IV.C.1d Cloning Single Wall Carbon Nanotubes for Hydrogen Storage

James M. Tour (Primary Contact),
Carter Kittrell
Rice University
Smalley Institute for Nanoscale Science and Technology
MS222
6100 Main Street
Houston, TX 77005
Phone: (713) 348-6246; Fax: (713) 348-6250
E-mail: tour@rice.edu; kittrell@rice.edu
Web site: http://www.jmtour.com

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

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

Contract Number: DE-FC36-05GO15073

Start Date: February 1, 2005
Projected End Date: January 31, 2010

Objectives

- Create a unique new nanoengineered fibrous storage media with specific uniform pore structure determined by the size of molecular crosslinkers.
- Measure hydrogen uptake in partnership with the National Renewable Energy Laboratory (NREL).
- Demonstrate the 2x steeper slope for Chahine's rule for H_2 uptake and the "nanopump" concept. Optimize pore spacing is ~0.8 nm.
- Improve solvent extraction methods to increase available pore volume.
- Develop non-acidic lithium/ammonia-based fiber expansion and cross-linking methods.
- Lithium intercalation of rigid nanotube scaffold enhanced metal binding of H_2 at room temperature (RT).

Technical Barriers

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

(A) System Weight and Volume
(C) Efficiency
(E) Charging/Discharging Rates
(J) Thermal Management
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Accomplishments

- Created 3-D nanoengineered carbon nanotube frame for direct hydrogen uptake and as a scaffold for metals for RT binding.
- Discovered and understood problems with solvent extraction.
- Developed expansion method for spun fiber and cross-linking method to make rigid scaffold and specifiable pore spacing.
- Discovered scaffold exhibits 2x steeper slope for H_2 uptake than Chahine's rule which extrapolates to 6.5 wt% uptake.
- Developed thermodynamic model calculation yields similar 6.5 wt% and 59 g/L.
- Developed new lithium/ammonia-based expansion and cross-linking as an alternative to avoid the difficulties of oleum solvent extraction.

✧ ✧ ✧ ✧ ✧

Introduction

For wide public acceptance, it is essential that the hydrogen "gas tank" in an automobile provide a similar range as today's gasoline tanks without occupying several times the volume. Physical adsorption of the H_2 molecule onto a material with high surface area minimizes the activation barrier and obviates the need for a catalyst (that would consume additional energy and could slow down the fill and release rates). More hydrogen is stored in less volume and much less pressure than in a tank without a sorbent. A porous nanoengineered framework of carbon nanotubes will provide the high surface area and have controlled pore size so that there is no wasted volume due to oversize pores. It is important that the hydrogen be packed tightly into the pores for maximum uptake, and this packing may be considerably enhanced by a favorable equilibrium constant, which occurs for the extended pi cloud of carbon nanotubes held apart with spacers. In addition, this scaffold can accommodate metal atoms, such as lithium, which have sufficient binding energy with hydrogen that it will adhere in the molecular form at or near RT.

Approach

We have recently developed a new type of nanoengineered materials, constructed from single wall carbon nanotubes (CNTs) that are used as molecular building blocks, which have unsurpassed uniaxial thermal conductivity, and these are spun to yield fibrous media. The fiber is expanded and is locked into place with bi-functional cross-linkers, which determine the tube-tube spacing, and, hence, provides uniform pore size between the aligned nanotubes. A correct-sized pore that can surround the hydrogen with sp^2 electron clouds considerably enhances the free energy of uptake into the pore to yield a large equilibrium constant. This forms a high temperature condensate, also termed a "nanopump" [1]. The uptake per unit area is essentially doubled compared to amorphous carbon adsorbents. The scaffold is now being developed as a support for lithium, and later transition metals for RT binding of molecular hydrogen. This nanoengineered scaffold provides a rigid support for unlimited cycling, a non-tortuous path for excellent gas flow kinetics, and high energy efficiency of H_2 uptake. The high density of this media is ~1g/cm^3 assures volumetric capacity will track gravimetric capacity.

