Overview of DOE Carbon-based Hydrogen Storage Materials Center of Excellence

2005 DOE Hydrogen Program Review

May 25, 2005

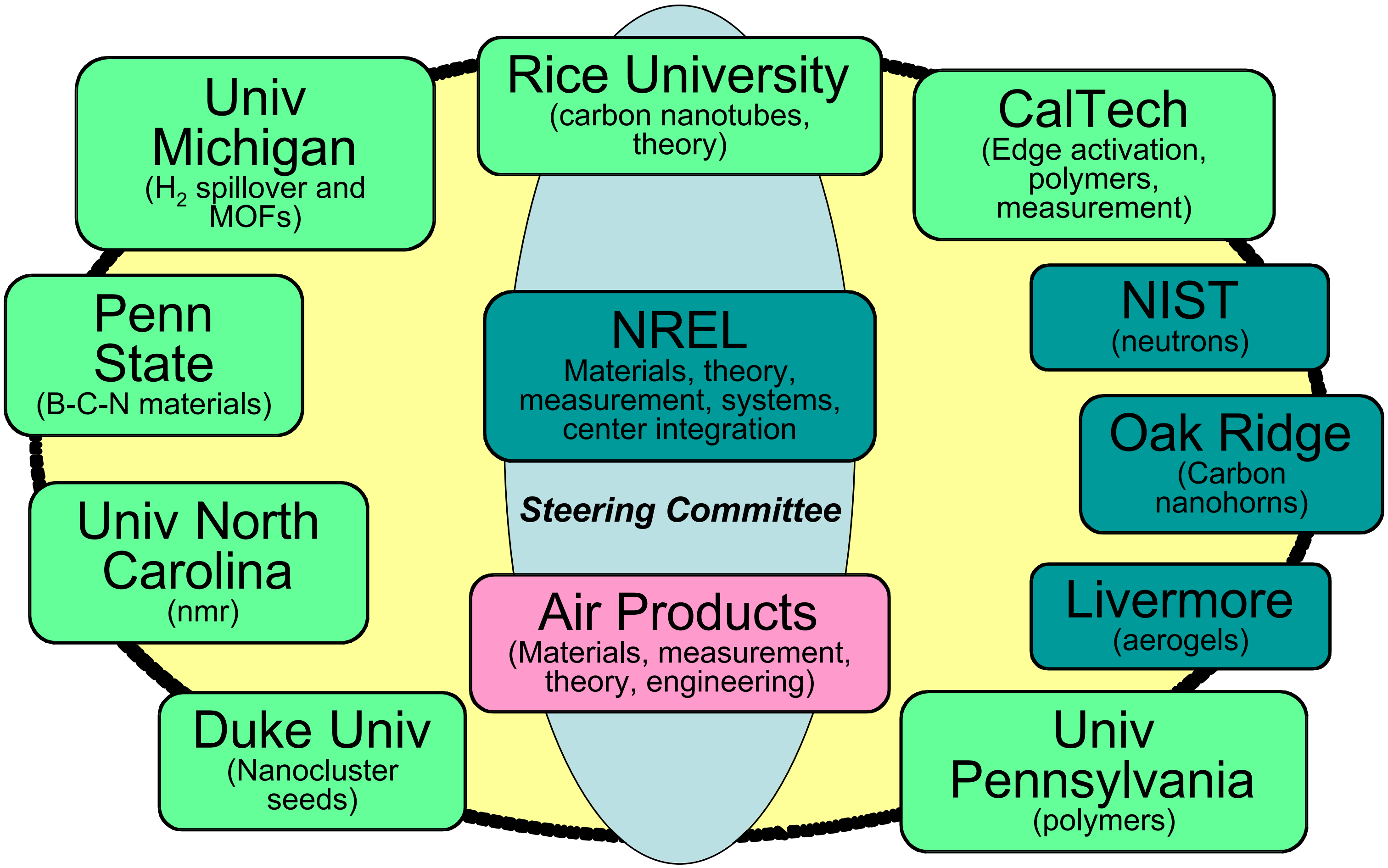
This presentation contains no proprietary information

STP 30

CbHS Center of Excellence Partners

9 university projects (at 7 universities), 4 government labs, 1 industrial partner

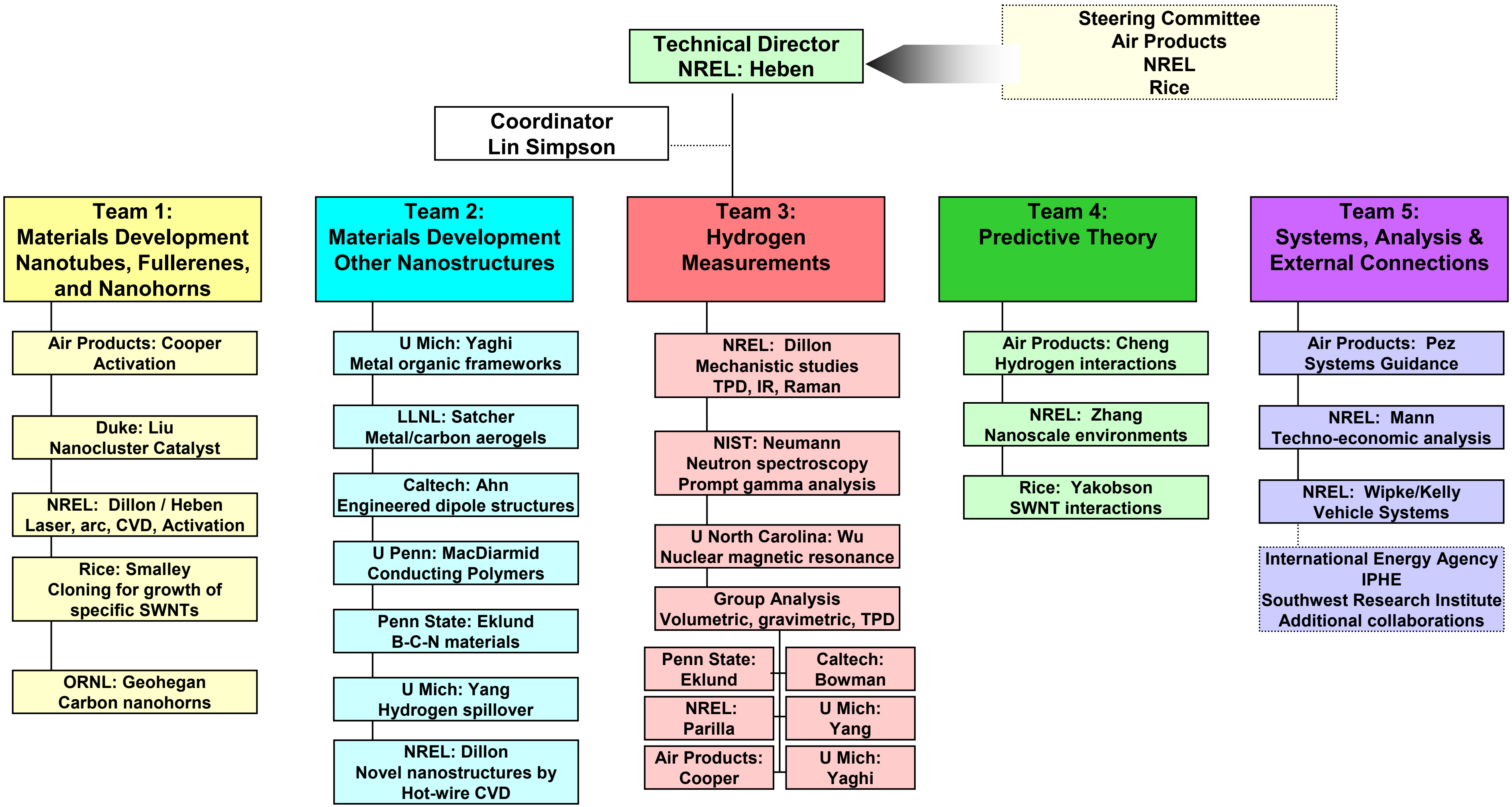
http://www.nrel.gov/basic_sciences/carbon_based_hydrogen_center.html



