Designing Microporous Carbons for Hydrogen Storage Systems

carried out in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

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Air Products and Chemicals, Inc.

2005 DOE HFCIT Annual Program Review

STP-43

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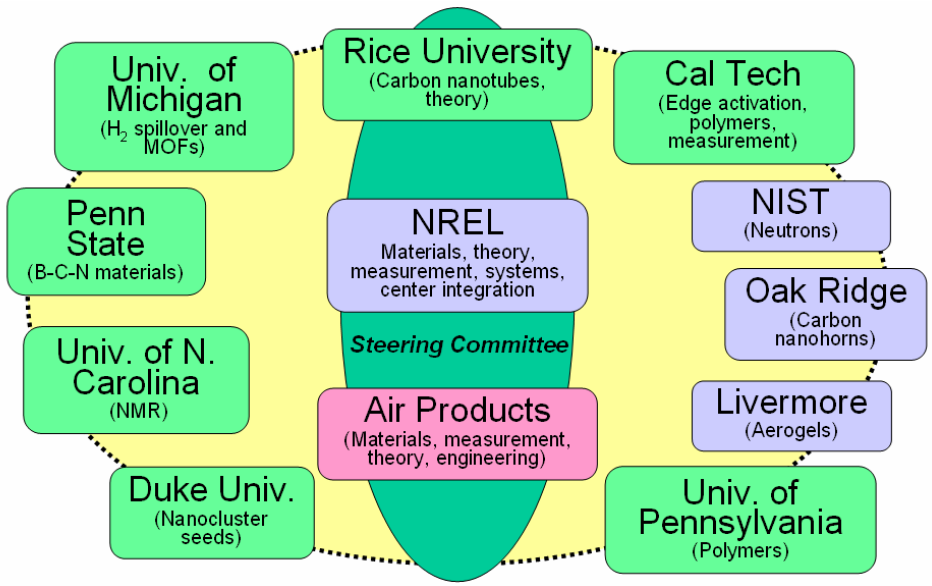
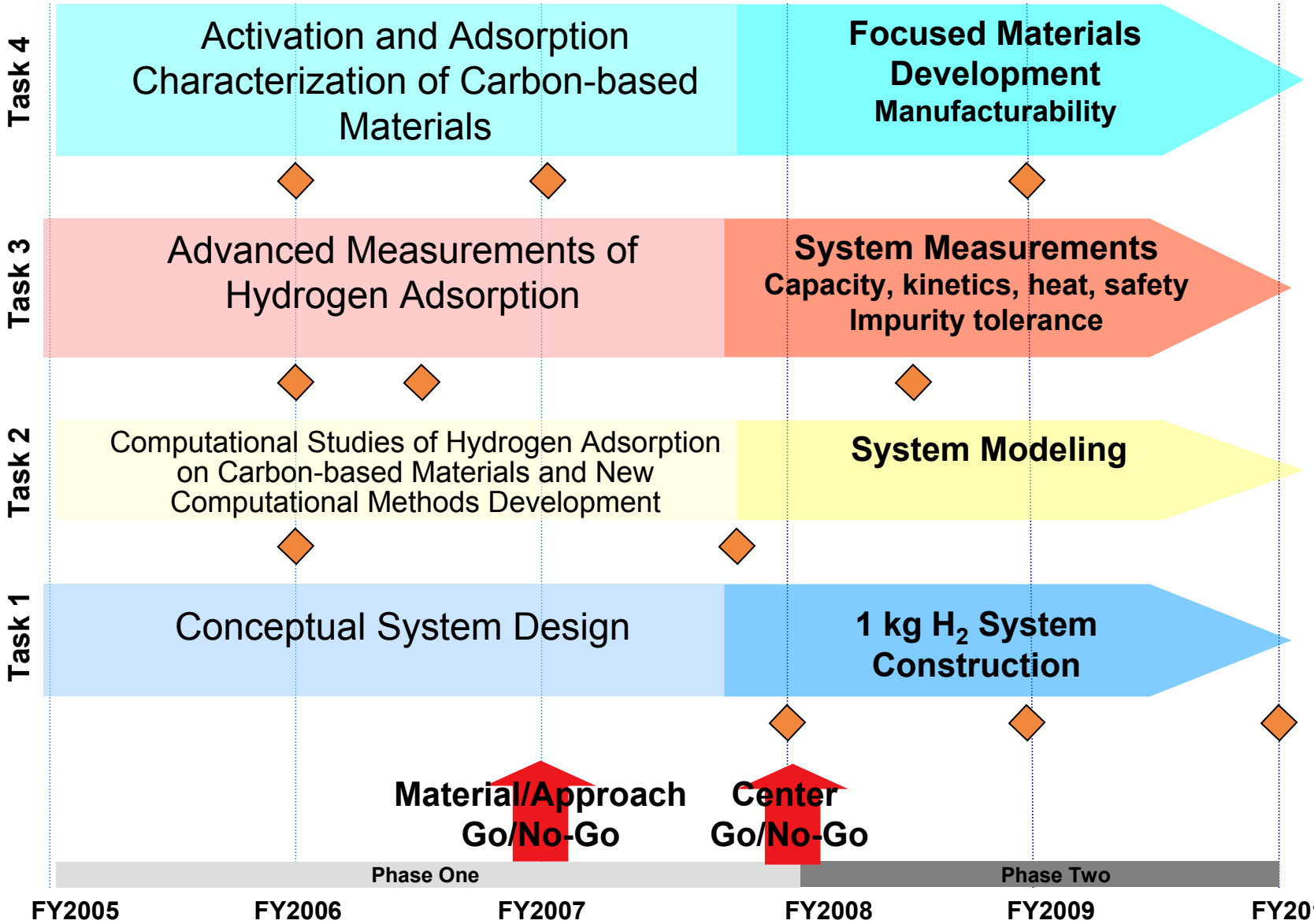
AIR PRODUCTS