Results

We have successfully created the nanoengineered CNT scaffold using a variety of techniques, and have been very consistent in reproducing the unusually high uptake of hydrogen per unit surface area. We have tested methods for using different cross-links to control pore size, with expansion ranging from 30% to 45%; up to 9 Angstrom pore spacing. The ability of hydrogen to pack densely when surrounded by an sp^2 pore of the correct size has been demonstrated theoretically [1] and we have focused on testing nanoporous structures. We have experimental evidence that this acts as a "nanopump" theoretically proposed by Gotthard Seifert's group (for nanoporous graphene). H_2 uptake measurements by NREL at 77 K shows a consistent pattern of about a 2x larger uptake per unit surface area (SA) using the Brunauer, Emmett, Teller (BET) test than expected for the standard "Chahine's rule" (Figure 1). The precision nanopore lends itself to a good understanding of the physisorption process, which is supported by a thermodynamic model for the uptake.

Chahine's Plot for Hydrogen Uptake

The experimental data are shown on plot of hydrogen uptake vs. BET SA (Figure 1). The standard slope, known as Chahine's rule, is 2 wt% for 1,000 m^2/gram of SA, and is typical of most carbon adsorbents. Our slope for the nanoengineered sp^2 pore, at 3.7% for 1,000 m^2/g, is nearly twice as steep at only 2 bar. We use a correction factor suggested by Michael Heben of NREL that is conservatively estimated at 1.3x for uptake for 40 bar. For 1,400 m^2/g external surface area, we project 3.7 slope x 1.4 x 1.3 correction = 6.5 wt% @ 1,400 m^2/g SA and 40 atm. The additional 1/3 of the surface area inside the nanotube will subsequently be made available by perforation of the nanotube wall.

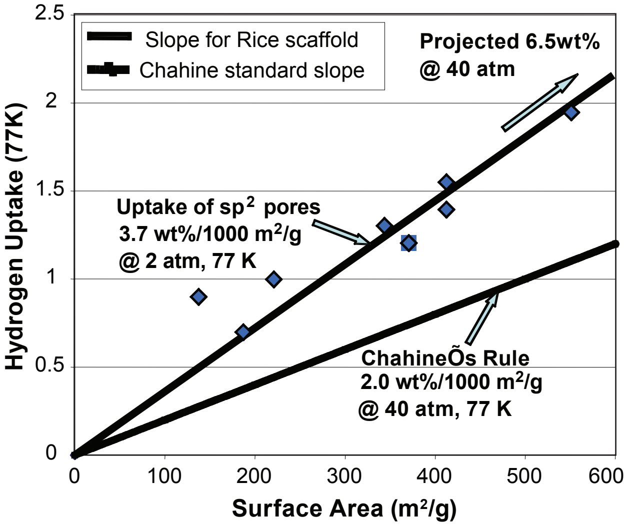

FIGURE 1. Enhanced Uptake in the Nanotube Scaffold (This shows that average uptake at 2 bar and 77 K provides a slope that is considerably steeper than that typical for carbon adsorbent materials. For the asymptotic pressure limit of 40 bar, our slope will be even steeper.)

Calculation for Hydrogen Uptake of our Fiber Scaffold

We have applied the methodology of Seifert [1] to the CNT scaffold, assuming that the pi cloud of the nanotube has the same sort of attraction for the hydrogen in the curved form as for a flat graphene sheet described by Seifert. Strong curvature actually enhances binding energy [2]. We started with $\Delta F = RT\ln K$, and the free energy for pore binding = 9.9 kJ/mole. For a temperature = 150 K, the equilibrium constant (corrected for fugacity) = 200. If the fill pressure is 30 bar, then this is 200 x 30 bar external => 6 kbar internal "pressure." The molar volume 6 kbar = 15.4 cm^3/mole [3]. The available volume for hydrogen is calculated to be = 0.5 cm^3, excluding single walled nanotubes (SWNTs). Therefore 15.4 cm^3/mole/0.5 = 31 cm^3/mole. Allow 15% volume for macroscopic flow channels for fast filling: x 1.15 for gas flow channels = 36 cm^3/mole. This will yield 55 mg/cm^3 H_2 volumetric uptake. We have measured the density of the 3-D SWNT scaffold to be consistently about 1 g/cm^3, and allow 15% for gas flow channels, this corresponds to 0.85 g/cm^3. Then 55 mg/cm^3/0.85 density then yields 6.5 wt% gravimetric uptake when all of the external surface area is made available. The calculated uptake and an extrapolation of the measured uptake are in agreement for the slope which is twice as steep as the "normal" Chahine's rule.

