorbent.

Accomplishments

- Successfully completed external review of the methods and equipment used to prepare and characterize carbon materials at the National Renewable Energy Laboratory (NREL). Reviewers concluded that NREL methods and results are accurate and thorough, and that the measured >2.5 wt.% hydrogen storage capacity of metal/nanotube hybrid materials is credible.
- Developed a method to rapidly calibrate the temperature-programmed desorption (TPD) apparatus.
- Verified reproducible capacity measurements on metal/nanotube hybrid materials using both TPD and volumetric techniques to within 5%.
- Developed and demonstrated novel surfactant method for synthesizing single-wall nanotubes (SWNT), achieving 3 wt.% to 3.13 wt.% hydrogen storage capacity on 8 samples.
- Initiated theoretical calculations which show that Fe forms a complex with carbon rings, stores H₂, and has H₂ binding energies in the desired range.

Future Directions

- Apply organometallic chemistry methods to activate solubilized SWNTs.
- Decouple cutting/metal incorporation steps, and investigate activation without metals.
- Develop and study materials for low-temperature, medium-pressure storage.
- Externally validate uptake results at Southwest Research Institute (SwRI).
- Demonstrate reproducible 4 wt.% storage by 4Q FY 2005 and 6 wt.% by 4Q FY 2006.
- Develop and demonstrate high-throughput measurement capabilities (multisample manifolds, optical and nuclear magnetic resonance spectroscopies, computational chemistry, combinatorial syntheses).
- Discover light frameworks, with a high site density per volume, with the correct energies to achieve DOE/HFCIT storage goals.
- Extend theoretical calculations to other transition metals and predict maximum metal loadings and resultant H₂ storage.
- Develop preliminary models to relate system-level performance to component and material capacities, particularly volumetric capacities.

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 Program state the critical needs and goals for 2005, 2010, and 2015. Nanostructured carbon materials have shown tremendous promise for breakthrough performance in many laboratories around the world, yet the capabilities of these materials remain controversial due to poor reproducibility in sample preparation and measurement. In addition to developing materials to meet DOE targets, the major focus of this project in FY 2004 was on reproducibility. Reproducible sample measurement and preparation methods will be developed to permit the optimization and thorough understanding of the interactions between hydrogen and carbon-based materials, with the goal of identifying an efficient, safe, cost-effective carbon-based technology that can meet the RD&D plan targets for on-vehicle hydrogen storage applications. This objective is in line with the DOE plan for achieving 4 wt.% storage capacity by the end of FY 2005 and making a Go/No-Go decision on carbon nanotubes (based on achieving 6 wt.% storage capacity) by the end of FY 2006.

Approach

The successful development of carbon materials for hydrogen storage will require (i) a detailed understanding of the mechanisms that give rise to adsorption interactions in the range of 20-40 kJ/mol; (ii) methods to fabricate materials having a high gravimetric density of sites displaying such interactions; and (iii) approaches to arrange these sites in space to enable high volumetric storage densities. Pure carbon SWNTs and SWNT-hybrid materials remain prime candidates for development because these materials can be formed into well-packed nanoporous solids and have electronic properties that may be controlled through nanotube geometry, the introduction of defects, attachment of electronic species, elemental substitution on the nanotube lattice, and the introduction of adventitious dopants or catalytic species. Other nanostructured

carbon materials such as nanohorns, multi-wall nanotubes (MWNTs), and metal oxide frameworks (MOFs) are also of interest because they provide additional systems in which adsorption interactions with hydrogen may be investigated and controlled. The study and optimization of these materials for hydrogen storage are the focus of this project.

In addition to the scientific and technical development aspects of the work statement, a principal issue for NREL in FY 2004 was that of reproducibility, stemming from three distinct issues:

- The credibility of NREL data presented in the well-known scatter plot which shows hydrogen storage uptakes between 2 and 8 wt.% on metal/SWNT hybrid materials
- A dearth of similar findings from different labs and a lack of consensus in the literature
- Inconsistent generation of high-capacity samples, i.e., poor reproducibility in materials processing and difficulty of scaling up current processing