Air Products and Chemicals – Participation in DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

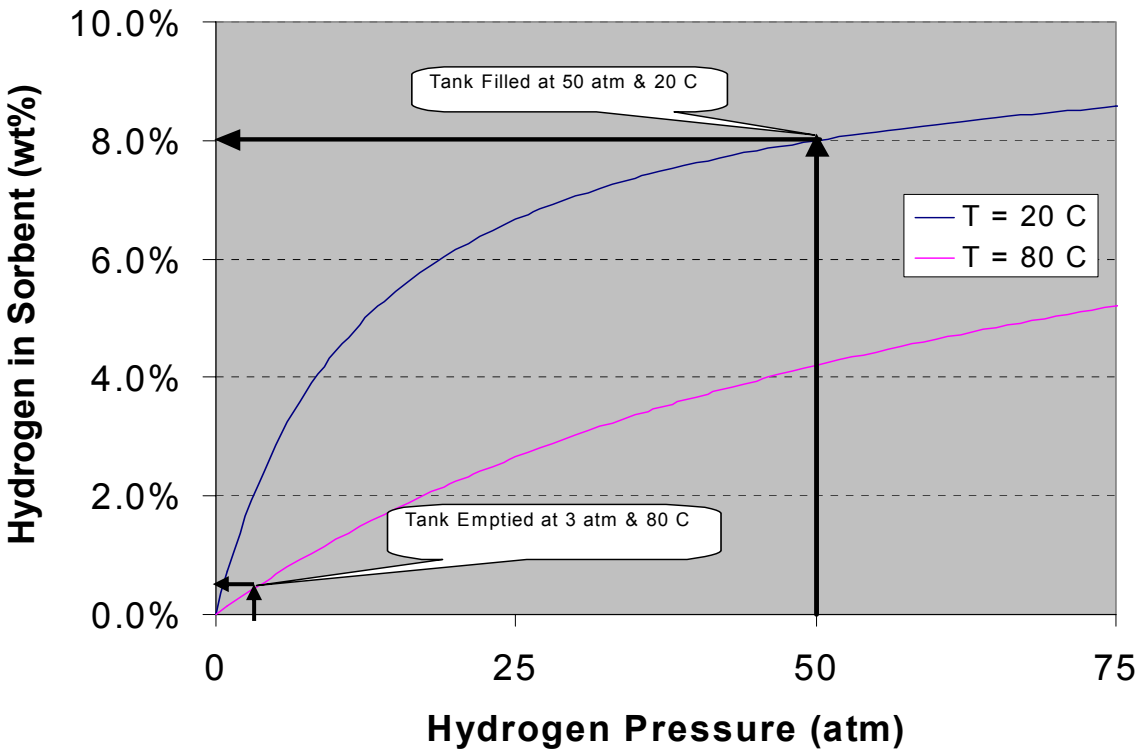
- **Conceptual System Design**
  - **System engineering guidance, heat integration**
- **Computational Studies of Hydrogen Adsorption on Carbon-based Materials and New Computational Methods Development**
  - **Develop accurate and efficient computational methodologies, to be shared with other partners**
  - **Mechanistic studies of hydrogen adsorption**
- **Advanced Measurements of Hydrogen Adsorption**
  - **Exploration of a novel low-cost, high-throughput technique**
  - **Measurement assistance for other center partners and confirmation of important adsorption results from other partners**
- **Activation and Adsorption Characterization of Carbon-based Materials**
  - **Novel approaches to carbon-based adsorbents in collaboration with other partners**