Solvent Extraction

We have developed the method to make nanoengineered SWNT scaffolds. Creation of stable expanded nanotube fiber arrays has been successfully done by swelling them in fuming sulfuric acid and then locking them into an array by cross-linking the sidewalls with bifunctional derivatives. This provides exposed surfaces that remain highly attractive for physisorption, which is good for hydrogen. However, the intercalating acid solvent is strongly attracted and also difficult to remove. One of our accomplishments is the understanding of the difficulty of removing the acid even with high temperatures (see Figure 2). The unusually tenacious physisorption of the expanded lattice will bind hydrogen strongly, but fully removing the expansion solvent has now become the next hurdle. Alternate means are currently being sought to remove the intercalated material without structural damage.

Lithium Expansion

The new lithium-based expansion of the SWNT fiber to produce the nanoengineered scaffold is a parallel effort with the already established expansion in oleum. The lithium ammonia chemistry provides a new method for crosslinking. We have experimentally shown that expansion of the spun fiber does take place comparably to that achieved by the oleum expansion method (Figure 3a.). The iodide-based cross-linking has also been achieved, which locks the expanded nanotubes in place. Raman spectroscopy has been obtained for the expanded fiber. The "roping peak" at 265 cm^{-1} frequency shift is greatly diminished for the expanded fiber, which is very strong evidence that the nanotubes have remained spaced apart after drying. We have designed and constructed the apparatus needed to provide precisely measured functionalization of the lithium metal to the expanded and cross-linked fiber (Figure 3b). This involves dissolving the lithium metal into liquid ammonia, and then transferring it under an inert atmosphere to a calibrated container, then transferring the measured amount of dissolved lithium metal to the reaction vessel containing the previously expanded scaffold fiber that will receive the measured amount of lithium. We have completed this apparatus, and will begin making the lithium functionalized scaffolds for hydrogen uptake tests (Figure 4).

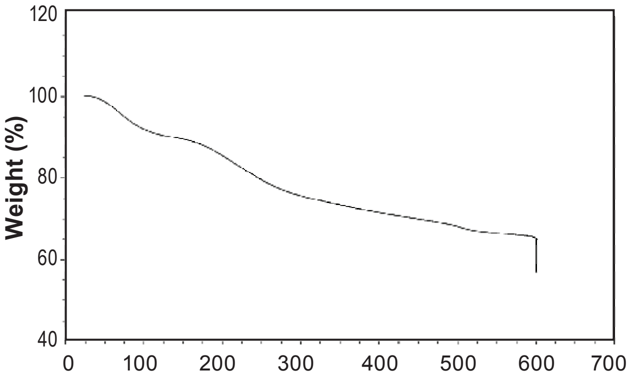

FIGURE 2. Thermogravametric analysis of the nanotube scaffold shows that a large amount of expansion solvent is not extracted after extensive washing. After heating to 600°C the fibers lose about 45 wt% which is acid and other non-nanotube material.

Conclusions and Future Directions

- The metal intercalated scaffold will adsorb at RT and low pressure, reducing system weight.
- The physisorption process has no energy barrier, minimizing energy consumption.

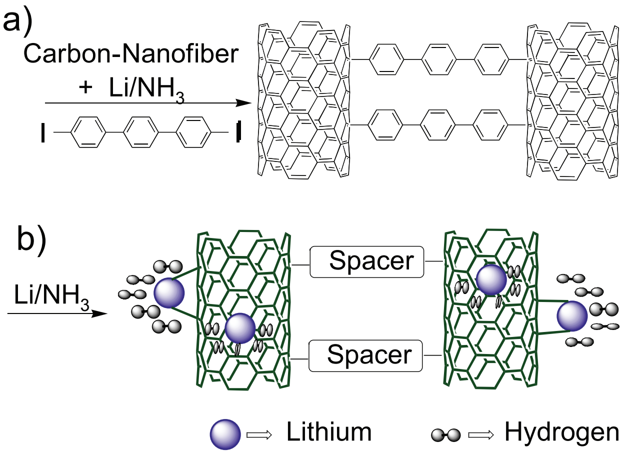

FIGURE 3. Alternate Means to Achieve 3D Nanoengineering
a) Nanotube fibers are expanded and crosslinked with lithium and terphenyl iodide. The lithium removes the iodine, and the terphenyl becomes a rigid spacer. b) In the second step, lithium is again introduced and the ammonia is evaporated away to leave the metal functionalized scaffold for hydrogen uptake at RT.