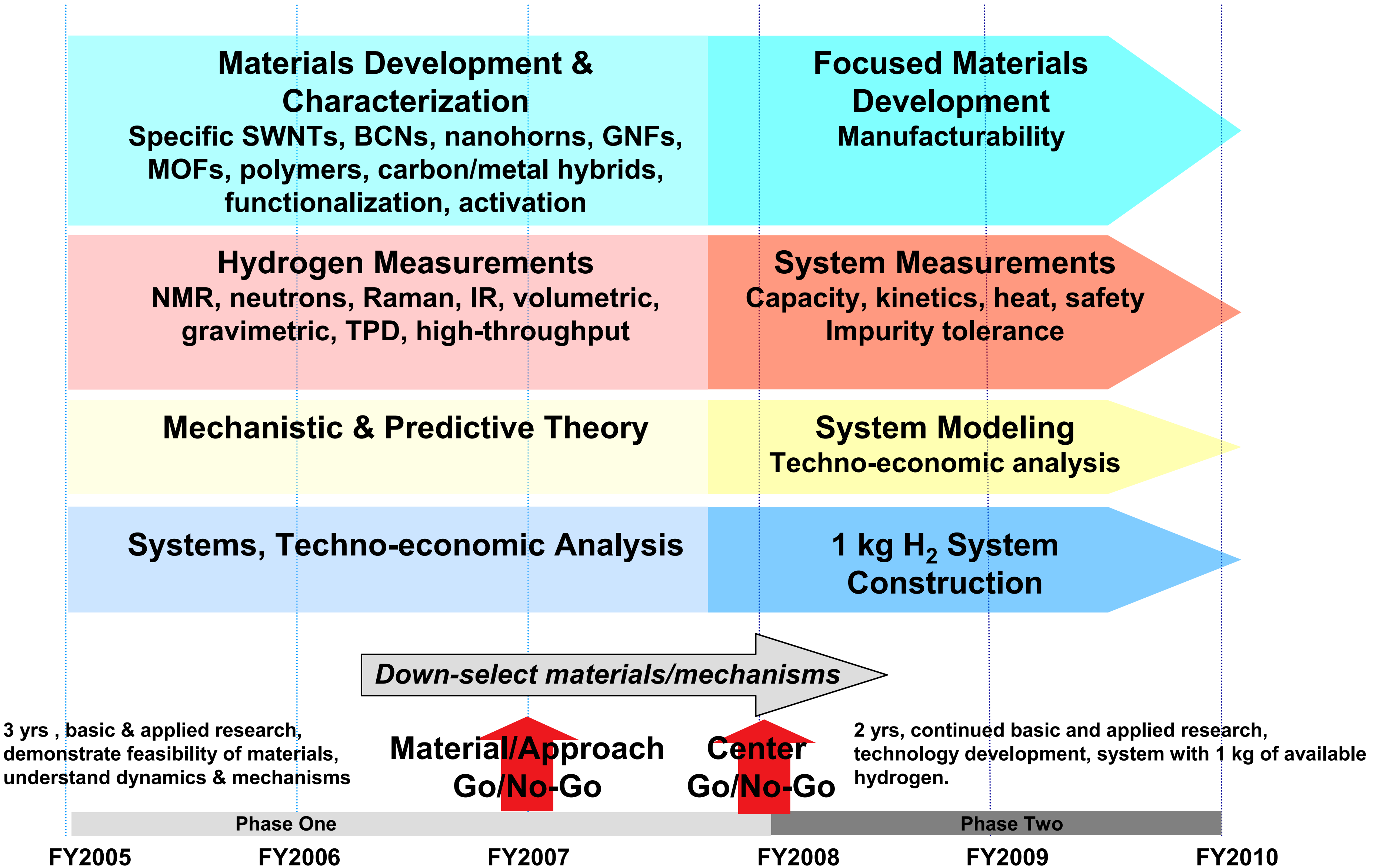
Themes of CbHS Center of Excellence

- Develop conducting and boron/carbon polymers, MOFs, carbon nanohorns, nanotubes and aerogels, and carbon-metal nanomaterials for on-vehicle storage
- Design and synthesize materials that bind hydrogen as either (i) weakly and reversibly bound atoms or (ii) as strongly bound molecules.
- Synthesize, test, develop light materials with high densities of appropriate binding sites per volume to meet DOE goals
- New concepts (e.g. conformal tanks with low T moderate P (<100 bar) operation, nanotube/hydride mixtures)

Center Organization



Work Plan and Timeline



Designing Microporous Carbons for Hydrogen Storage Systems

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

Alan C. Cooper, Hansong Cheng, and Guido P. Pez

Air Products and Chemicals, Inc.

2005 DOE HFCIT Annual Program Review

STP-43

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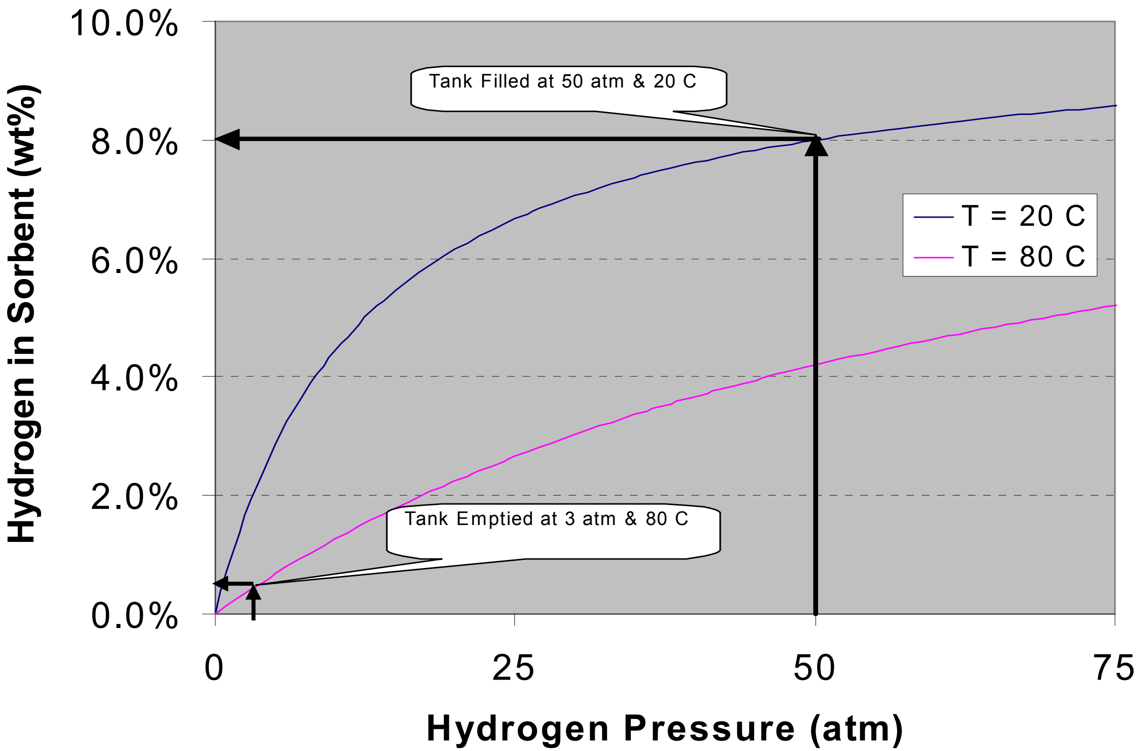
AIR PRODUCTS

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**

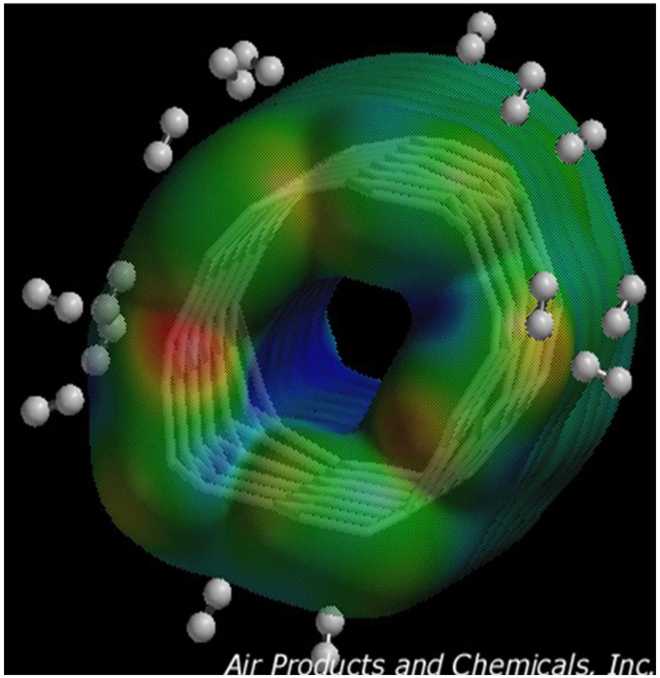
Gravimetric hydrogen capacity is linked to the heat (ΔH) and the entropy (ΔS) of H_2 sorption, which determine the strength and extent of equilibrium binding to the sorbent, and to the volumetric space per unit mass of sorbent that is accessible to hydrogen capture. The sorbent (S) and H_2 equilibrium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

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

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

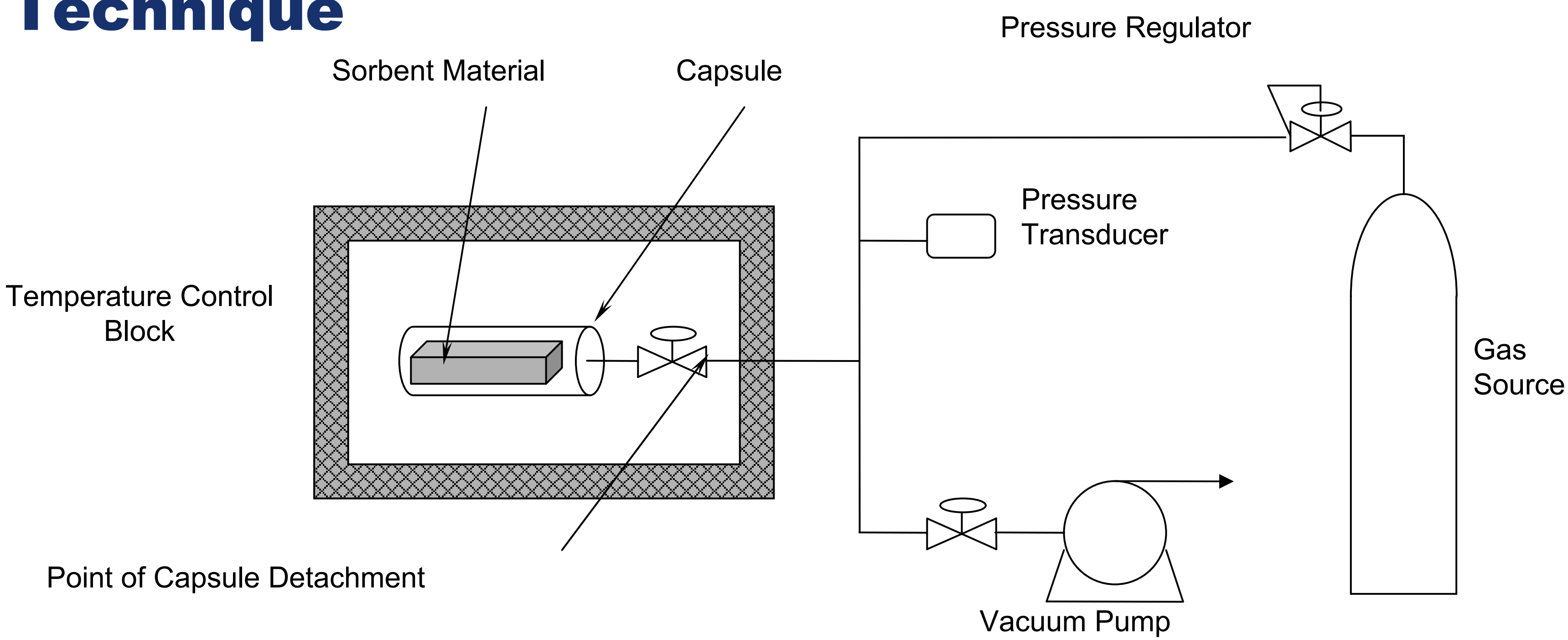
- H spillover onto carbon nanomaterials (nanofibers, nanotubes, etc.)
  - Objectives: evaluate energetics for H spillover, identify chemisorption pattern, kinetics
  - Methods: Monte Carlo, DFT, MD
  - Potential collaborators: Rice University U. of Michigan, NREL