Results

Hydrogen Capacity Measurements

External Review

During FY 2004, NREL worked with the DOE Technology Development Manager and the Hydrogen Storage Tech Team (of the FreedomCAR and Fuel Partnership) to design a plan that would permit external reviewers to thoroughly evaluate the analytical methods used by NREL. NREL hosted two scientists (Dr. M. Miller from Southwest Research Institute and Prof. R. Gorte from the University of Pennsylvania) while they reviewed all aspects of material preparation and characterization as well as the methods and equipment used to measure hydrogen adsorption on small samples at NREL. The reviewers concluded that NREL methods and results are accurate and thorough, and that the observed hydrogen storage performance of metal/nanotube hybrid materials is credible (Miller and Gorte, 2004). Although 8 wt.% storage capacities were not observed during the site visit, over 2.5 wt.% was observed, and this in and of itself is a record for room-temperature and low-pressure (~600 Torr) storage of hydrogen in metal-activated

Table 1. Data Obtained during External Review

| Sample | Technique | Wt% H ₂ total | Wt% alloy | Wt% H ₂ tubes |
|---------------------------|-----------|--------------------------|-----------|--------------------------|
| Pure #1, cut #1, piece #1 | TPD | 2.62 | 68.0 | 2.88 |
| Pure #1, cut #1, piece #2 | TPD | 2.39 | 66.4 | 2.17 |
| Pure #1, cut #1, piece #3 | Vol (abs) | 1.93 | 63.9 | 0.92 |
| Pure #1, cut #1, piece #3 | Vol (des) | 2.13 | 63.9 | 1.48 |
| Pure #1, cut #2, piece #1 | TPD | 1.90 | 41.0 | 1.48 |
| Pure #2, cut #1, piece #1 | TPD | 1.09 | 22.4 | 0.68 |
| Pure #2, cut #2, piece #1 | Vol (abs) | 1.51 | 45.8 | 0.67 |
| Pure #2, cut #2, piece #1 | Vol (des) | 1.50 | 45.8 | 0.65 |
| Pure #2, cut #2, piece #2 | TPD | 1.18 | 40.4 | 0.29 |
| Pure #3, cut #1, piece #1 | TPD | 1.06 | 43.3 | -0.04 |
| Pure #3, cut #1, piece #2 | Vol (abs) | 0.87 | 35.7 | 0.00 |
| Pure #3, cut #1, piece #2 | Vol (des) | 1.19 | 35.7 | 0.46 |

SWNTs (see Table 1). Moreover, the panel stated that “analytical methodologies are well established” and “TPD and volumetric techniques were demonstrated to be accurate and repeatable based on reference standards.” Consequently, it was concluded that the “large variances in H₂ uptake for SWNT materials are not related to analytical methodologies.” A particular finding of note was that NREL was able to determine the amount of hydrogen on small TiH₂ samples (1 to 10 mg) within 2% accuracy, via a blind fashion, by both the volumetric and temperature-programmed techniques. This finding establishes NREL hydrogen measurement equipment as being among the most accurate available (Miller and Gorte, 2004).

Volumetric H₂ Capacity Measurement Procedure Development

The differences observed between the TPD and volumetric H₂ capacity measurements during the in-house review were attributed to differences in the degas methodology used to prepare samples. Specifically, the methods used to produce a clean adsorbent surface prior to performance of a hydrogen uptake measurement may contribute to the observed variation in the hydrogen adsorption capabilities of samples. Previously, a new flow-through sample cell was developed to improve the degassing procedure by minimizing any sample degradation that may occur while lab gasses are desorbed. We are initiating a systematic study to determine if the flow-through cell can eliminate any sample degradation that we suspect is the cause of any discrepancy between the volumetric and TPD measurements. Additionally, new sample processing techniques (discussed below) have not only improved sample reproducibility, homogeneity and H₂ storage