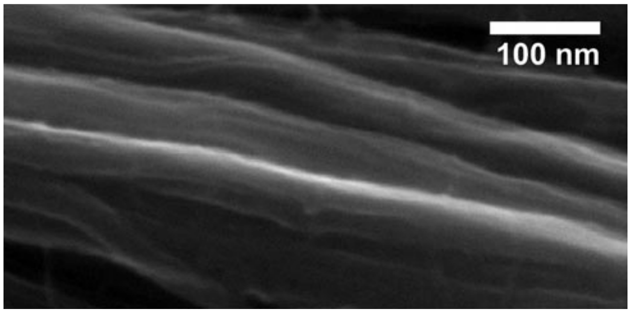

FIGURE 4. A High Resolution SEM, 200,000x Shows the Preservation of the Excellent Alignment of the Nanotube Fiber that has been Expanded and Crosslinked in the Lithium Ammonia Reagent, scheme in Figure 3

- Non-tortuous path and no catalyst allow for fast charge/discharge.
- SWNTs are the best thermal conductors for efficient removal of heat of adsorption.
- The engineered nanopore provides uniform surface binding and uptake explained by a thermodynamic model.
- Expansion and crosslinking of fiber spun from SWNTs makes rigid scaffold for hydrogen uptake.
- Controlled expansion has been shown ranging from 30% to 45% with up to 9 Angstrom pore spacing.
- The 3D nanoengineered scaffold exhibits 2x greater uptake per unit surface area than most. Scaffold exhibits 2x steeper slope for H_2 uptake than Chahine's rule, which extrapolates to 6.5wt% uptake.
- Thermodynamic model calculation yields similar 6.5wt% and 59 g/L.
- Lithium/ammonia based expansion and cross-linking provide an alternative to avoid the difficulties of oleum solvent extraction.
- We plan to improve solvent extraction methods for continued 2x enhanced uptake.
- We plan to continue to explore alternative expansion methods.
- We will test the air-free lithium intercalation apparatus.
- We will begin tests on hydrogen uptake on the metal functionalized nanotube scaffold for RT binding.

Relevant Group Publications

1. Smalley, R. E.; Li, Y.; Moore, V. C.; Price, B. K.; Colorado, R., Jr., Schmidt, H. K.; Hauge, R. H.; Barron, A. R.; Tour, J. M., "Single Wall Carbon Nanotube Amplification: En Route to a Type-Specific Growth Mechanism," *J. Am. Chem. Soc.* **2006**, *128*, 15824-15829.

2. Price, B. K.; Tour, J. M., "Functionalization of Single-Walled Carbon Nanotubes On Water," *J. Am Chem. Soc.* **2006***, 128,* 12899-12904.

3. Stephenson, J. J.; Sadana, A. K.; Higginbotham, A. L.; Tour, J. M., "Highly Functionalized and Soluble Multi-Walled Carbon Nanotubes by Reductive Alkylation and Arylation: the Billups Reaction," *Chem. Mater.* **2006**, *18*, 4658-4661.

References

1. Graphene nanostructures as tunable storage media for molecular Serguei Patchkovskii, John S. Tse, Sergei N. Yurchenko, Lyuben Zhechkov, Thomas Heine, and Gotthard Seifert, *PNAS* 2005;102;10439-10444 (2005).

2. Hansong Cheng, Alan C. Cooper, Guido P. Pez, Milen K. Kostov, Pamela Piotrowski, and Steven J. Stuart, "Molecular Dynamics Simulations on the Effects of Diameter and Chirality on Hydrogen Adsorption in Single Walled Carbon Nanotubes," *J. Phys. Chem. B*, 109, 3780, (2005).

3. R. L. Mills, D. H. Liebenberg, J. C. Bronson, and C. Schmidt, "Equation of State of Fluid n-H_2 from PVT and Sound Velocity Measurements to 20 kbar," *J. Chem. Phys, 66*, 3078, (1977).