

Cloning Single Wall Carbon Nanotubes for Hydrogen Storage

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Project ID
#ST05: Tour

Overview

Timeline

- Start-Feb 2005
- Finish-Jan 2010
- 40% complete

Budget

- Total project funding
- DOE share \$1,715,990
- Contractor share\$428,997
- Funding received in FY05-\$300,000 plus \$82,000 cost share
- Funding for FY06-\$300,000 plus \$82,800 cost share
- Funding for FY07- \$300,000
- \$85,697 cost share

Barriers

- General
 - A. Cost.
 - B. Weight and Volume
 - C. Efficiency
- E. Refueling Time
- Reversible Solid-State Material
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of H Physi- and Chemisorption

Partners

NREL, Air Products,
Duke, Penn. St and
Oak Ridge National Lab
Yakobson/Hauge Rice

DOE 2010 Targets for Storage System

- Gravimetric 0.06 kg H₂/kg
- Volumetric 0.045 kg H₂/m³

Objectives

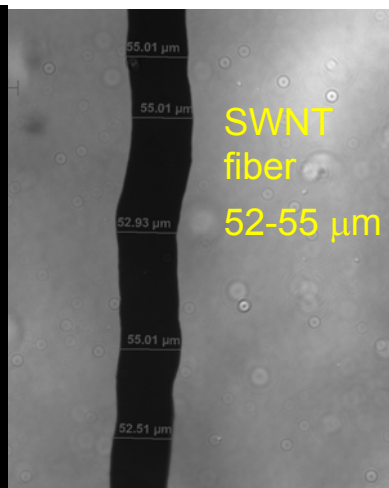
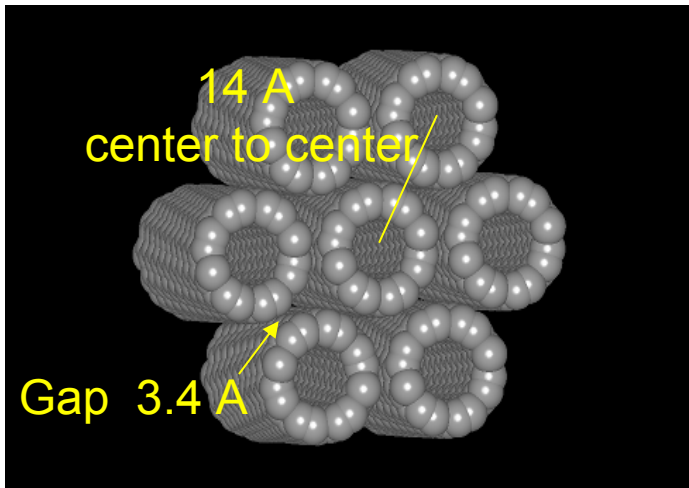
- **FY 2006:**
- **Create a unique new nanoengineered fibrous storage media with uniform pore structure determined by the size of molecular crosslinkers**
- **Develop reliable spinning of 100% sp² fibers of SWNTs with subsequent expansion in oleum**
- **Develop crosslinking methodologies to make a rigid scaffold**
- **Begin testing of H₂ uptake with NREL**

- **FY 2007:**
- **Investigate the 2x steeper slope for Chahine's rule for H₂ uptake and the concept of high temperature condensate. Determine uptake properties of the precision sp² pore**
- **Develop alternative spinning methods and solvent extraction methods to increase available pore volume**
- **Develop non-acidic lithium/ammonia based fiber expansion and cross-linking methods to circumvent oleum acid extraction problems and generalize the nanoengineered sp² pore methodology**
- **Begin development of lithium intercalation of rigid nanotube scaffold for Kubas-type binding of H₂ at ambient temperatures**

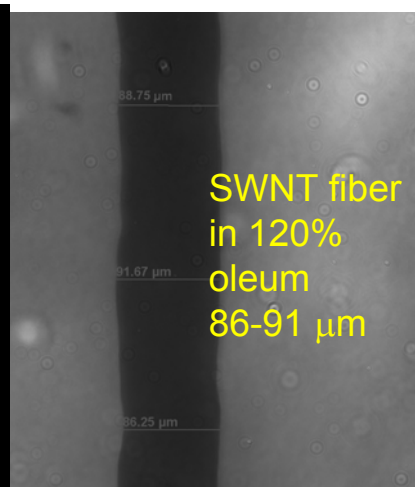
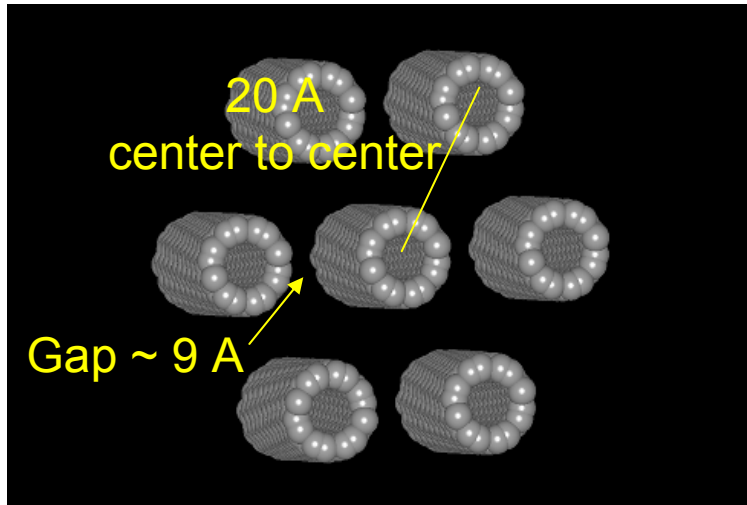
Approach