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

AIR PRODUCTS

Advanced Measurements of Hydrogen Adsorption: 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

CLONING SINGLE WALL CARBON NANOTUBES FOR HYDROGEN STORAGE

Richard E. Smalley
Carbon Nanotechnology Laboratory
Rice University

A Participant in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

May 23, 2005

DOE 2005 Hydrogen Program Annual Review
Washingtion, D.C., May 23, 2005

Project ID #

General Objectives:

Develop methods for producing type-selected SWNT

Produce particular SWNT types for hydrogen storage evaluation

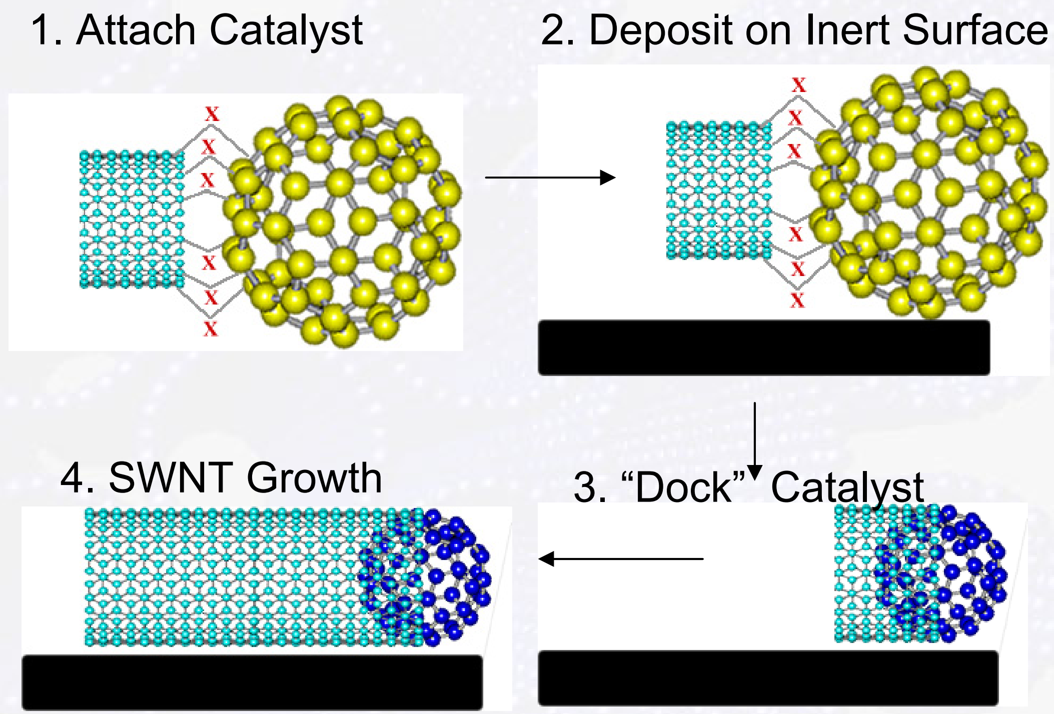
Scale production technology & deliver optimized SWNT material for prototype hydrogen storage system development

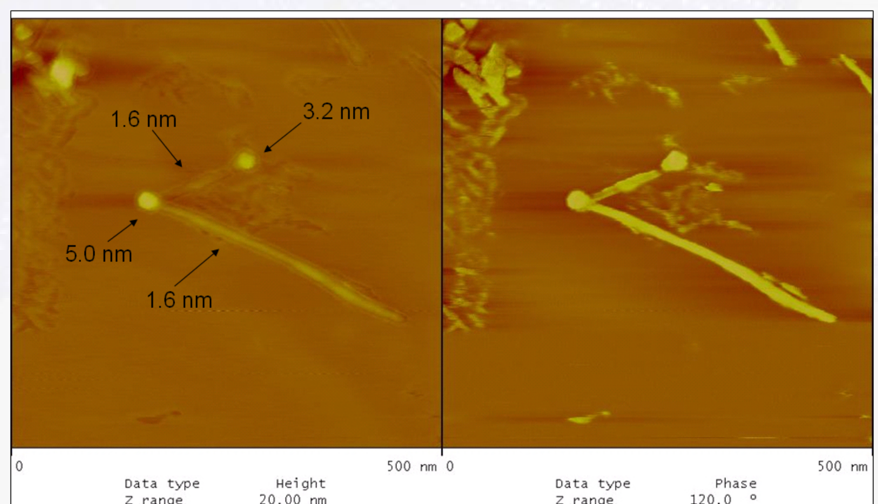
SWNT Seeded Growth

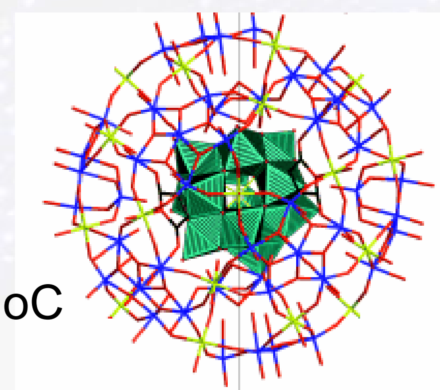
Current Results

Key Starting Materials
- Have FeMoC Catalyst
- Have Short SWNT Seeds
- Have Soluble SWNT

Key Process Steps
- In-Solution Attachment
- Controlled Deposition
- Catalyst Docking
- Reductive Etching
- Limited Growth
- *Luxuriant Growth is Next !!*







FeMoC

Controlling the Diameter of Single Walled Carbon Nanotubes for Hydrogen Storage

-Carried in the “DOE Center pf Excellence on Carbon-Based Hydrogen Storage Materials”

Lei An and Jie Liu

Duke University

05/23/2005

Project ID # STP35

This presentation does not contain any proprietary or confidential information

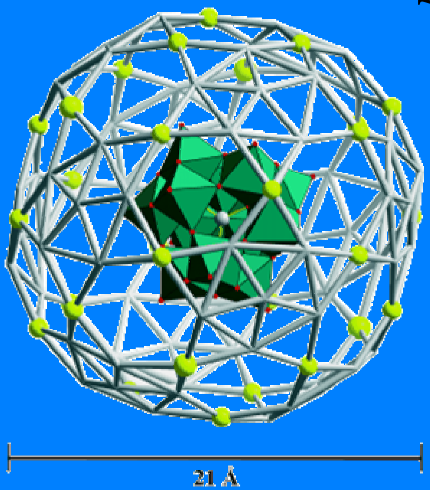
Approach 1: Using Molecular Cluster as Catalysts to Control the Diameters of SWNTs

Motivation:

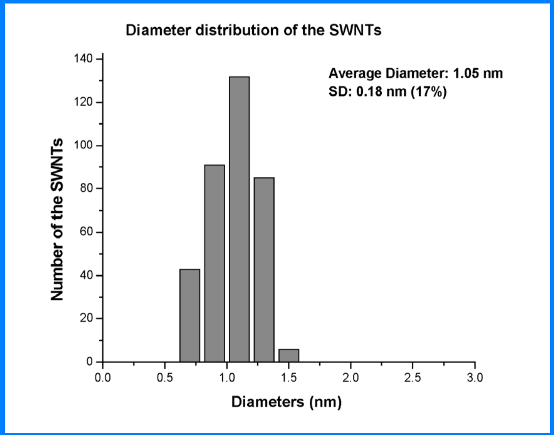
- The diameter of single walled carbon nanotubes is controlled by the size of catalyst nanoparticle during the initiation stage of the growth. If the diameter of the catalysts can be controlled, the diameter of the nanotubes can be controlled.
- Molecular clusters are molecules with identical number of metal atoms in each cluster, making them perfect catalysts for the growth of uniform nanotubes.
- The growth of uniform nanotubes were demonstrated before by our group using one type of clusters (Figures on the right).

Things to Do:

- Making smaller nanotubes using smaller cluster molecules (Next Page)
- Developing method to produce gram quantity of uniform nanotubes.