Carbon-based Hydrogen Storage Center: Work Plan and Timeline



Conceptual System Design: System Engineering Model of Adsorption



- **Langmuir isotherm model assumes a ΔH of -25 kJ/mol and ΔS of -105 J/mol·K**
- **The "tank" can deliver 7.56 wt. % H_2 under these modeling conditions**

Gravimetric hydrogen capacity is linked to the heat (ΔH) and the entropy (ΔS) of H_2 sorption, which determine the strength and extent of equilibrium binding to the sorbent, and to the volumetric space per unit mass of sorbent that is accessible to hydrogen capture. The sorbent (S) and H_2 equilibrium is expressed as:

$$S(s) + H_2(g) \underset{}{\overset{K}{\rightleftharpoons}} S \bullet H_2(s) \text{ where } K = [S \bullet H_2] / [S] P_{H_2} \qquad (atm^{-1})$$

AIR PRODUCTS

New Computational Methods: Results and Future Development

- **Results: Curvature dependent force field – tested and available to CoE partners**

The calculated optimal distribution of H_2 and the average adsorption energy (kcal/mol) per H_2
The uncertainty of the averaged adsorption energy is approximately ±0.5 kcal/mol

nanotube (n,m)	SWNT diameter (Å)	0.4 wt. % H_2 loading		3.0 wt. % H_2 loading		6.5 wt. % H_2 loading	
		endo/exo ratio	ΔE_{ad} (kcal/mole)	endo/exo ratio	ΔE_{ad} (kcal/mole)	endo/exo ratio	ΔE_{ad} (kcal/mole)
(3,3)	4.068	0:100	5.7	0:100	4.9	0:100	3.7
(5,5)	6.780	0:100	5.1	20:80	2.4	30:70	1.7
(9,9)	12.204	0:100	3.8	40:60	1.4	50:50	1.1
(5,0)	3.914	0:100	5.3	0:100	5.1	0:100	2.8
(10,0)	7.828	0:100	4.8	20:80	2.1	30:70	0.9
(15,0)	11.743	0:100	3.3	30:70	1.1	50:50	0.6
(8,4)	8.285	0:100	4.3	20:80	1.9	30:70	0.6

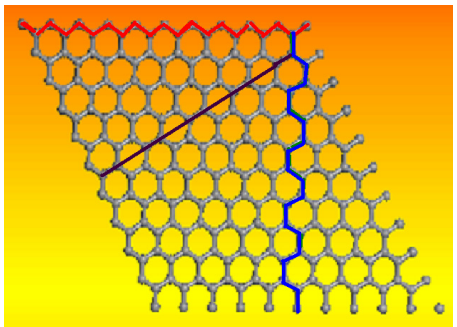
H. Cheng, A.C. Cooper, G.P. Pez, M.K. Kostov, P. Piotrowski, S.J. Stuart *J. Phys. Chem. B* 109, 3780 (2005)

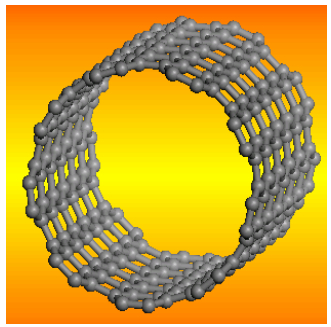
- **Results: Constant NPT molecular dynamics: implemented in the AIREBO simulation package**
- **Future methodology development:**
  - **Reliable & transferable force field development**
  - **Grand Canonical Monte Carlo (GCMC) simulations: under development in AIREBO**
  - **Density functional theory with correct dispersion forces: to be implemented in SIESTA**