- **A framework with nanoengineered pores is constructed from single wall carbon nanotubes that are used as molecular building blocks, which have unsurpassed uniaxial thermal conductivity, and spun to yield fibrous media**
- **The fiber is expanded and is locked into place with bifunctional cross-linkers which determine the tube-tube spacing, and hence uniform pore size between the aligned nanotubes; adjustable pore size for optimum uptake (Yakobson theory)**
- **A correct-sized pore that can surround the hydrogen with sp² electron clouds considerably enhances the free energy of uptake into the pore to yield a large equilibrium constant. This is a high temperature condensate, (AKA supercriticality or “nanopump”)**
- **This leads to a much steeper slope for Chahine’s rule, whereby the uptake per unit area is considerably enhanced**
- **The scaffold will also be used as a support for Kubas-type binding of H₂ to metals such as lithium, titanium and scandium (Yakobson theory) for room temperature uptake**
- **This nanoengineered scaffold provides a rigid support for unlimited cycling, a non-tortuous path for excellent gas flow kinetics, and high efficiency for carbon adsorption and a rigid support for RT uptake of H₂ on Li, Sc, Ti**
- **High density media ~1g/cm³ assures volumetric capacity does not lag gravimetric capacity**

Background FY06 : Expanded fiber



- Start with SWNT spun fiber
- Nanotubes are closely spaced due to strong van der Waals attractive forces.



- SWNT Bundle, swollen in 120% H_2SO_4 (Oleum)
- Increases the tube-tube spacing
- Uniform coating of the acid that intercalates onto the walls of each SWNT for uniform expansion

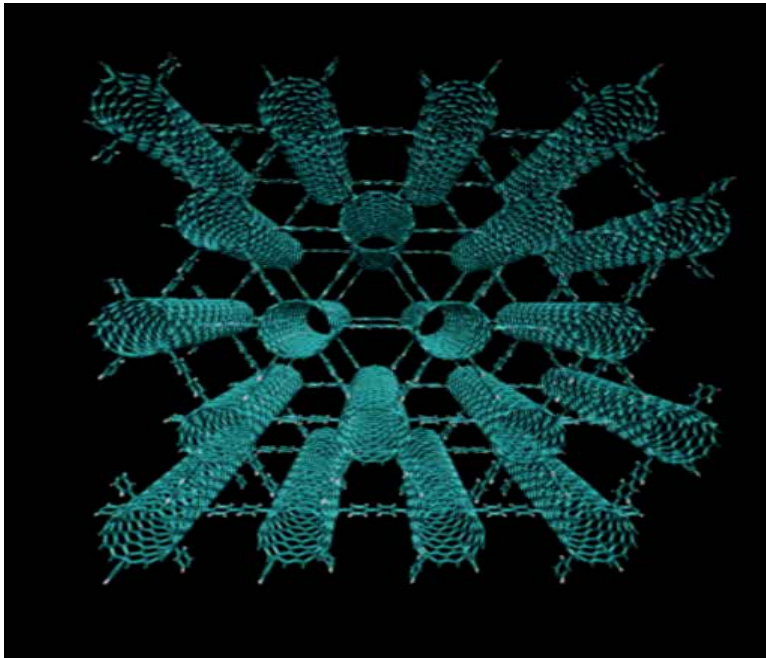
Uniform expansion of the aligned nanotubes followed by cross-linking provides a uniform pore so that all pores can be optimized for binding free energy and maximum H_2 uptake

Accomplishment: The Nanoengineered SWNT Scaffold

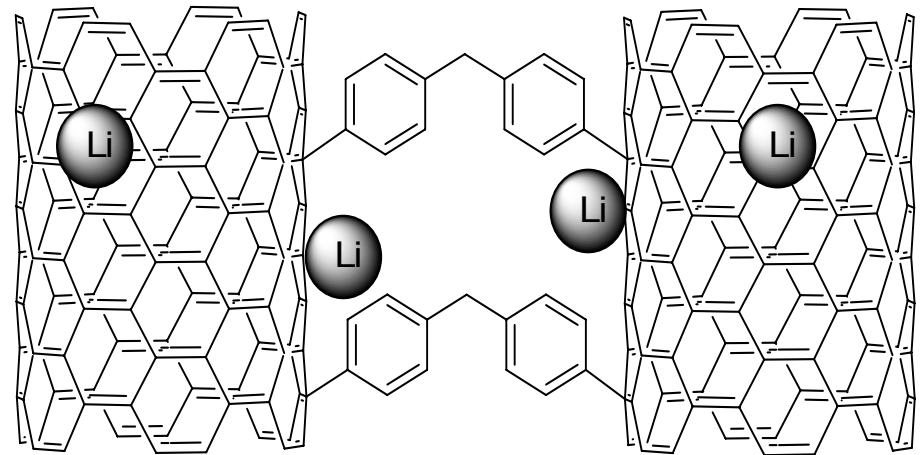
Nanoengineering:

Developed methodology to make these nanostructured materials possible, with adjustable pore sizes needed for maximum hydrogen storage capacity.

The cross-linker determines the pore size. Many sizes cross-linkers are available.