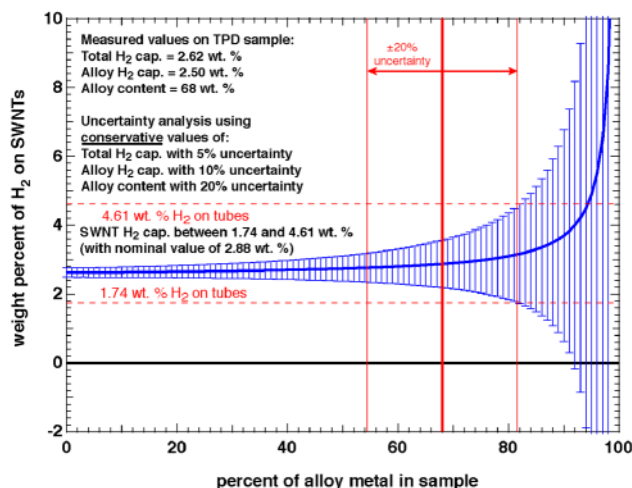


Figure 1. Uncertainty analysis graph for the 2.62 total H₂ wt.% sample shows that the nanotubes nominally are storing 2.88 wt.% H₂. Using very conservative estimates on the uncertainty in the measured values, we estimate that the true value will lie between 1.74 and 4.61 wt.%. The prime conclusion is that the nanotubes are participating in the hydrogen uptake.

capacity, but they also have made the samples more immune to degradation during the degas procedure. Given this progress, we expect to meet the upcoming milestone of achieving better agreement between the TPD and volumetric instruments. Work is continuing on understanding the relationship between the observed performance of a given sample and the sample degas procedure in the volumetric apparatus.

Uncertainty Analysis

For nanotube samples that contain a fraction of a metal hydride, it is critical to determine how much of the stored hydrogen is on the metal fraction and how much is on the nanotube fraction. Furthermore, given these measurements and their associated uncertainties, it is important to determine whether the amount stored on the nanotube fraction is significant, i.e., when the uncertainties are propagated in the calculation, can we say with certainty that hydrogen is being stored on the nanotubes. Figure 1 shows the amount of hydrogen stored on the nanotubes as well as the uncertainty for the amount of hydrogen stored on the nanotubes. This allows researchers to quickly ascertain the quality of the sample under test for both

the TPD and the volumetric methods. Results from the uncertainty analysis show significant SWNT uptake on two of nine samples; in addition, lower metal contents result in less uncertainty and higher overall gravimetric performance.

Rapid Calibration Method for TPD

The conventional method used to calibrate the TPD apparatus is quite laborious and time consuming, often requiring 5 - 10 different standard samples over a range of weights and as much as a week to complete. Furthermore, such calibration must be performed periodically to account for long-term changes in the characteristics of the vacuum system and the response of the detector. NREL designed and built a computer-controlled leak that allows precise amounts of hydrogen (or any other gas) to be metered into a vessel over a wide dynamic range. This new, highly accurate calibration method can be performed in an *in situ* fashion in tens of minutes once preliminary set-up has been accomplished. Furthermore, the new method can be considered a primary calibration that can be checked against the secondary methods that require standard samples. This is a general advance in the area of hydrogen measurement science that will facilitate measurement of hydrogen content on a wide variety of novel, nanostructured hydrogen storage materials. We are currently preparing publications on these advances and plan to work with parties interested in employing these techniques.

Advances in Preparation and Analysis Methodologies

Identifying Nanotube Distributions

SWNT samples typically consist of an agglomeration of many different types of nanotubes. Theory and experiment suggest that the specifics of the nanotube type (diameter and chirality) may impact the hydrogen adsorption thermodynamics and the maximum available capacities. We have implemented a photoluminescence excitation spectroscopy technique developed by Weisman at Rice University to assess the distribution of semiconducting SWNTs within purified samples. These data will enable us to build a link between hydrogen adsorption performance and the structural properties of the nanotubes.

Increased Purification Throughput

The purification rate of SWNTs has been limited by a step in which solid materials are removed from an acid solution by filtration. Until now, the filter disk had to be small (25 mm) to permit release of the resultant nanotube paper. Recently, we discovered that nanotube papers could be released from larger filter disks by physical stretching. Incorporating this approach with filter papers as large as 80 mm, we increased the potential purification throughput by a factor of ~10. To date, we have realized a throughput enhancement of ~5.

Improved Reproducibility and H₂ Storage Capacity

Production of the nanotube/metal hybrid has suffered from a lack of reproducibility, and absorbents have hovered around 2 - 2.5 wt.% H₂ capacity. A new approach has been to add surfactants to the cutting process to keep the nanotubes from reagglomerating. Two postulated benefits of this modification are (1) having the nanotubes better exposed to the energy of the ultrasonic horn, resulting in more thorough cutting, and (2) permitting better access for the alloy nanoparticles to decorate and interact with the tubes. We have noticed a definite improvement in the reproducibility and an increase in the observed H₂ storage capacity. Both of these are illustrated in the data of Figure 2, which shows several points clustered around the 3 wt.% threshold, including 8 points at or above 3 wt.%.