AIR PRODUCTS

New Computational Methods Development: Curvature-Dependent Force Field

- *Bonding Interaction*: Brenner's bond order potential for C-C, H-H
- *Nonbonding Interactions*: must be curvature dependent





(9,9) d = 12.2Å

(2,2) d = 2.7Å

H. Cheng, A.C. Cooper, G.P. Pez *Nano. Lett.* **3**, 585 (2003)

$$\sigma(r) = f(r)\ \sigma_{sp^2} + [1 - f(r)]\ \sigma_{sp^3}$$

$$\varepsilon_{exo}(r) = f(r)\ \varepsilon_{sp^2} + [1 - f(r)]\ \varepsilon_{sp^3}^{head\text{-}on}$$

$$\varepsilon_{endo}(r) = f(r)\ \varepsilon_{sp^2} - [1 - f(r)]\ \varepsilon_{sp^3}^{side\text{-}on}$$

$$f(r) = \left(1 - \frac{r_o}{r}\right)^{\lambda} \qquad 0 < f(r) < 1$$

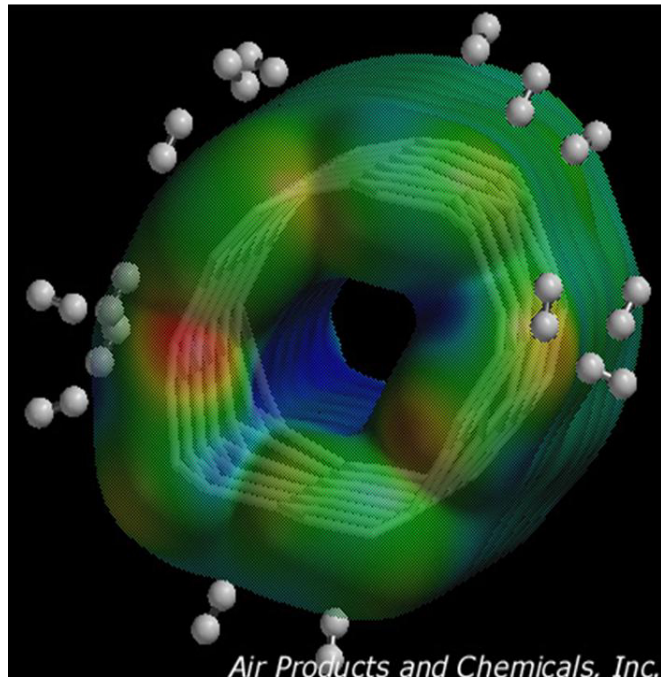
M. K. Kostov, H. Cheng, A. C. Cooper, G. P. Pez *Phys. Rev. Lett.* **89**, 6105 (2002)

AIR PRODUCTS

Computational Studies of Hydrogen Adsorption on Carbon-based Materials

- **H_2 adsorption in carbon nanomaterials (nanotubes, nanohorns, nanofibers, etc.)**
  - **Objectives: study storage capacity at given pressure and temperature and identify material properties key to adsorption**
  - **Methods: NPT-MD, GCMC**
  - **Potential collaborators: Rice University, NREL**

- **H spillover onto carbon nanomaterials (nanofibers, nanotubes, etc.)**
  - **Objectives: evaluate energetics for H spillover, identify chemisorption pattern, kinetics**
  - **Methods: Monte Carlo, DFT, MD**
  - **Potential collaborators: Rice University U. of Michigan, NREL**