The nanotube rigid space frame scaffold
(B. Yakobson)

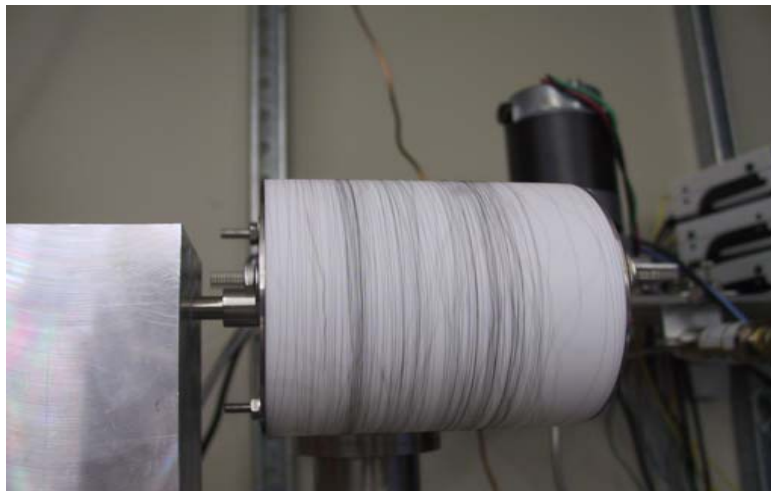
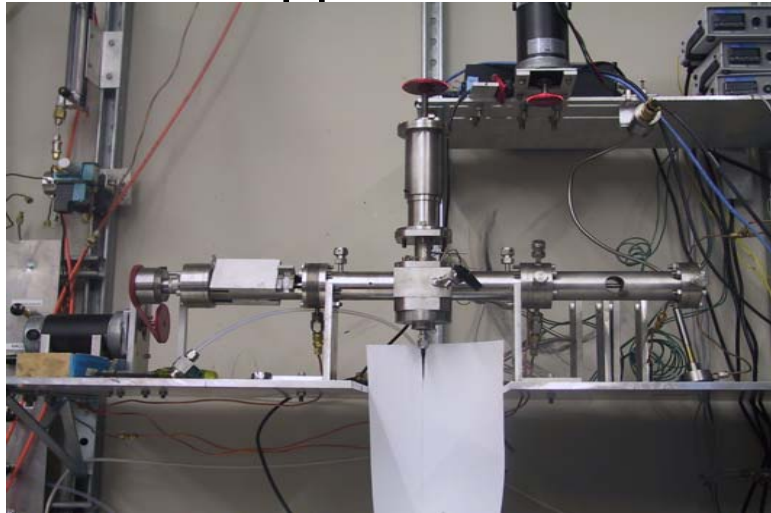


Addition of lithium atoms to the sidewalls of the nanotube scaffold for Kubas-type binding at ambient temperature. Larger pore sizes may be needed

Single wall carbon nanotubes are used as molecular building blocks to make scaffolds that surround the physisorbed H₂ with an sp² hybridized pi cloud for enhanced binding, and support lithium or transition metals for Kubas-type binding at room temperature.

Accomplishment: Fiber spinning in oleum

Fiber Spinning Apparatus



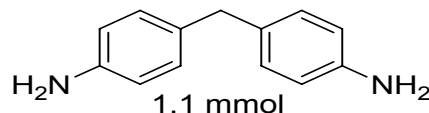
- **Upper-** Laboratory engineered SWNT fiber spinning apparatus extrudes 100% pure carbon fibers from an oleum suspension.
- **Lower-** Single continuous SWNT fiber wound up on the take up drum -- production: 2g/hour.
- Feed stock for current expansion and cross linking to make the nanoengineered structure
- New approach now being tested: spin fiber directly into oleum, bypassing drying step,
- Then go directly into bath(s) for crosslinking chemistry and cleaning, then wind up on drying spool

Conventional wet spinning techniques provide feedstock for the nanotube scaffold; bypass drying step for continuous production

Expect to be fully scalable to produce 3D nanoengineered media to meet DoE targets

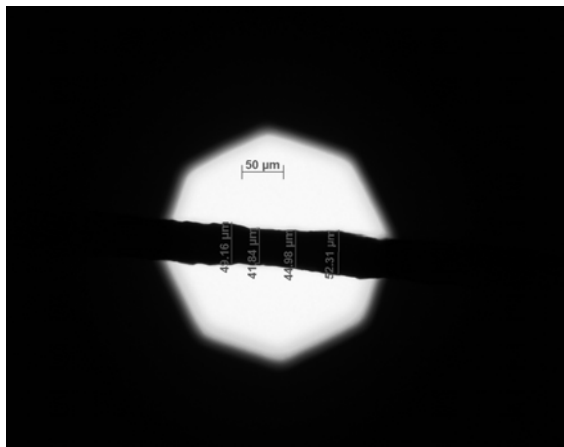
Accomplishment: Expanded and crosslinked fiber

SWNT Fiber
No mounting

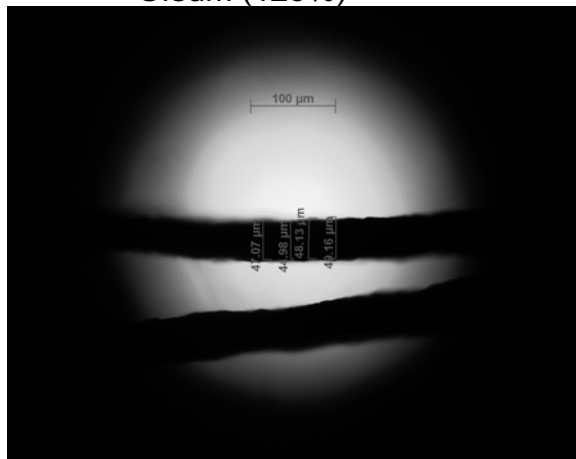


NaNO₂
AIBN
Oleum (120%)