Low-Pressure, Low-Temperature Adsorption Measurements

NREL successfully developed the procedures and equipment to extend the temperature range for adsorption measurements down to the liquid nitrogen region. Lower-pressure operation would permit the use of conformable storage systems. Because of the high sensitivity of our volumetric apparatus due to its small volume, extending the temperature range to lower temperatures was non-trivial. By precisely controlling the temperature gradients along the sample tube, we were able to overcome this difficulty. This new instrumental capability will support studies directed at ascertaining the low-pressure, low-temperature capabilities of novel

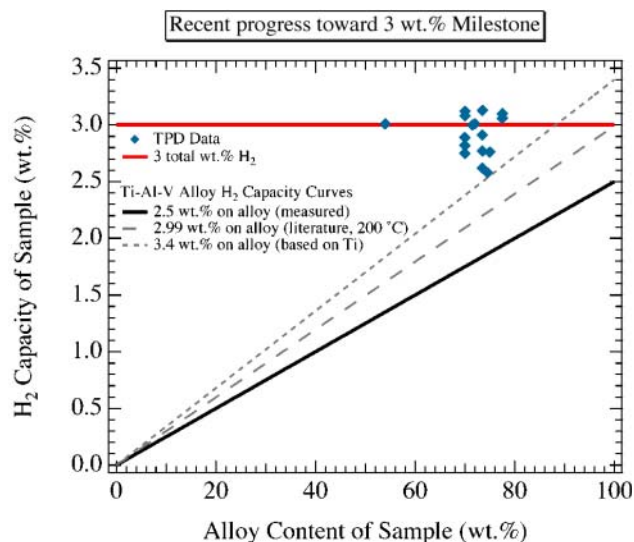


Figure 2. Adding surfactant to the sample-cutting/alloy-introduction process has allowed improvements in the reproducibility and an increase in the hydrogen storage capacity in the hybrid material, as is shown in the graph where several points are clustered near the 3 wt.% total storage capacity threshold. Direct measurements on the alloy have consistently yielded 2.5 wt.% H_2 storage capacity, and this is represented by the dark thick line in the graph, which shows the expected capacity if the metal alone was responsible for the hydrogen uptake.

adsorbents such as the metal-doped carbon aerogel samples that we have obtained from our collaborators at Lawrence Livermore National Laboratory.

Carbon Materials Development, Mechanistic and Computational Studies

Carbon materials are made at NREL by laser vaporization, chemical vapor deposition (CVD), hot-wire CVD, and arc-discharge. The various production methods can be adjusted to produce SWNTs, MWNTs, nanohorns, and other nanostructured carbons, with or without included dopant or catalytic species. Variations in synthetic conditions produce tubes of differing chirality and electronic type (semiconducting or metallic), diameter, and defect densities. Mechanistic and computational investigations of the as-produced and purified SWNTs and MWNTs will aid in understanding the behaviors of other carbon nanostructures.

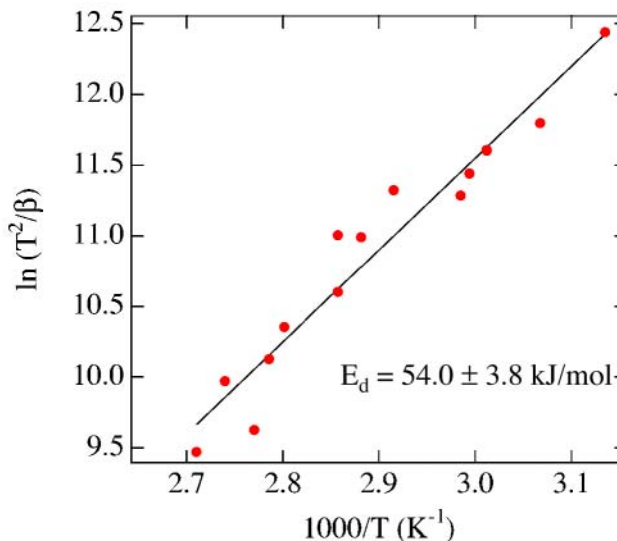


Figure 3. Desorption activation energy ($\ln T_m + E_d/RT_m$) from TPD measurements of the H_2 adsorption on as-synthesized MWNT materials with Fe catalyst suggests that the adsorption process is first order and has an energy of 54 kJ/mol.