$[H_xPMo_{12}O_{40} \subset H_4Mo_{72}^{VI}Fe_{30}^{III}(CH_3COO)_{15}O_{254}(H_2O)_{98}].60H_2O$



L. An, J. M. Owens, L. E. McNeil, and J. Liu, *JACS*, **124**, 13688-13689, (2002).

Optimization of SWNT Production and Theoretical Models of H_2-SWNT Systems For Hydrogen Storage

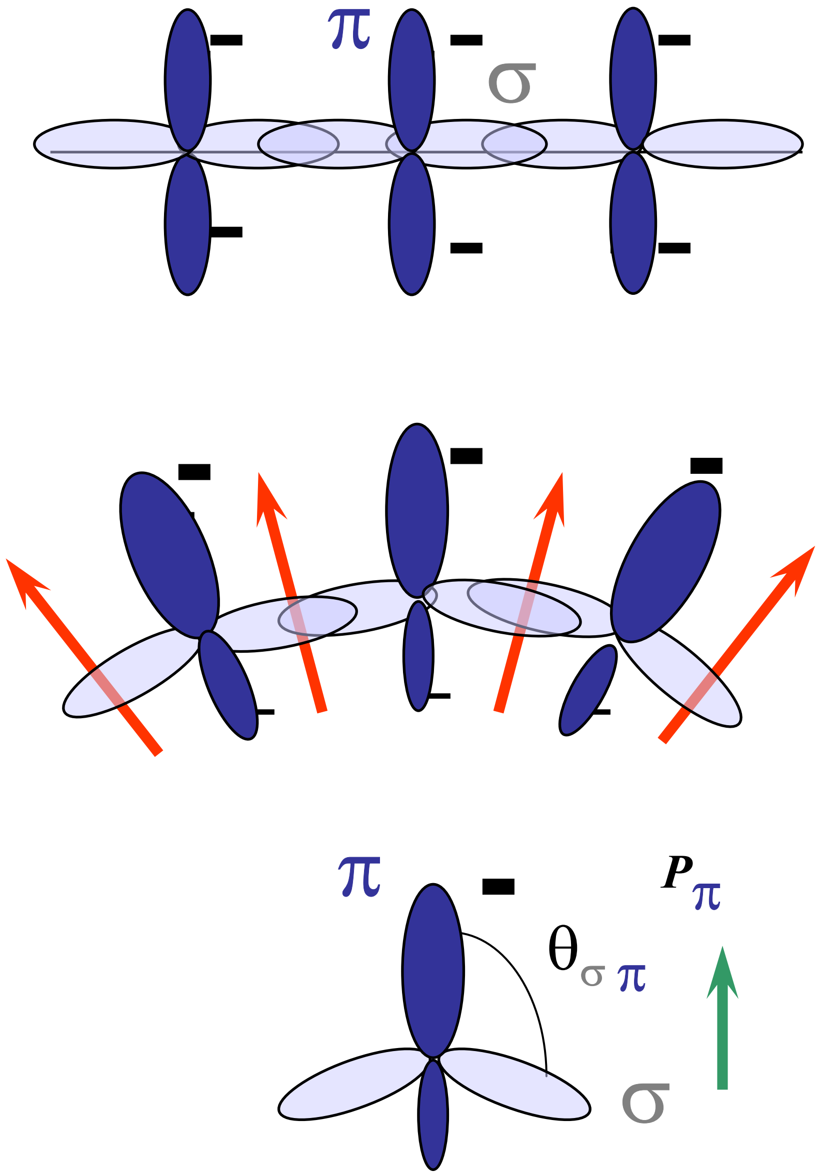
Carried out in the DOE Center of Excellence on Carbon-based Hydrogen Storage

Boris Yakobson and Robert Hauge

Rice University

May 25, 2005

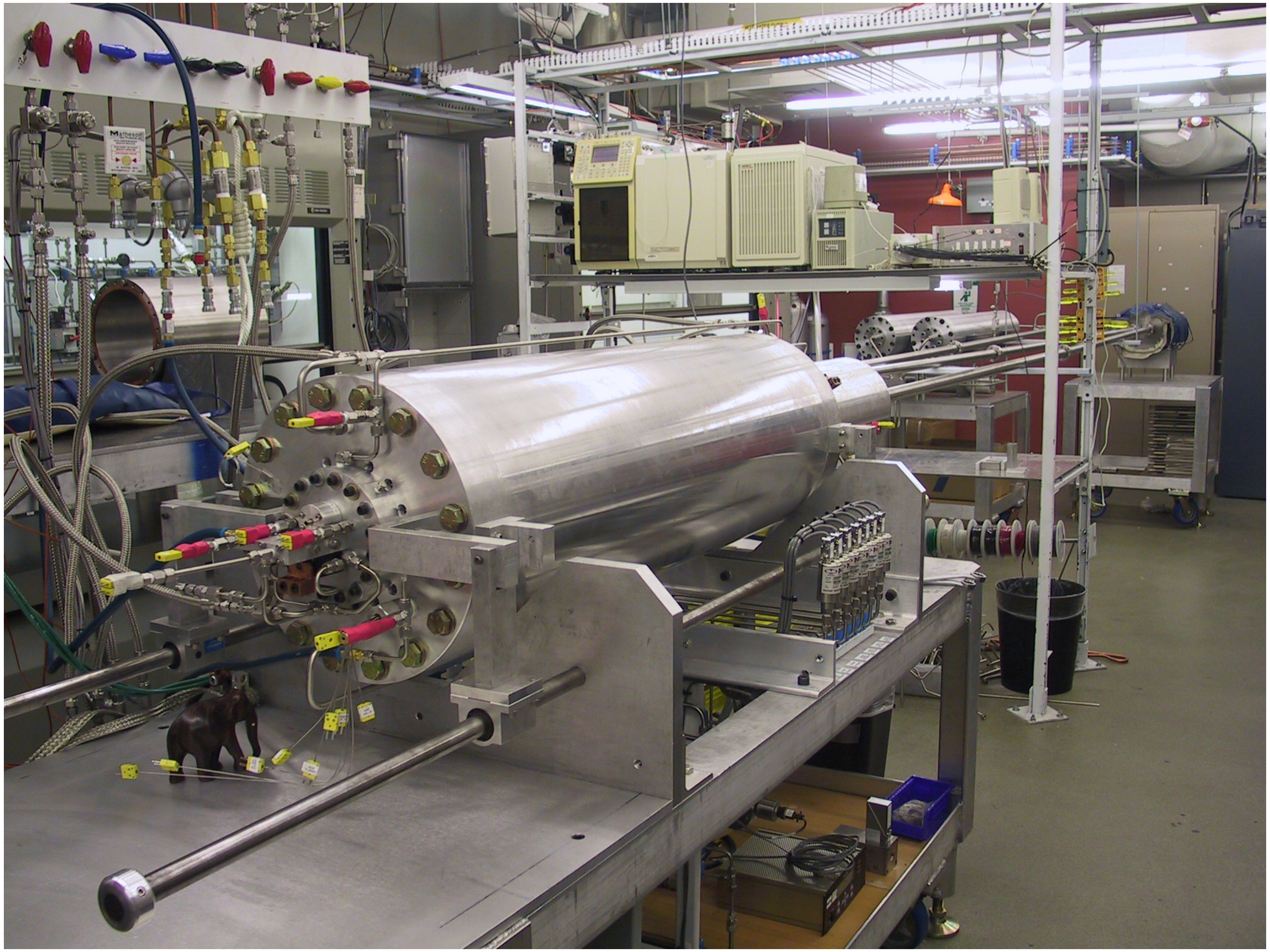
Project ID #STP38



Will further explore curvature-induced polarization and evaluate local field and their ability to change the energy of physisorption

Preliminary/past work
Yakobson *et al.*,
Chem Phys Lett v **360**, p 182

HiPco Reactor



Enhanced Hydrogen Dipole Physisorption

Channing Ahn, R. H. Grubbs and R. C. Bowman, Jr.
California Institute of Technology
with DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

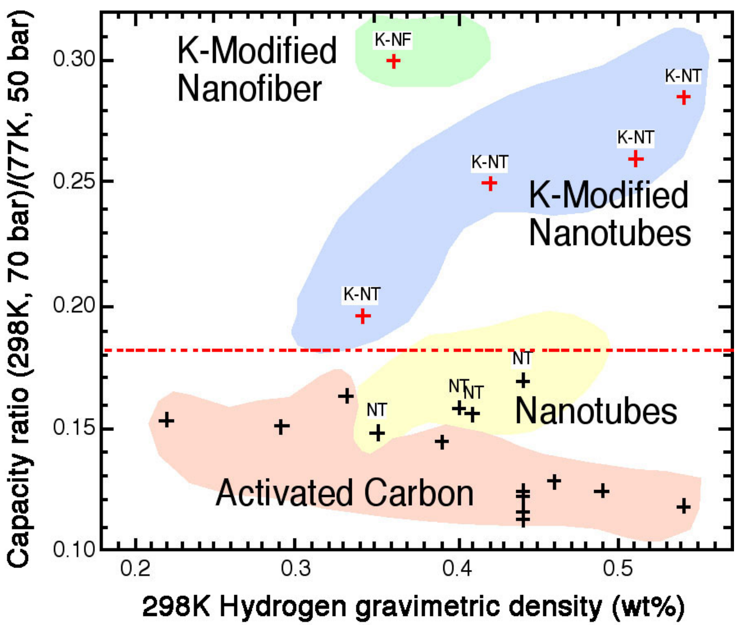
May 23-26, 2005

This presentation does not contain any proprietary or confidential information

Project ID # STP34 AHN

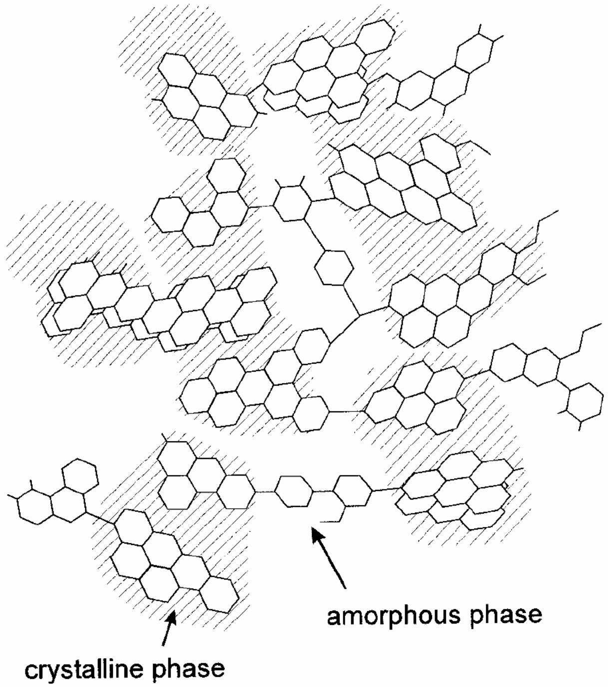
Approach

A. Local charge site polarization
(alkali metal modified carbons)



Ratio of hydrogen to carbon that can be accommodated in alkali-metal modified nanotubes. Note that in normal carbons, the ratio of hydrogen to carbon capacity of RT/77K is 1:6 while this ratio is 1:4 when the sorption potential is changed through K additions.