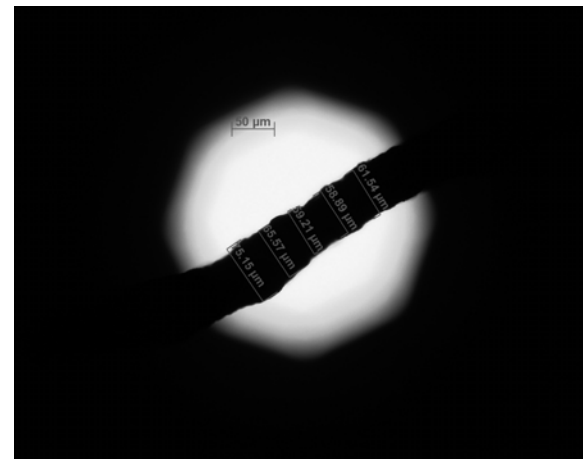
Crosslinked Fiber



Standard
47 μm



Oleum only
47.3 μm

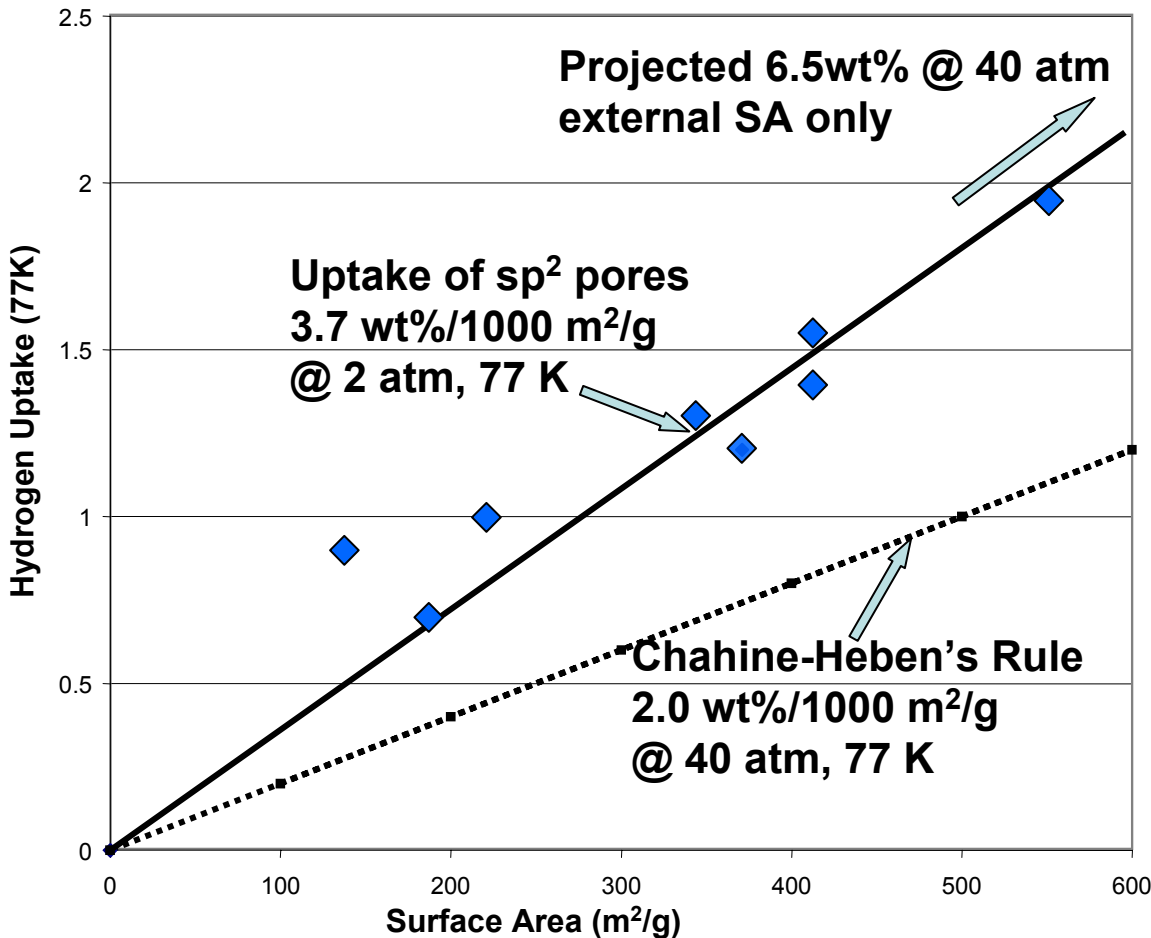


Cross-Linked Fiber 64.6 μm
Diameter increased ~ 30%

Without the cross-linkers (middle, oleum only) the fiber collapses back after extraction
The nanoengineered medium (right) is a self-supporting, readily handled object.
Crosslinked swollen fiber exhibits a 30% increase in diameter & corresponds to a 7 Å pore
Expansion up to a 9 Å pore has been obtained.

**The crosslinking chemistry is the key to a permanent & rigid 3D nanoengineered scaffold.
Different expansion conditions and cross-linkers create different pore sizes.**

Chahine-Heben's Rule vs. Nanoengineered scaffold



— Slope for Rice scaffold
····· Chahine standard slope

- Our average uptake at **2 bar** and 77 K provides slope that is considerably steeper than that typical for carbon
- For the **asymptotic** pressure limit, our slope will be even steeper
- Using the **Heben Approximation** (x1.3-1.5 correct 2 atm to 40 atm): 3.7 slope x 1.4 x 1.3 Heben = **6.5wt% @ 1400 m²/g & 40 atm** (only external SA considered)
- Our nanotube wall perforation to be incorporated later: Internal ~1/3 of total SA not considered here

Uptake per unit surface area (SA) twice as large as for most carbon materials. Persists for different types of samples. Data corresponds with the “nanopump” theory of G. Seifert. Pores packed with high density hydrogen; volumetric uptake tracks gravimetric

