III.D Carbon Materials

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

A.C. Dillon, P.A. Parilla, T. Gennett, K.E.H. Gilbert, J.L. Blackburn, Y.-H. Kim, Y. Zhao, S.B. Zhang, J.L. Alleman, K.M. Jones, T. McDonald, and Michael Heben (Primary Contact)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401
Phone: (303) 384-6641; Fax: (303) 384-6655; E-mail: michael_heben@nrel.gov

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

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 $H_2$, and has $H_2$ 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 $H_2$ 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Technique</th>
<th>Wt% H₂ total</th>
<th>Wt% H₂ alloy</th>
<th>Wt% H₂ tubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure #1, cut #1, piece #1</td>
<td>TPD</td>
<td>2.62</td>
<td>60.0</td>
<td>2.88</td>
</tr>
<tr>
<td>Pure #1, cut #1, piece #2</td>
<td>TPD</td>
<td>2.79</td>
<td>99.4</td>
<td>2.17</td>
</tr>
<tr>
<td>Pure #1, cut #1, piece #3</td>
<td>ViD (ads)</td>
<td>1.03</td>
<td>63.9</td>
<td>0.92</td>
</tr>
<tr>
<td>Pure #1, cut #2, piece #1</td>
<td>TPD</td>
<td>1.13</td>
<td>63.9</td>
<td>1.48</td>
</tr>
<tr>
<td>Pure #2, cut #1, piece #1</td>
<td>TPD</td>
<td>1.09</td>
<td>24.4</td>
<td>0.68</td>
</tr>
<tr>
<td>Pure #2, cut #2, piece #1</td>
<td>ViD (ads)</td>
<td>1.51</td>
<td>45.0</td>
<td>0.67</td>
</tr>
<tr>
<td>Pure #2, cut #2, piece #2</td>
<td>ViD (des)</td>
<td>1.50</td>
<td>45.0</td>
<td>0.65</td>
</tr>
<tr>
<td>Pure #3, cut #1, piece #1</td>
<td>TPD</td>
<td>1.06</td>
<td>43.3</td>
<td>-0.04</td>
</tr>
<tr>
<td>Pure #3, cut #1, piece #2</td>
<td>ViD (ads)</td>
<td>0.97</td>
<td>35.7</td>
<td>0.00</td>
</tr>
<tr>
<td>Pure #3, cut #1, piece #2</td>
<td>ViD (des)</td>
<td>1.39</td>
<td>35.7</td>
<td>0.46</td>
</tr>
</tbody>
</table>

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 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 \( \text{H}_2 \) Storage Capacity**

Production of the nanotube/metal hybrid has
suffered from a lack of reproducibility, and
absorbents have hovered around 2 - 2.5 wt.% \( \text{H}_2 \)
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 \( \text{H}_2 \)
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.% \( \text{H}_2 \) 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 \( \text{H}_2 \) 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.

\( \text{H}_2 \) 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 \( \text{C}_{36} \) fullerene,
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 substitutitional 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).

- Variance may relate 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 H$_2$ storage capacity to 3 wt.% have been made.

**References**


**FY 2004 Publications/Presentations**


2. Dr. Phil Parilla gave an invited presentation at the Society of Automotive Engineers conference on the Implications of the Hydrogen Economy.


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.

**Special Recognitions & Awards/Patents Issued**