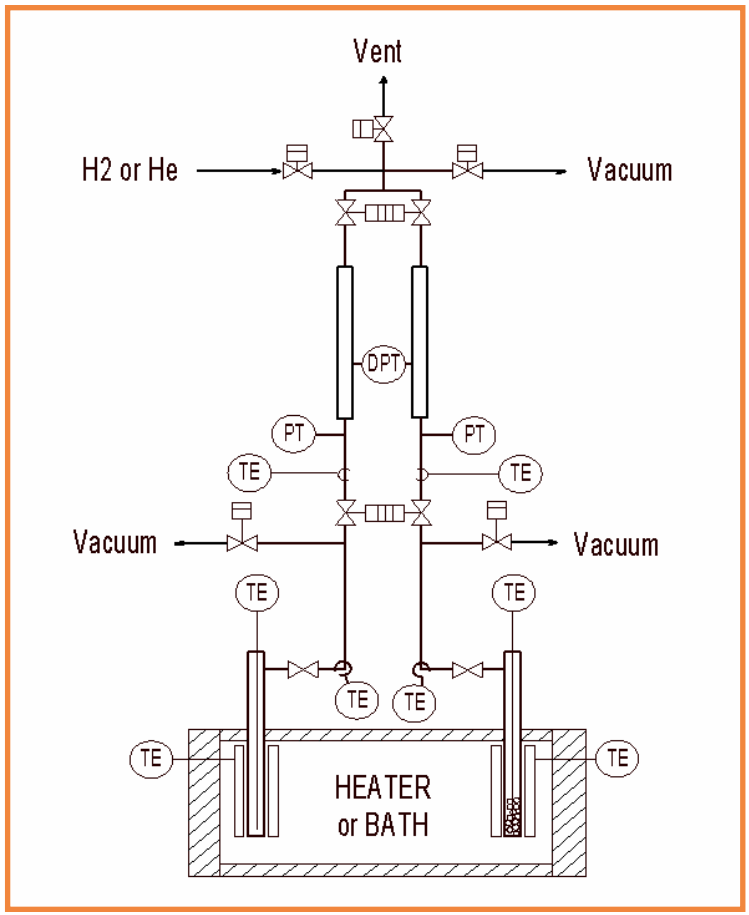


Electrostatic potential mapped to the electron density of a deformed (5,5) singlewalled carbon nanotube

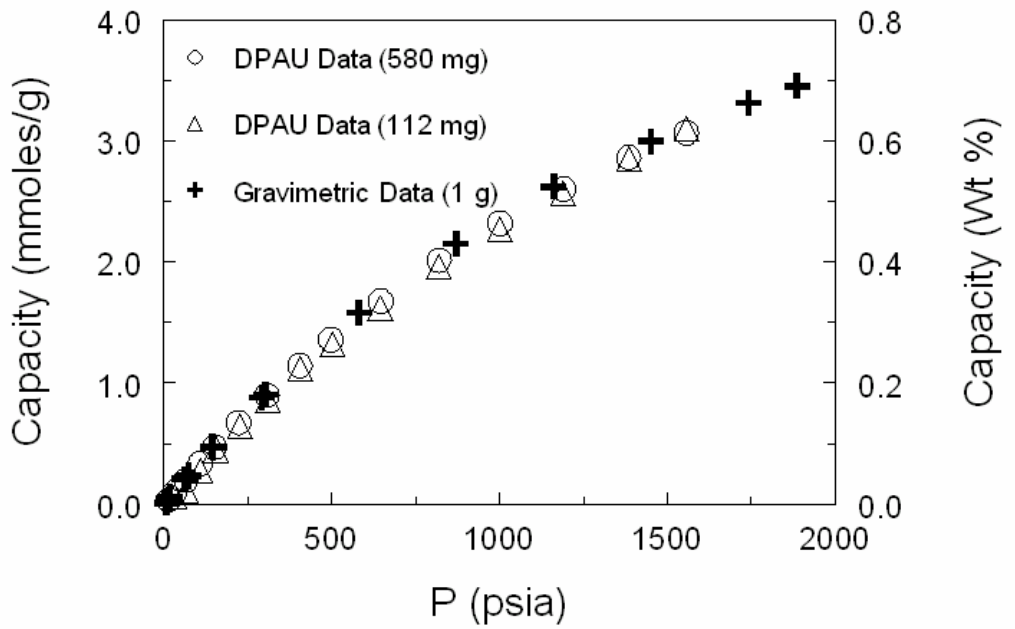
AIR PRODUCTS

Advanced Measurements of Hydrogen Adsorption: Differential Pressure Adsorption

Differential Pressure Adsorption Unit (DPAU)