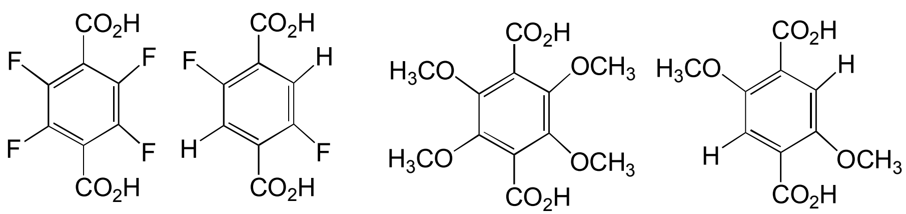
B. Polarization at heterogeneities
(activated carbons, graphites)



Engineer a high edge termination structure from graphite through mechanical attrition, and activate these edge sites with hydrogen or oxygen to promote high surface area hydrogen sorption.

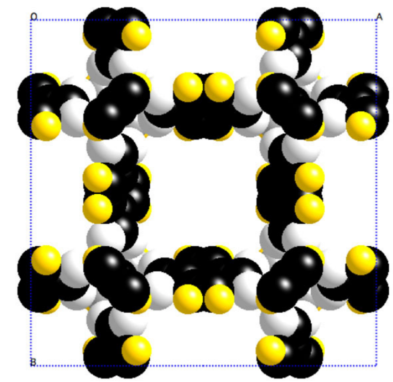
Approach, cont'd

C. Modification of metal organic framework electron structures

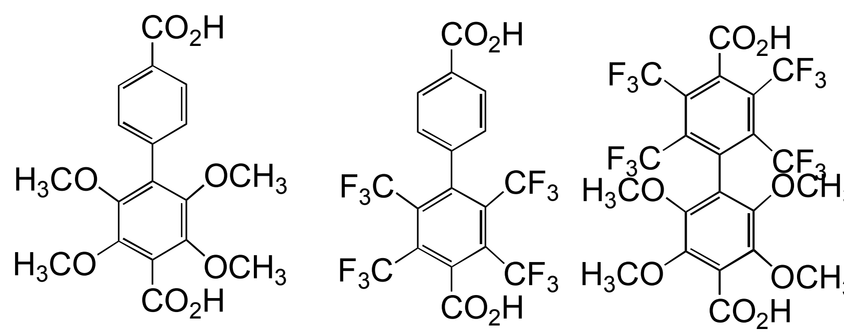


A B C D

Above is a series of diacid structures that would be used in conjunction with MOF structure linkers in order to test the principle of enhanced edge site potentials for enhanced hydrogen sorption with symmetric polarization change.



MOF-5 unit cell



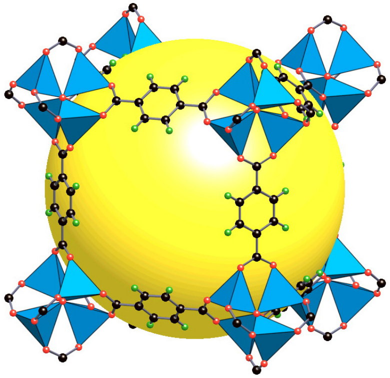
Above are asymmetric polarization structures that will be used to verify hydrogen sorption properties

Examination of the Physical Aspects of Hydrogen Storage in MOFs

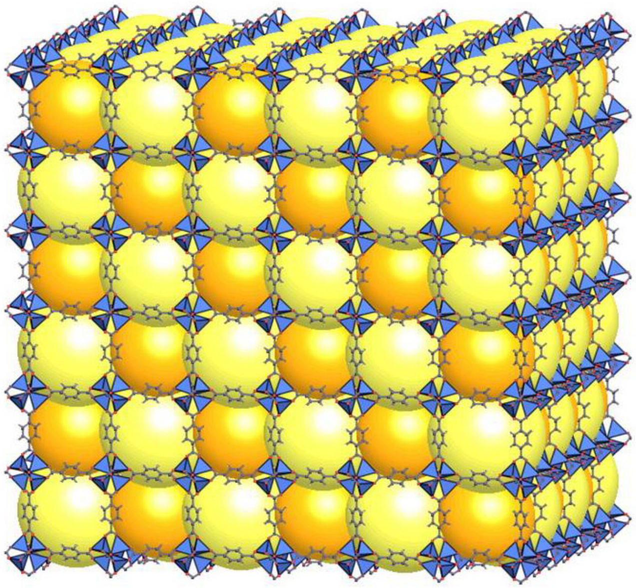
Omar M. Yaghi and Adam J. Matzger
Department of Chemistry
University of Michigan
Ann Arbor, MI 48109

Project ID #
ST39 Yaghi

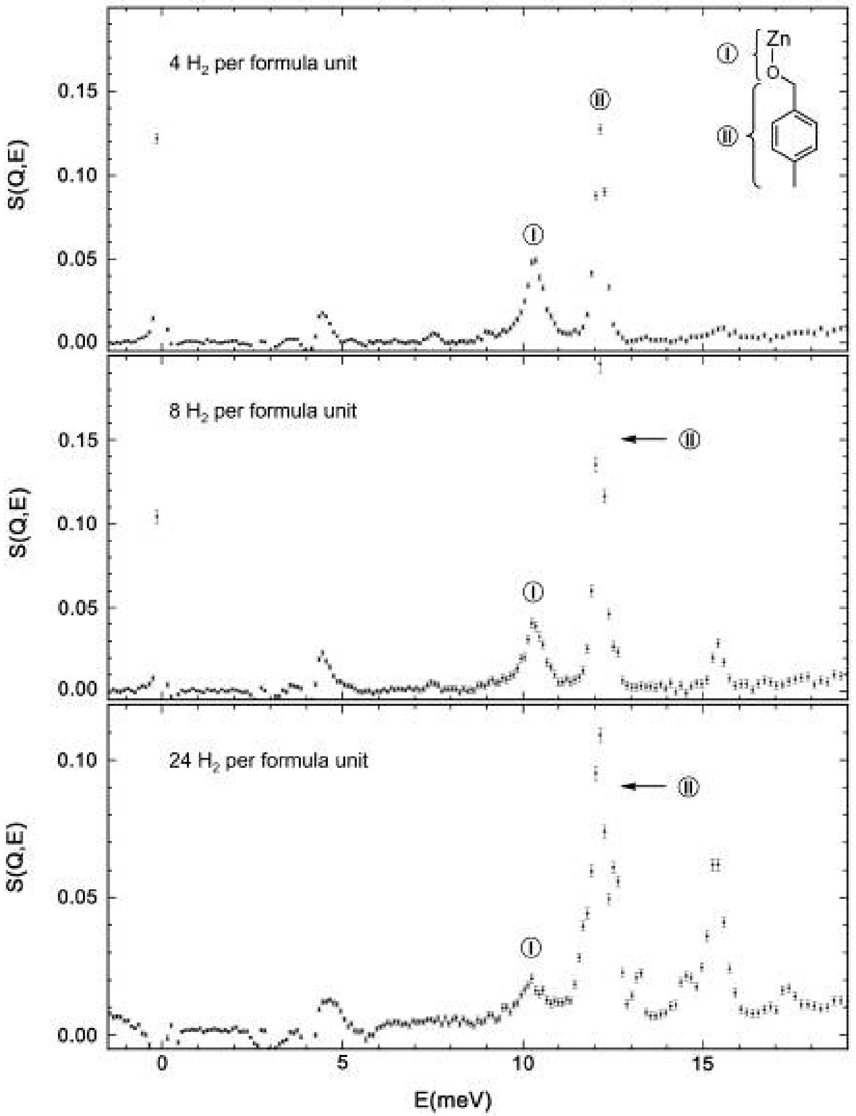
Inelastic Neutron Scattering of H_2 in MOF-5