Accomplishment: Predicted uptake from theory

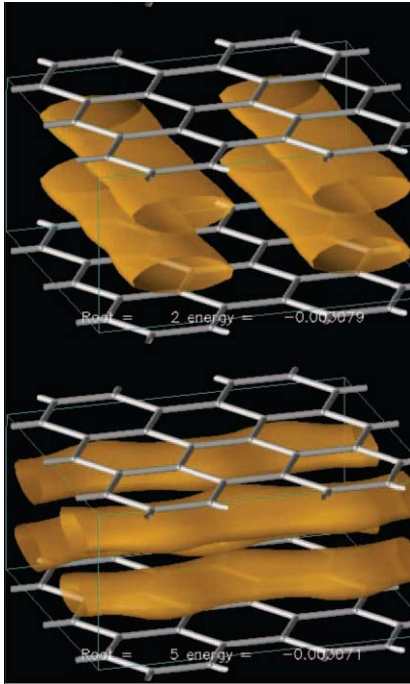


Figure adapted from Seifert, PNAS-102, 10439 2005.

Probability densities of translational nuclear Hamiltonians of hydrogen in spaced graphene for two wavefunctions. The free energy is about doubled for the correct pore spacing, leading to the “nanopump” effect.

Calculation for our fiber: $\Delta F = RT \ln K$

Free energy for pore binding = 9.9 kJ/mole; $T = 150 \text{ K}$
[calculated from binding enthalpy: Eklund 2002]

Equilibrium constant (corrected for fugacity) = 200

200 x 30 bar external => 6 kbar internal “pressure”

Molar volume 6 kbar = 15.4 cm³/mole [Mills 1977]

Available volume: = 0.5 cm³.

(Excludes SWNT frame & internal pores)

15.4 cm³/mole/0.5 = 31 cm³/mole

(x 1.15 for gas flow channels = 36 cm³/mole)

=> 55 mg/cm³ H₂ volumetric uptake

Density of the 3-D SWNT scaffold is 1 g/cm³,

Allow 15% for gas flow channels => 0.85 g/cm³.

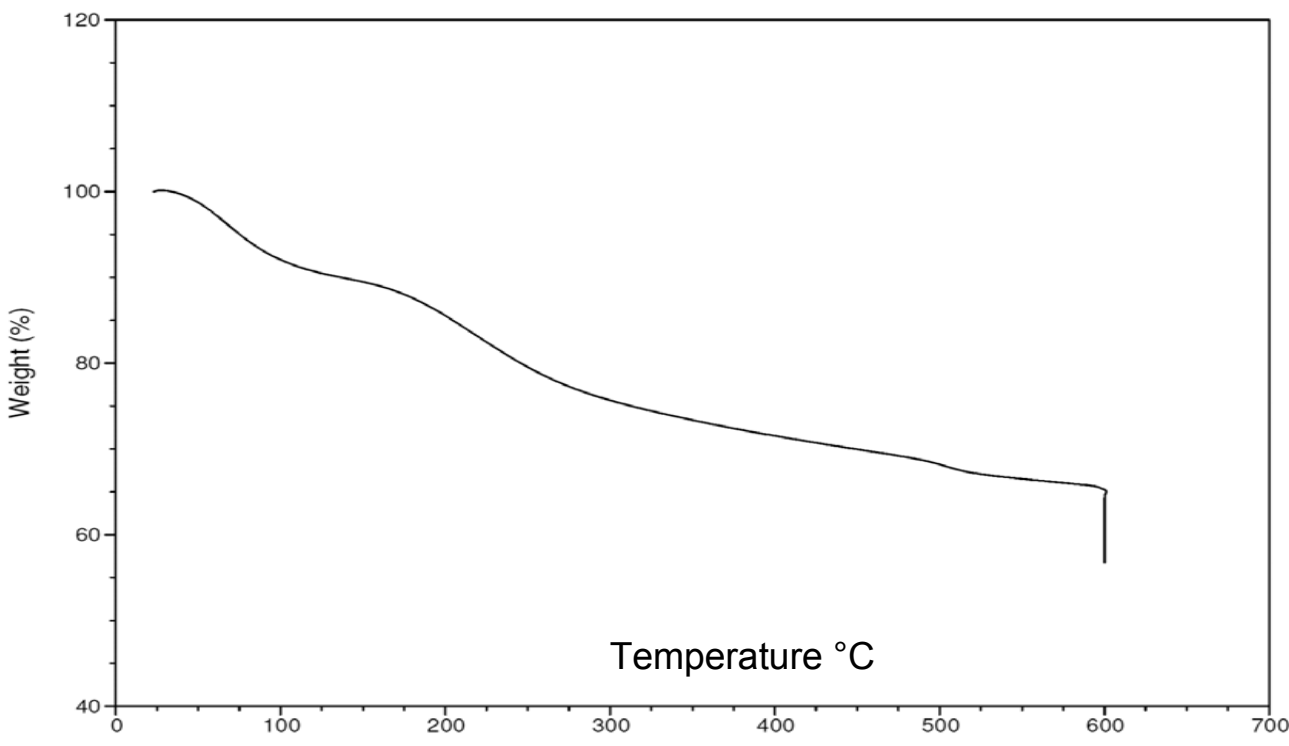
55 mg/cm³/0.85 density =>

=> 6.5 wt% gravimetric

Correct size sp² carbon pores show an enhanced equilibrium constant which leads to high density hydrogen filling the pores.

Calculated uptake shows that our experimental observations using nanoengineered scaffolds are consistent with this predicted enhancement

Accomplishment: Determined cause of hindered access



Thermogravimetric analysis shows 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

Problem: the SWNT pores are very sticky, and the energy gained by collapse of the matrix that can squeeze out the solvent is no longer available; further evidence of rigid cross linking; Water is not effective for extraction.