H_2 Storage in Metal-Tipped MWNTs

Multi-wall carbon nanotubes with Fe nanoparticles at their tips grown by hot-wire chemical vapor deposition have shown a small amount of hydrogen adsorption at near-ambient temperatures by TPD (~ 0.01 wt.%). Despite the small amount of adsorbed hydrogen, the findings are mechanistically important as they clearly indicate the necessity of having metal particles in intimate contact with sp-hybridized carbons to enable near-ambient temperature hydrogen adsorption. The binding energy of the adsorbed hydrogen was measured using temperature-programmed desorption by varying the heating rate over more than one order of magnitude and plotting the temperature for the peak desorption according to an Arrhenius-type relation. The binding energy was found to be ~ 54 kJ/mol, a value that is in the range between simple physisorption and chemisorption, as is required for a vehicular hydrogen storage system (see Figure 3).

In an effort to simulate behavior of the metal-tipped MWNTs, two different sets of calculations were performed using the Vienna Ab-initio Simulation Package (VASP). One set of calculations utilized a system in which an Fe atom was included substitutionally on the lattice of a C_{36} fullerene,

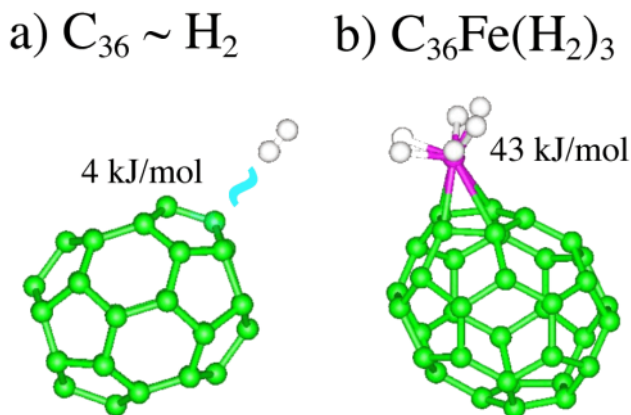


Figure 4. Effect of Fe Adatom on Hydrogen Adsorption on C_{36} (a) H_2 on pure C_{36} : only weak physisorption (~ 4 kJ/mol) is predicted to occur; (b) Fe adatom complexes with H_2 and results in hydrogen bonding with the Fe (~ 43 kJ/mol) but not with the carbon.

while the second set of calculations was performed with an Fe atom that was bonded onto one of the carbon atoms of the C_{36} fullerene. It is important to note that these are model systems designed to provide mechanistic insight. They are not necessarily target materials for use in eventual hydrogen storage systems. The models must be kept relatively simple and atomistically small given the computational intensity and sophistication of the simulation package. In the first case, we found that the presence of the Fe atom had no effect on the ability of nearby carbon atoms to bind hydrogen, but that the Fe species itself could bind up to three elongated H_2 molecules to form $C_{36}Fe(H_2)_3$ via a back-donation of electrons in a manner similar to that seen for Kubas-type compounds (Kubas, 2001) (see Figure 4). In this case, we have found another example of an “enhanced physisorption” in which dihydrogen is non-dissociatively bound to the Fe with an energy of ~ 50 kJ/mol. We note that this value is in good agreement with the value obtained from the TPD measurements for Fe-tipped MWNTs. In the second model, we found that a first H_2 molecule can be bound only to the Fe site. Once again, as with the substitutional Fe, the H-H bond length is stretched (~ 0.9 Å) in comparison to a free H_2 molecule (0.75 Å). Subsequent molecules dissociate and can break Fe-C bonds and also bind to carbon atoms that are distant from the Fe species.

Thus, in this second case we have an example of what can be termed “hydrogen spillover”.

Assessment of Novel Materials

A recent publication has described the synthesis of a Cu-based microporous metal oxide matrix (MMOM) material and the evaluation of the material as a hydrogen storage adsorbent (Pan et al., 2004). A hydrogen storage capacity of ~ 1.5 wt.% was found at room temperature and overpressures of ~ 100 atm using a volumetric technique. We have synthesized this material and a related Ti-based material and performed TPD measurements to evaluate the distribution of binding energies for hydrogen. Preliminary experiments on the Cu-based material show an enhancement in the physisorption population, but more complete experiments are required to determine if the capacity claims are valid. Volumetric measurements remain to be done. We have also begun measurements on metal-doped carbon aerogel samples obtained from Lawrence Livermore National Laboratory.