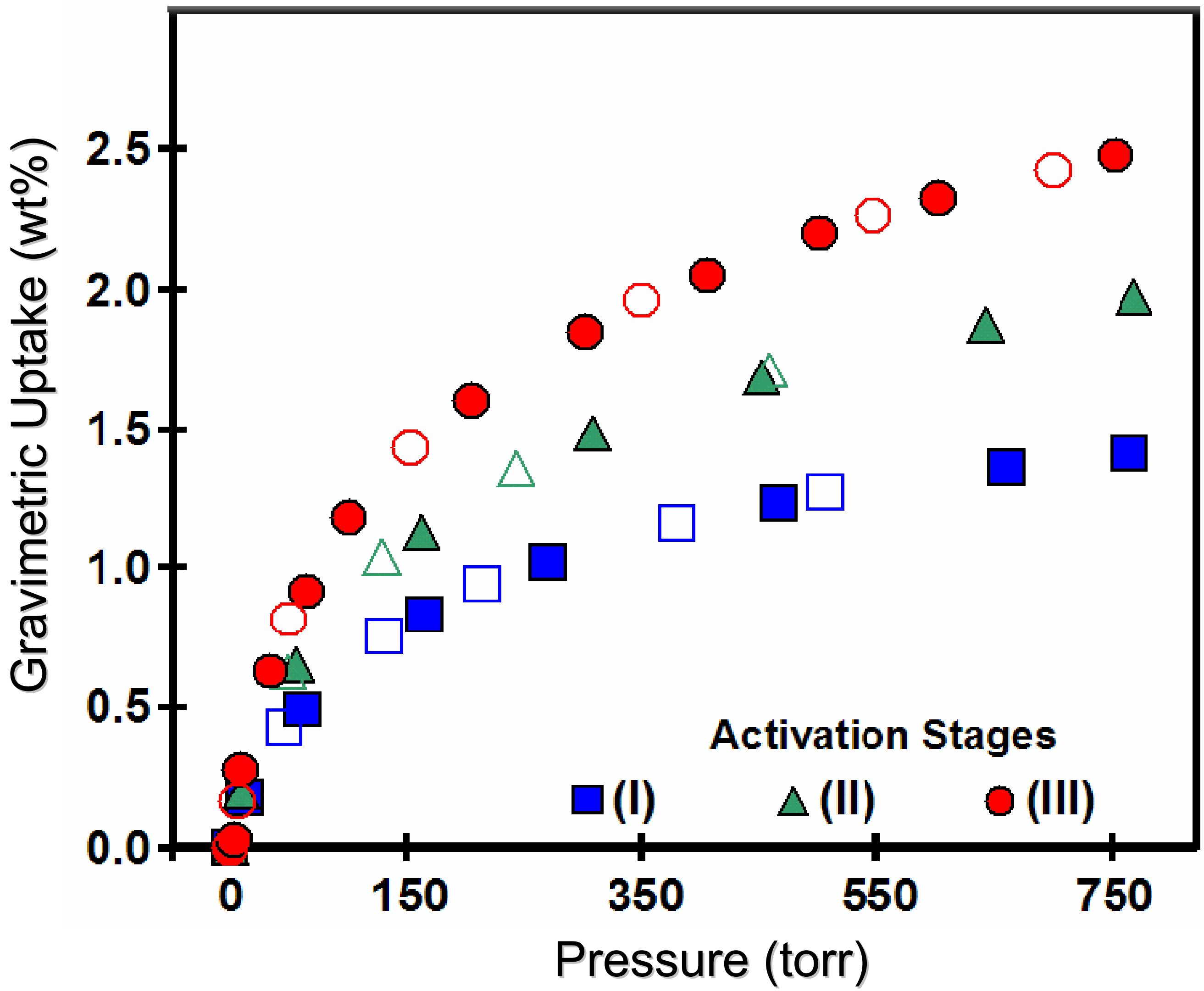
Smallest repeat unit of MOF-5

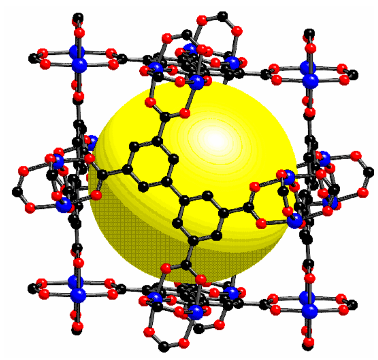


Extended structure of MOF-5



MOF-505 H_2 (77 K) Sorption Isotherms– Activation Study





MOF-505

Conducting Polymers as New Materials For Hydrogen Storage

Alan G. MacDiarmid
University of Pennsylvania

Part of the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

May 24, 2005

STP42

KEY PARTS FROM CHO'S* PAPER

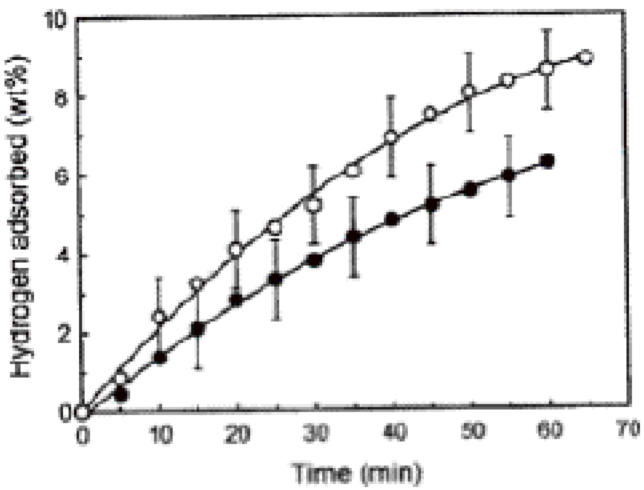


Figure 1. The amount of H_2 in wt. % for both (•) the PANI and (O) the Ppy treated with concentrated hydrochloric acid. The measurement was started after evacuation at 473 K and subsequently at room temperature at least 0.13 Pa.

Table 1. Summary of the hydrogen storage in metal hydrides, multiwalled carbon nanotubes and the acid treated conducting polymer measured using the same adsorption apparatus.

Sample	Press. (atm)/ Temp. (K)	Wt. %
† $MmNi_{4.7}Al_{0.3}$	10 ~ 20 / 298	1.2
† $MmNi_{4.8}Al_{0.2}$	10 ~ 20 / 298	1.3
$Ti_{0.7}Zr_{0.3}$ $Mn_{1.0}Cr_{0.9}Ni_{0.02}Fe_{0.03}$	10 ~ 20 / 298	2.0
MWNT	90 / 298	0.8
HCl-Treated PANI	90 / 298	6.0
HCl-Treated Ppy	90 / 298	8.0

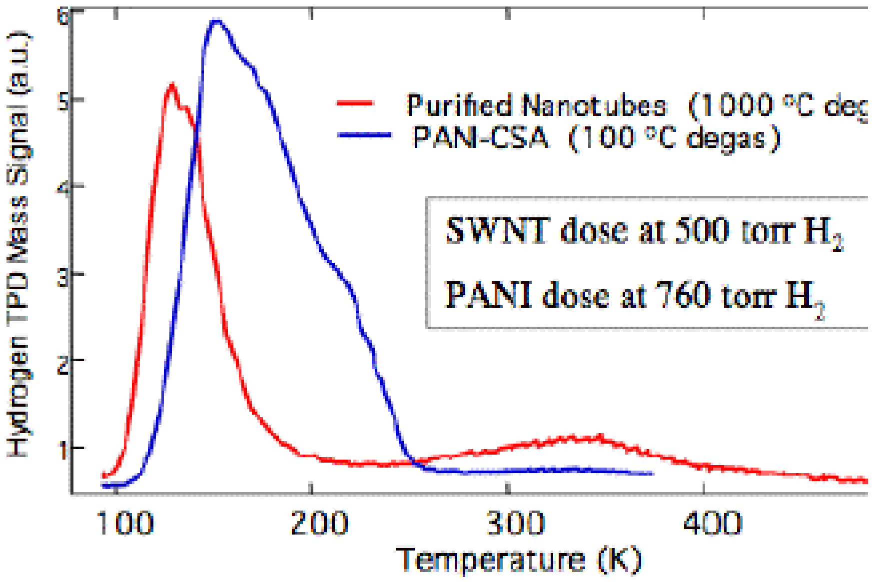
† = "Mischmetals", i.e., a mixture of the early lanthanide metals including

- Commercial (Aldrich) polyaniline (PANI) and polypyrrole used.
- The hydrogen storage can also be varied widely depending on the method of the modification process of the polymer using the concentrated hydrochloric acid, specifically, the exchange or removal level of the dopants, the drying temperature and the rigidity of the polymer backbone.

Results

Comparison of Conducting Polymers to SWNTs

- Very preliminary Temperature Programmed Desorption (TPD) studies by M. Heben Group at DOE labs, Golden, CO
- Polyaniline nanofibers doped with CSA (Camphorsulfonic Acid), PANI-CSA (one phase w/Triton X100 and stirring doped)
- Investigating the report By Cho et al.* of 6 wt% storage in PANI



- PANI-CSA: extremely broad desorption peak (~ -165 °C to -25 °C) with a shoulder at ~ -60 °C. This could indicate the presence of a variety of different binding sites and though it is not room temperature, it is quite accessible throu standard cooling methods.
- Potential roles of the surfactant and dopant are considered to be of very great importance for further study.