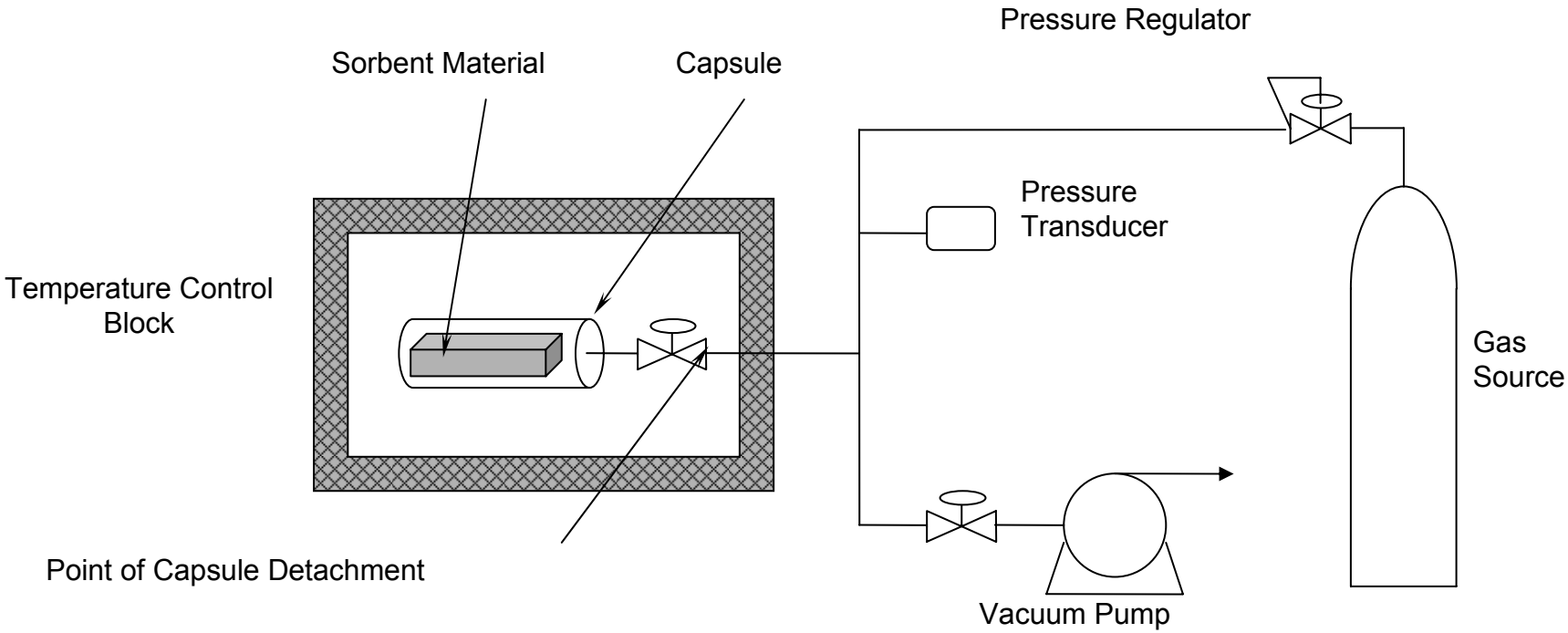


H_2 Sorption on Activated Carbon (25°C)



- **Differential pressure measurement more accurate than standard (absolute pressure) volumetric adsorption**
- **Equally accurate at low and high pressures (up to 120 bar)**
- **High temperature helium pycnometry will enable accurate hydrogen isotherms (unit under construction)**

Advanced Measurements of Hydrogen Adsorption: Exploration of a Novel Low-cost, High-throughput Sorption Measurement Technique



- Direct method that measures the total amount of hydrogen (sorbed + gaseous) stored in a pressurized vessel containing a sorbent
- Measurements can be performed at ambient to high temperatures and high hydrogen pressures
- Inexpensive technique (requires an accurate analytical balance)
- Potential for high throughput screening