Solutions to be tested to increase H₂ uptake:

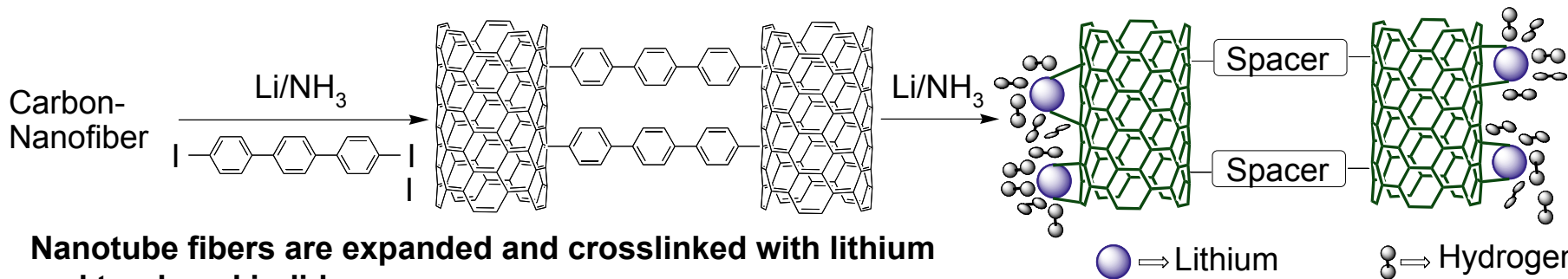
- 1. Use a better solvent to extract the oleum**
- 2. Find a non-protic intercalating acid, such as SO₂ClF, SO₂Cl₂, SO₃**
- 3. Use non-acidic expansion method, such as lithium/ammonia**

Accomplishment: Nanoengineering with Lithium

- Lithium metal dissolves in liquid ammonia and this is used as an expansion solvent for the carbon nanotube spun fiber
- A di-iodide cross-linker reacts with the lithium and covalently bonds to the sidewalls; this chemistry was also pioneered at Rice University
- The highly volatile ammonia solvent is more readily removed than H_2SO_4
- Raman spectra show near elimination of the “roping peak” radial breathing mode at 265 cm^{-1} (10,2) [Doorn 2004] which shows that the SWNTs have now become physically spaced apart from each other and hence have become a nanoengineered object
- This scaffold may be used directly for hydrogen uptake, or as a scaffold for Kubas-type binding
- A precision lithium doping apparatus has been designed and is under construction; this can be used on both oleum expanded and lithium expanded scaffolds

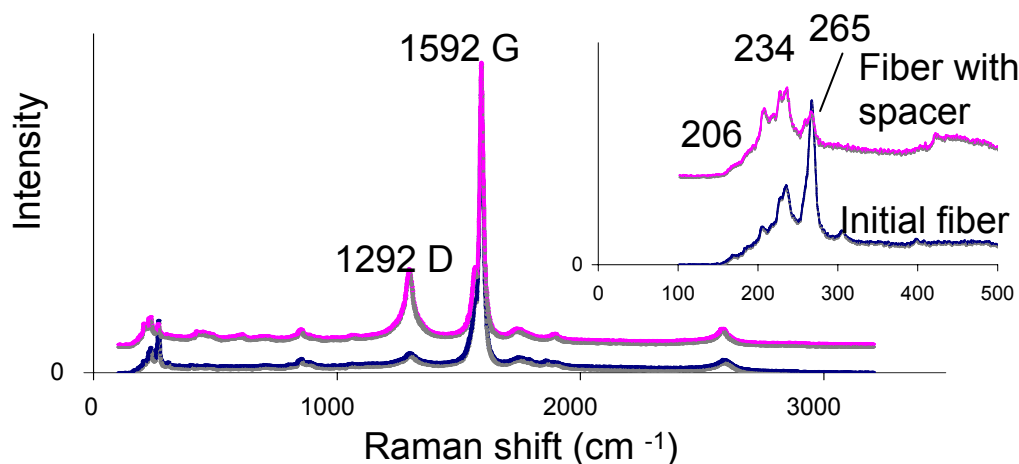
This new method just developed for the 3-D scaffold shows generality of the nanoengineered concept; there is more than one route to construction of the scaffold. Either scaffold is suitable for lithium/transition metal doping for enhanced Kubas-type binding at RT

Accomplishment: New nanoengineered spacer

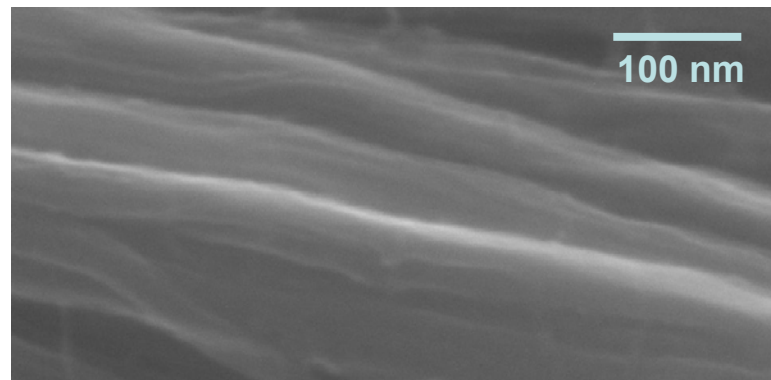


Nanotube fibers are expanded and crosslinked with lithium and terphenyl iodide.