Synthesis and Processing of Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

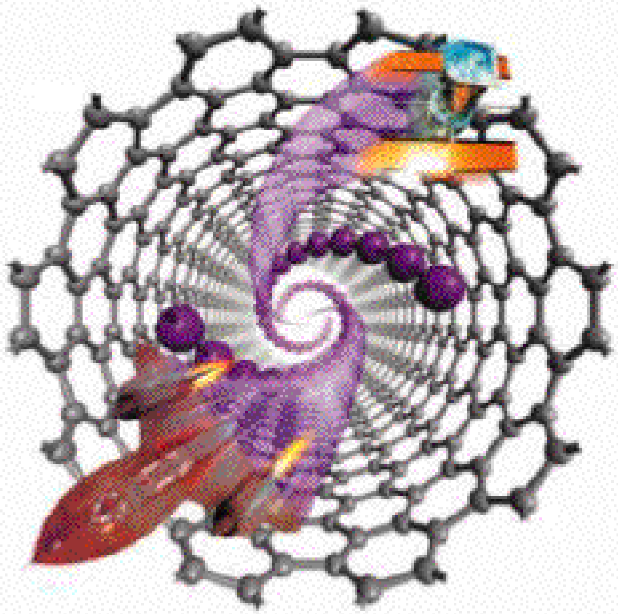
a participant in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials
DOE Hydrogen Program Annual Review, Washington, D.C., May 23, 2005

David B. Geohegan
Alex Puretzky*
Ilia Ivanov*
Hui Hu
Hongtao Cui
Christopher M. Rouleau
Zuqin Liu#

Condensed Matter Sciences Division
Oak Ridge National Laboratory

**Materials Science & Engineering Dept.,*
University of Tennessee

#Center for Nanophase Materials Sciences



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Project ID#
STP32

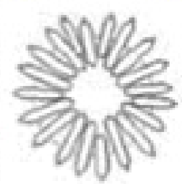
OAK RIDGE NATIONAL LABORATORY
U.S. DEPARTMENT OF ENERGY

P.O.C. David Geohegan, odg@ornl.gov

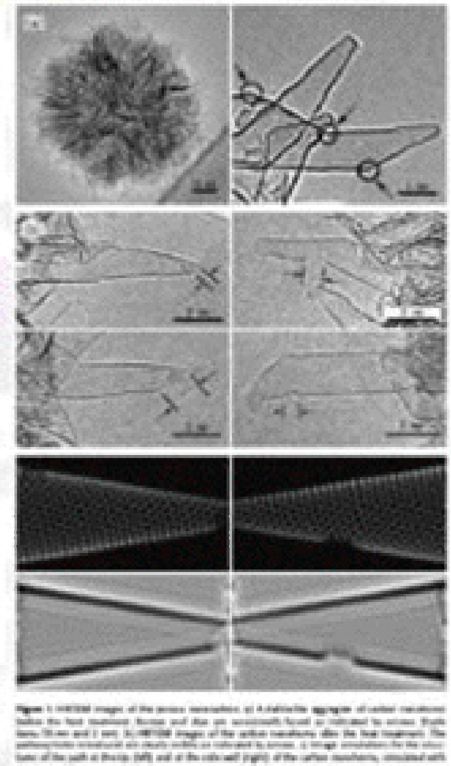
UT-BATTELLE

Why Single-Wall Carbon Nanohorns (SWNH)?

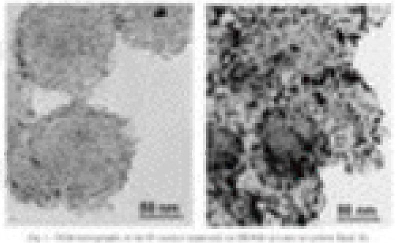
- SWNH excellent as both storage vessels and catalyst supports
  - single-walled carbon structures like single-walled carbon nanotubes
    - huge surface area
    - visible in TEM
    - can be produced *without* metals
    - can be produced mixed with SWNT and metals to probe spillover mechanism
  - Two modes of storage
    - outer surface - initially exposed
    - inner surface accessible by opening pores
    - tiny "bottles" for storage
  - Excellent catalyst supports - for gas storage, fuel cells
    - nanohorn structure restricts catalyst aggregation, supporting finer catalysts at lower weight loadings
    - demonstrated by Iijima's group at NEC
      - first commercial methanol fuel cell now in production for laptops



Schematic diagram of nanohorn aggregates. [Bekyarova'02]



TEM of SWNH as produced and after heat treatment [Aijima AM'04]



Pt nanoparticles on nanohorn aggregates (left) vs. carbon black (right). [Yoshitake PRB'04]

Study of Hydrogen Storage in Advanced Boron and Metal Loaded High Porosity Carbons Carried Out in the "DOE/NREL Center of Excellence on Carbon-based Hydrogen Storage Materials"

M. Chung, H.C. Foley, and P.C. Eklund

The Pennsylvania State University

5/23/2005

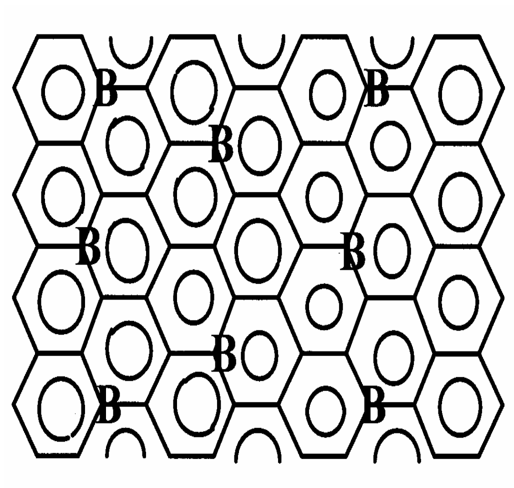
This presentation does not contain any proprietary or confidential information

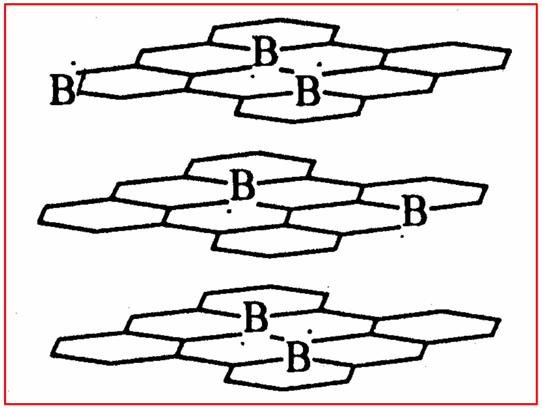
Project ID STP#36

Approach

- Synthesis of C-B-M Materials
  - Pyrolysis of Molecular Precursor *(Professor Mike Chung)*
  - Inclusion Reactions with Preformed High SSA Carbons *(Professor Henry Foley)*
  - Very High Temperature Gas Phase Synthesis *(Professor Peter Eklund)*
- Synthesis of highly micoporous C-B-M material by three separate routes.
- Characterization of the short- and long-range structure, the microporosity and SSA
- Evaluation of these materials for hydrogen sorption behavior.
- Optimization of the SSA for specific C-B-M materials of technological relevance

C/B Materials (B-substituted C)





- C and B with similar atomic size with trivalent coordination,
  - C/B material can maintain graphitic structure.
- B (electron deficiency) serves as p-type dopant
  - Increase π-electron delocalization and surface activities.

Metal-doped Carbon Aerogels for Hydrogen Storage

- Joe H. Satcher, Jr., Theodore F. Baumann,
- Julie L. Herberg, Robert S. Maxwell
- *Lawrence Livermore National Laboratory*

- 05/24/05
- Project ID# STP-31
- DOE Center of Excellence on Carbon-based H_2 Storage Materials

This presentation does not contain any proprietary or confidential information

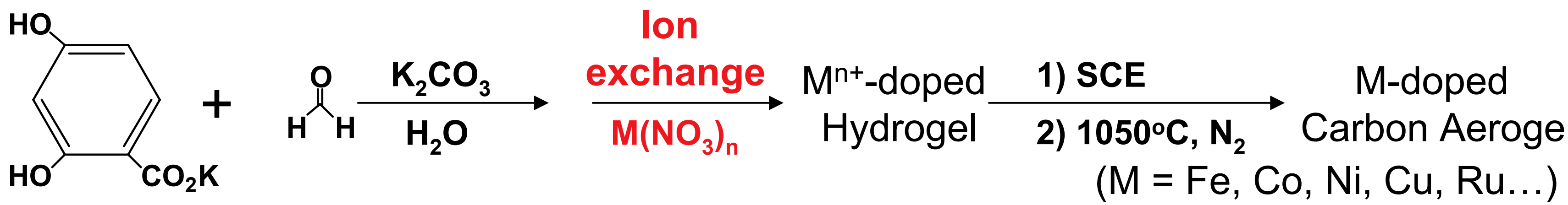
Work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48

Project Objectives

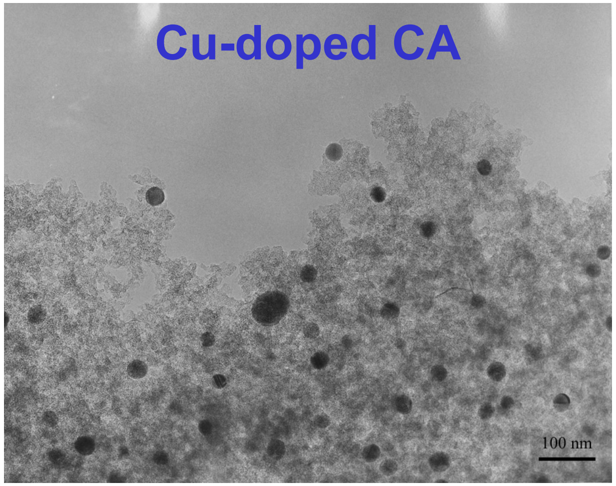
- To develop new nanostructured carbon materials that meet the targets set by DOE for hydrogen storage:
  - Novel metal-doped carbon aerogels (MDCAs) will be prepared, characterized and evaluated for their hydrogen storage properties
  - Mechanisms associated with hydrogen physisorption and chemisorption in these carbon-based materials will be investigated using advanced nuclear magnetic resonance (NMR) techniques
- Insights gained from MDCA systems should also be beneficial to the other nanostructured carbon systems, leading to the design of an optimized carbon-based material for hydrogen storage

Current Technical Status

- **Incorporation of metal species into aerogel framework using sol-gel precursors containing ion exchange sites :**
  - **General technique that can be used to incorporate a variety of metals**



- **Physical Properties:**
  - Density Ranges: 150-400 mg/cm^3
  - Surface Areas: 500-900 m^2/g
  - Metal Content: 1-10% by weight
- **Metal nanoparticles form during carbonization (5 to 60 nm)**



Satcher, J. H.; Baumann, T. F., *US Patent 6 613 809*, **2003**.