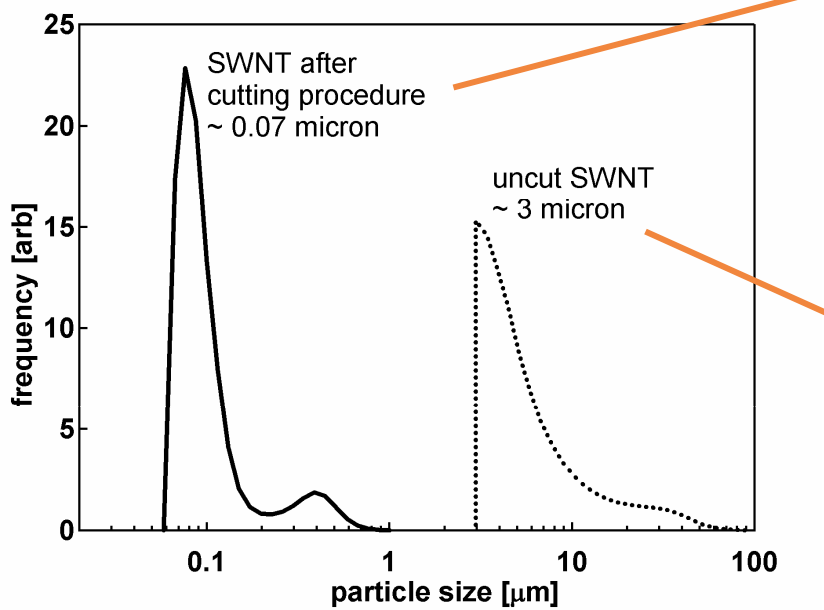
AIR PRODUCTS

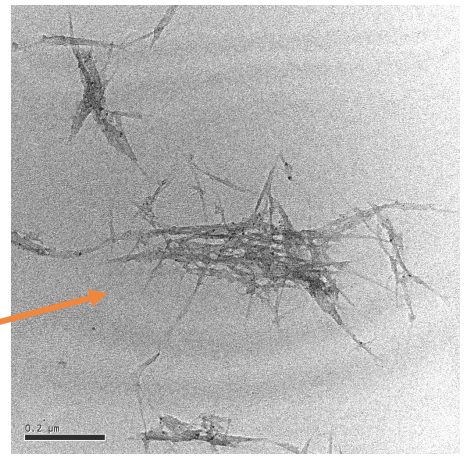
Activation and Adsorption Characterization of Carbon-based Materials: Potential Collaborations

- Hydrogen adsorption on small diameter singlewalled carbon nanotubes
  - Potential collaborations: Rice University, Duke University, NREL
- Boron and nitrogen incorporation into carbon nanostructures
  - Potential collaboration: Penn State University
- Doping of carbon nanotubes
  - Enhancing heat of adsorption of hydrogen as indicated by predictive computational modeling
  - Potential collaboration: California Institute of Technology

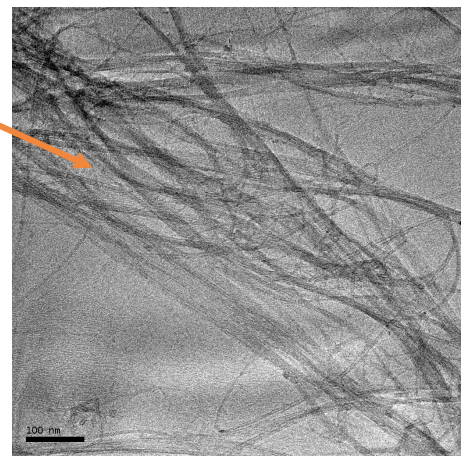
Activation and Adsorption Characterization of Carbon-based Materials: "Tailoring" Singlewalled Carbon Nanotubes for Hydrogen Storage

Laser light scattering profile of SWNT samples before (dotted line) and after (solid line) a non-destructive cutting procedure





Transmission Electron Microscopy



Overview

Timeline

- Project start date FY05
- Project end date FY09
- New start

Budget

- Total project $3,539,750
  - DOE share $2,842,540 (80%)
- FY05 funding $300,000

Barriers

- Technical Barriers- Hydrogen Storage
  - A. Cost
  - B. Weight and Volume
  - C. Efficiency
  - E. Refueling time
  - M. Hydrogen Capacity and Reversibility
  - N. Lack of Understanding
  - O. Test Protocols
  - Q. Thermal Management

Partners

- Current interactions: NREL
- Anticipated collaborations: Rice University, Duke University, University of Michigan