Next Step: Lithium atoms are now being added for Kubas-type binding of hydrogen at ambient temperature



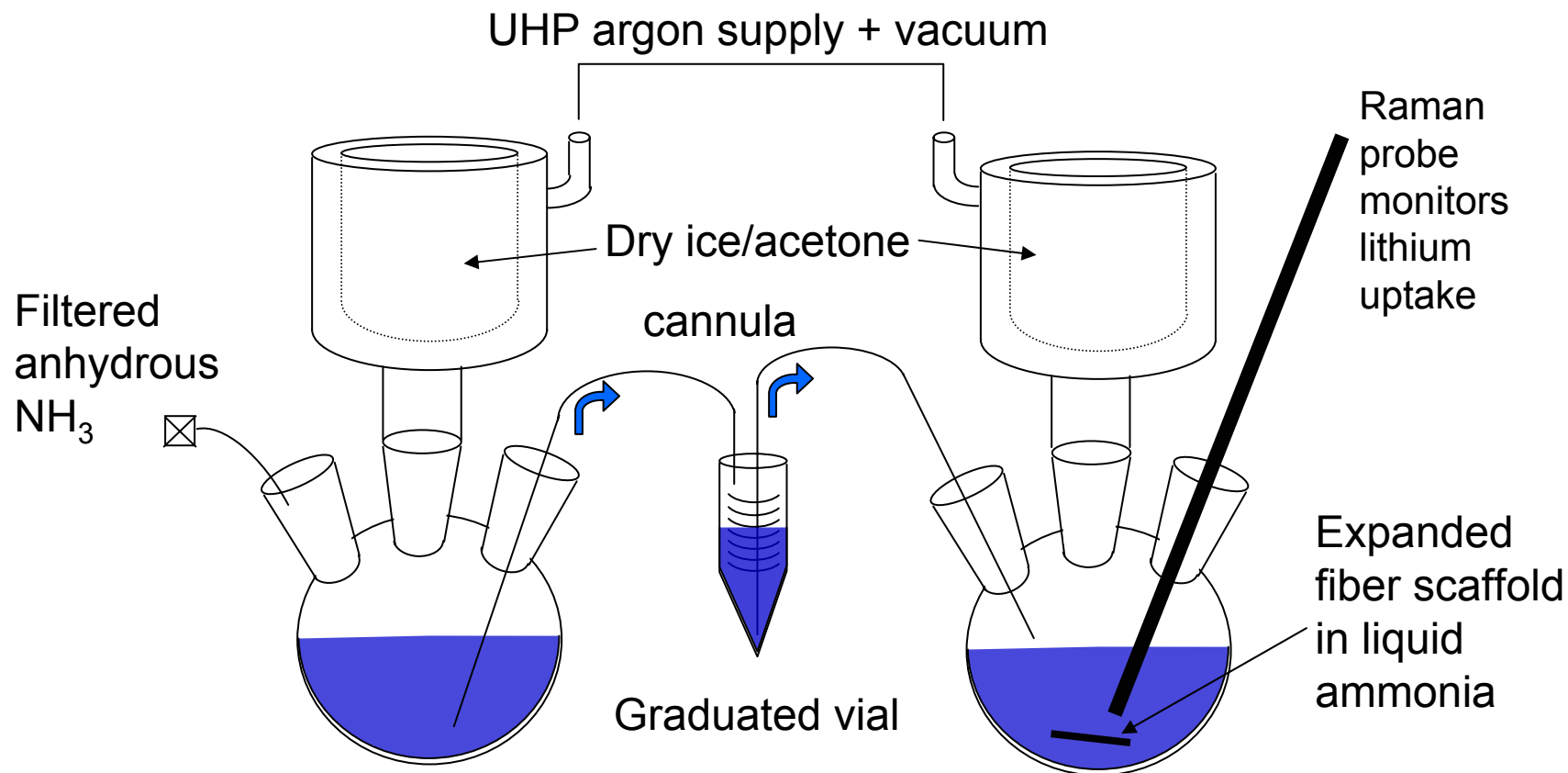
Raman spectra (Ex 780 nm); Enhanced “D” peak proves covalent bonding, loss of “roping” peak at 265 cm⁻¹ proves nanotubes are individually spaced apart.



High Resolution SEM, 200,000x shows excellent alignment of the expanded nanotube fiber

For Kubas-type binding to be optimized, tube-tube spacing must be optimized. The pore size is dependent on the number of phenyl groups in the linker: This number is in turn determined by the molecule on purchase order.

Accomplishment: Lithium intercalation apparatus



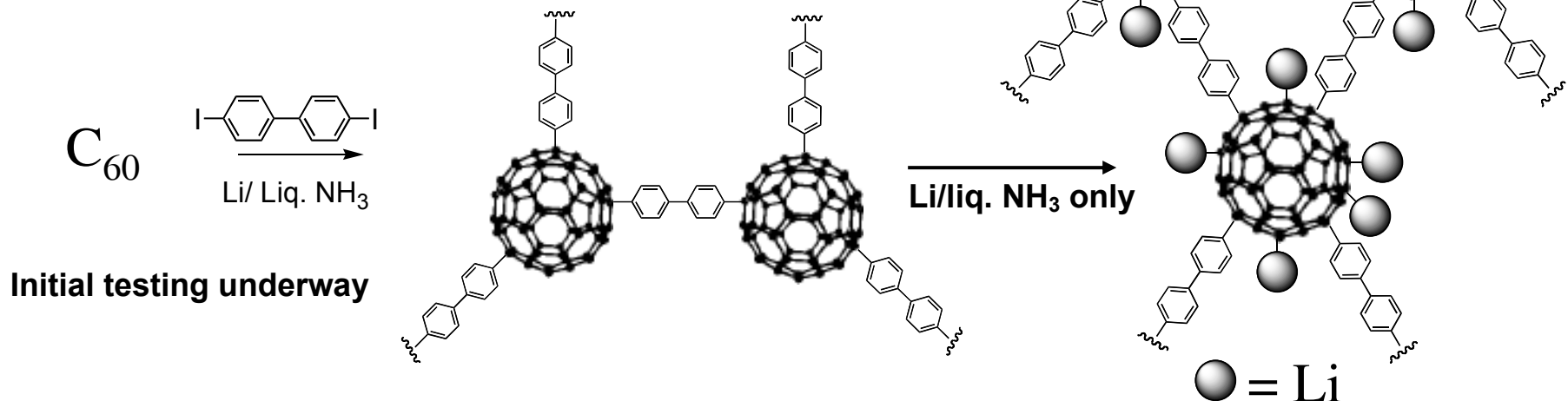
NH_3 is inserted into chilled flask preloaded with Li granule. Li-NH_3 mixture of known concentration is transferred to graduated vial and a measured amount is transferred to chilled flask with nanofiber and Raman probe. Insulation not shown.