Future plans include a shift away from only SWNTs to exploring novel materials. NREL was selected to participate in a Center of Excellence on Carbon-Based Materials for Hydrogen Storage, which was competed through DOE's "Grand Challenge" solicitation released in 2003. The new center brings together a team of seven universities, three government labs, and one industrial partner to accelerate work on hydrogen storage in carbon materials over the next five years, subject to congressional appropriations.

Conclusions

- Hydrogen uptake values for alloyed SWNTs as reported by the NREL team during peer review were deemed credible.
- NREL's TPD and volumetric techniques were demonstrated to be accurate and repeatable based on a reference standard and showed excellent correlation between techniques using similar samples.
- Large variances in H_2 uptake for SWNT materials are not related to analytical methodologies.

- They are likely due to the stochastic nature of sample processing (synthesis, purification, cutting, dopant uptake).
 - Variances may related to the sensitivity of samples to degradation during the degas cycle.
 - TPD measurements and computational modeling show the binding energy of multi-wall carbon nanotubes with Fe nanoparticles at their tips to be ~50-55 kJ/mol, which is in the range between simple physisorption and chemisorption as is required for vehicular hydrogen storage systems.
 - A definite improvement in the reproducibility and an increase in the observed H₂ storage capacity to 3 wt.% have been made.
4. A.C. Dillon gave an invited talk at the MRS Fall Meeting in Boston, December 2, 2003, entitled, "Hydrogen Adsorption on Multi-Wall Nanotubes Produced by Continuous Hot Wire Chemical Vapor Depositions Sheds Light on the Mechanism of Enhanced H₂ Adsorption on Graphitic Structures Containing Small Quantities of Transition Metals."
 5. Anne Dillon gave an invited talk at the 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004, titled, "Continuous Hot Wire Chemical Vapor Deposition of Carbon Single-Wall Nanotubes and Employing Raman Spectroscopy to Qualitatively Evaluate the Purity of Bulk Single-Wall Nanotube Materials."

References

1. Miller, M.A., Gorte, R. "Carbon Nanotube Sorption Science – External Peer Review of NREL Activities." Special Report (Revised), SwRI Project No. 18.03.03.05064. Prepared for U.S. Department of Energy Office of Hydrogen, Fuel Cells & Infrastructure Technologies. March 1, 2004.
2. Kubas, G.J., J. Organo-metallic Chem. 635 (2001) 37-68.
3. L. Pan, M.B. Sander, X. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath, J.K. Johnson, J. Am. Chem. Soc. 2004, 126, 1308-1309.
6. Katie Gilbert gave a talk at the Annual APS March Meeting 2004, March 22-26, 2004, Montreal, Quebec, Canada, titled, "A Highly Accurate Method for Measuring Hydrogen Storage Capacities."
7. Tom Gennett gave a talk at the 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004, titled, "Removal of Graphite Encapsulated Metal Particles for the Purification of SWNT Materials."
8. Mike Heben was invited to present at the National Nanotechnology Initiative Workshop on Nanoscience Research for Energy Needs, held March 16-18, 2004, in Crystal City, Virginia. Two brief presentations were given to highlight the importance of nanoscience for finding solutions to energy-related problems.

FY 2004 Publications/Presentations

1. "Single-Wall Carbon Nanotube Growth in a Volumetrically Confined Arc-Discharge System," co-authored by Kale Franz selected for publication in Volume 4 of DOE's Journal of Undergraduate Research.
2. Dr. Phil Parilla gave an invited presentation at the Society of Automotive Engineers conference on the Implications of the Hydrogen Economy.
3. M.J. Heben presented a talk at the International Energy Agency meeting on hydrogen storage in Hawaii, November 16-20, 2003.

Special Recognitions & Awards/Patents Issued

1. International Patent Application "Carbon Nanotube Heat-Exchange Systems," T.J. Hendricks, M.J. Heben
2. Patent Application "Hot-Wire Production of Carbon Multi-Wall and Single-Wall Nanotubes," A.C. Dillon, J.L. Alleman, A.H. Mahan