A special apparatus is needed to quantitatively add lithium in the liquid ammonia to the 3-D scaffold fiber. This will produce the lithium doping to test Kubas-type H_2 uptake

Accomplishment: A new model system for pore size

Pore size is adjustable by the number of phenyl groups in the cross-linker.

Step 1. Use lithium + biphenyl iodide to link buckyball into a matrix. Suitable for testing the “nanopump” concept and enhanced binding when the nanopore spacing is just right



Step 2. Add lithium atoms dissolved in ammonia. Suitable for testing Kubas-type binding where all substrates are identical (C_{60})

1. A model system to test Kubas-type binding and H_2 uptake in relation to pore size with well-defined molecular size mode cross-linking.
2. Test bed as a prototype self-assembly technique for nanotubes; ease of solvent removal and scalability provides another means to construct the 3-D nanotube scaffold.

Project Summary

Technical Accomplishments and Progress

- Created 3-D nanoengineered scaffold for direct hydrogen uptake and as a scaffold for metals used for Kubas-type binding
- Developed expansion method for spun fiber & cross-linking method to convert single wall carbon nanotubes into a nanoengineered scaffold; new no-dry spinning process under development for continuous production
- Tested methods for using different cross-links to control pore size, with expansion ranging from 30% to 45%; up to 9 Angstrom pore spacing
- Discovered our nanotube scaffold exhibits 2x steeper slope for H₂ uptake than predicted by Chahine-Heben rule (at U. Quebec, Trois-Rivieres & NREL) which extrapolates to 6.5wt% uptake (does not including internal tube pores)
- Calculated from theory & thermodynamic model an uptake for sp² pores of 6.5wt% and 55 g/L; similar to extrapolation of our experimental uptake
- Discovered and understood problems with solvent extraction associated with oleum expansion solvent
- Developed new lithium/ammonia based expansion and cross-linking as an alternative to bypass the difficulties of oleum solvent extraction
- Designed lithium intercalation apparatus to start Kubas-type binding tests

Future Work – FY2007

- Fully develop the sp^2 3D nanoengineered carbon nanotube fibrous pore material & determine the relations between the pore size, expansion methodology and size of cross-linking compound
- Develop alternate solvent extraction and spinning methods, and self-assembly, to greatly reduce problem of residual solvent
- Determine the nature of the nanopump mechanism for high density pore storage by supercritical uptake of hydrogen, and obtain experimental support for the theoretical model
- Continue testing of hydrogen uptake measurements to determine if the 2x steeper slope for Chahine's rule [Chahine 2001] remains linear up to 1000 m^2/g and 4wt%. Determine if this is consistent with theory
- Continue development alternative expansion and cross-linking methods using lithium/ammonia expansion and varied polyphenyl cross-linkers; Test for hydrogen uptake
- Complete lithium doping apparatus and began Kubas-type binding experiments with lithium-doped nanotube scaffold, & test for H_2 uptake

Future work - FY2008

- Re-engineer the 3D scaffold with enlarged pores for generalized Kubas binding of lithium and transition metals; use the rigid frame for testing high cycle reproducibility >90%, fast kinetics, and energy efficiency.
- Determine if the 2x steeper slope Chahine's rule for sp^2 nanoengineered pores continues as we approach 6wt% & if the experimental results support the "nanopump" concept.
- Scale sample size and production sufficient for full range of pressure and temperature hydrogen uptake testing, and binding energy determination with our HSCoE partners
- Test and optimize pore size for lithium doping and hydrogen uptake at room temperature.
- Develop transition metal binding to the nanotube scaffold for Kubas-type binding on titanium and scandium, compare to theory.
- Develop sidewall perforation techniques compatible with our nanoengineered fiber to make the inside of the nanotubes accessible to metal doping and increased hydrogen uptake.

Summary Table

<u>On-Board Hydrogen Storage System Targets</u> (**Data is based on material only, not system value)					
Storage Parameter	Units	2010 System Target	FY05 materials**	FY06 Result materials**	FY07 Result nanoengineered fiber**
Specific Energy	kWh/kg (wt. % H ₂)	2.0 (6 wt.%)	0.43 1.3 wt%	0.97 2.9 wt%	0.67 2.0wt%
Volumetric Energy Capacity)	kWh/L	1.5	0.43	0.97	Density = 1 0.67
Desorption Temperature			>77K	>77K	>77K
Plateau Pressure			Measured at 2 bar	Fit to 30 bar	Measured at 2 bar

The FY06 Result is from heavily oxidized SWNT material which predates the new nanoengineering effort, and the isotherm measured at two bar was extrapolated to 30 bar.

The FY07 is the uptake as measured at 2 bar.

References

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