Baumann, T. F. et al *Langmuir*, **2002**, *18*, 7073; *Langmuir*, **2002**, *18,* 10100; *J. Non-Cryst. Solids* **2003**, *317*, 247 *J. Non-Cryst. Solids*, **2003**, *318, 223*.

Hydrogen Storage in Graphite Nanofibers and the Spillover Mechanism

A Study Carried Out in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

Anthony J. Lachawiec, Gongshin Qi and Ralph T. Yang (P. I.)

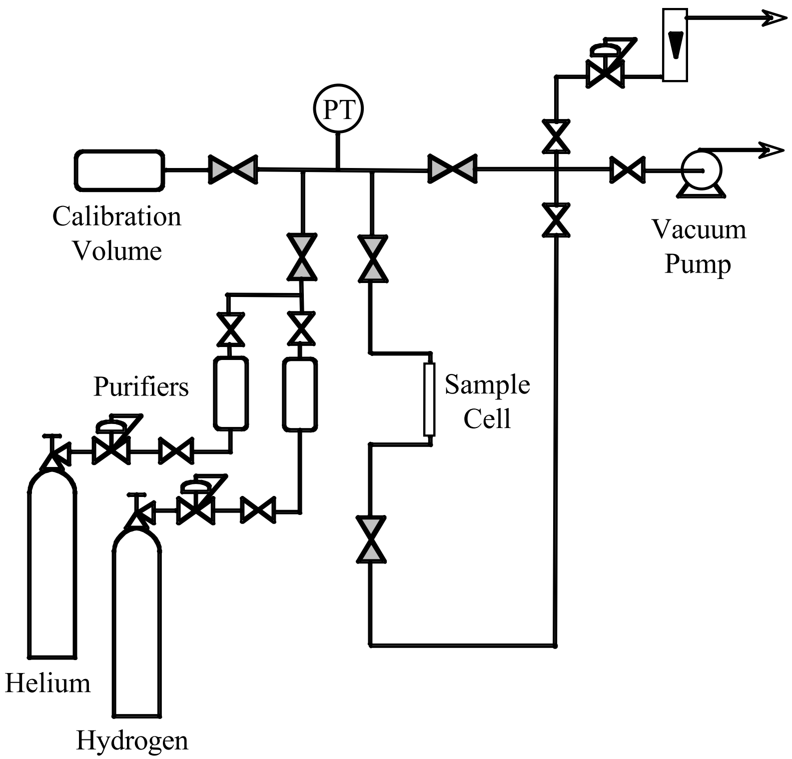
University of Michigan

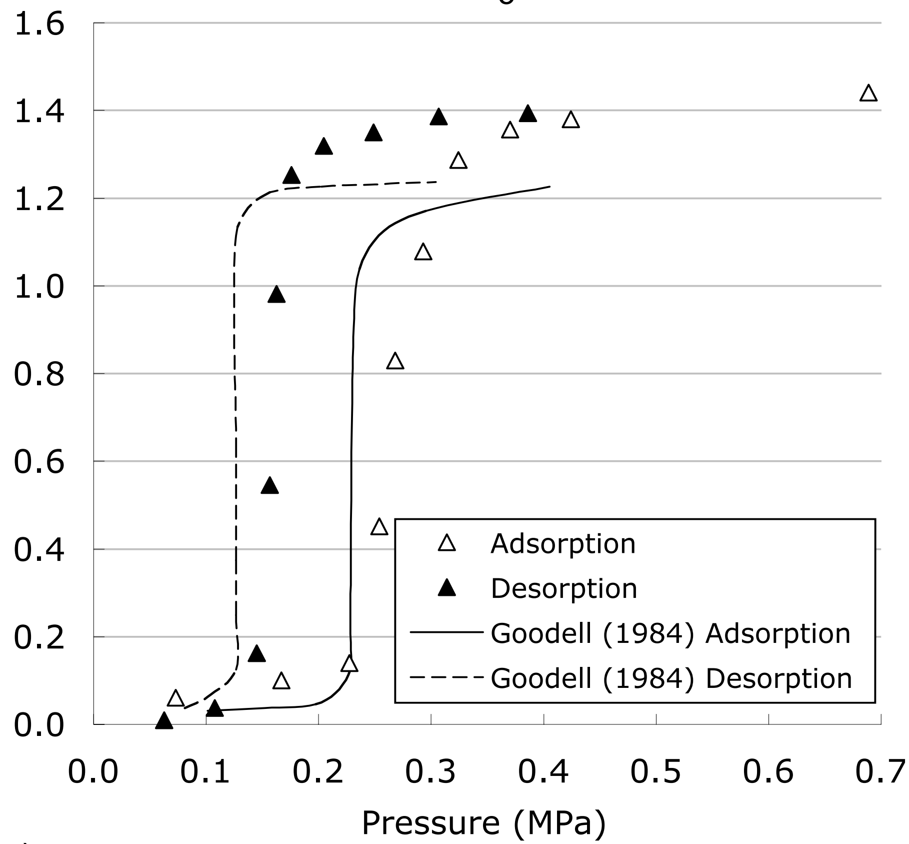
Department of Chemical Engineering

23-24 May 2005

STP40

High Pressure Measurement





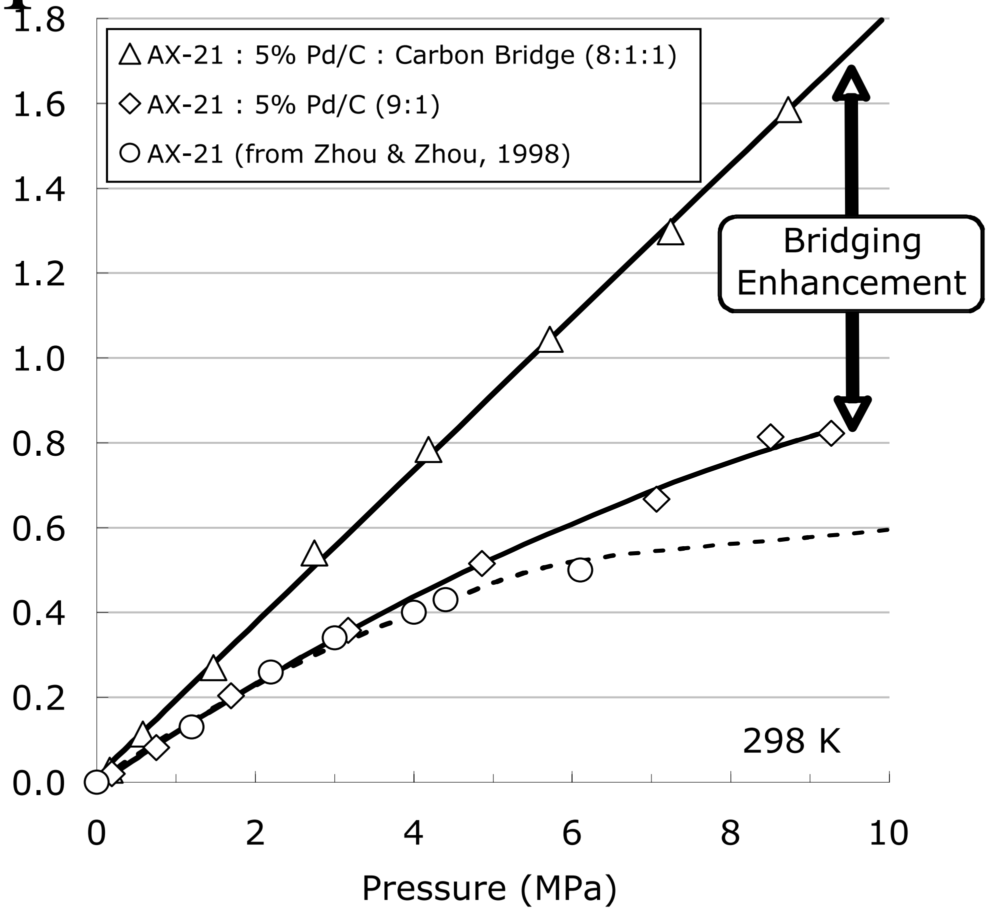
- Calibrated Volumetric System ($LaNi_5$ & $TiAl_{0.12}V_{0.04}$)
- In-situ Pretreatment to 1023 K (750 C)
- Adsorption Measurements to 12 MPa (1800 psia)

Source: Goodell (1984) *J. Less-Common Met.* 99, 1

University of Michigan
Department of Chemical Engineering

High Pressure Spillover Enhancement

- Extension of low-pressure work
- Identical trends observed at high pressure
- Completely reversible adsorption at 298 K
- Adsorption capacity tripled at 10 MPa (only 1.3 times without bridges)
- 1.8 wt% capacity at 10 MPa without optimization



Sources: AX-21 Bridge Data: Unpublished Work, Lachawiec, Qi & Yang (2005)
AX-21 Isotherm: Zhou & Zhou (1998) *Chem. Eng. Sci.* 53, 2531

UNIVERSITY OF MICHIGAN
Department of Chemical Engineering

Characterization of Hydrogen Adsorption by NMR

"DOE Center of Excellence on Carbon-based Hydrogen Storage Materials"

Yue Wu
Department of Physics and Astronomy
And
Curriculum in Applied and Materials Sciences
University of North Carolina, Chapel Hill

May 23-26, 2005

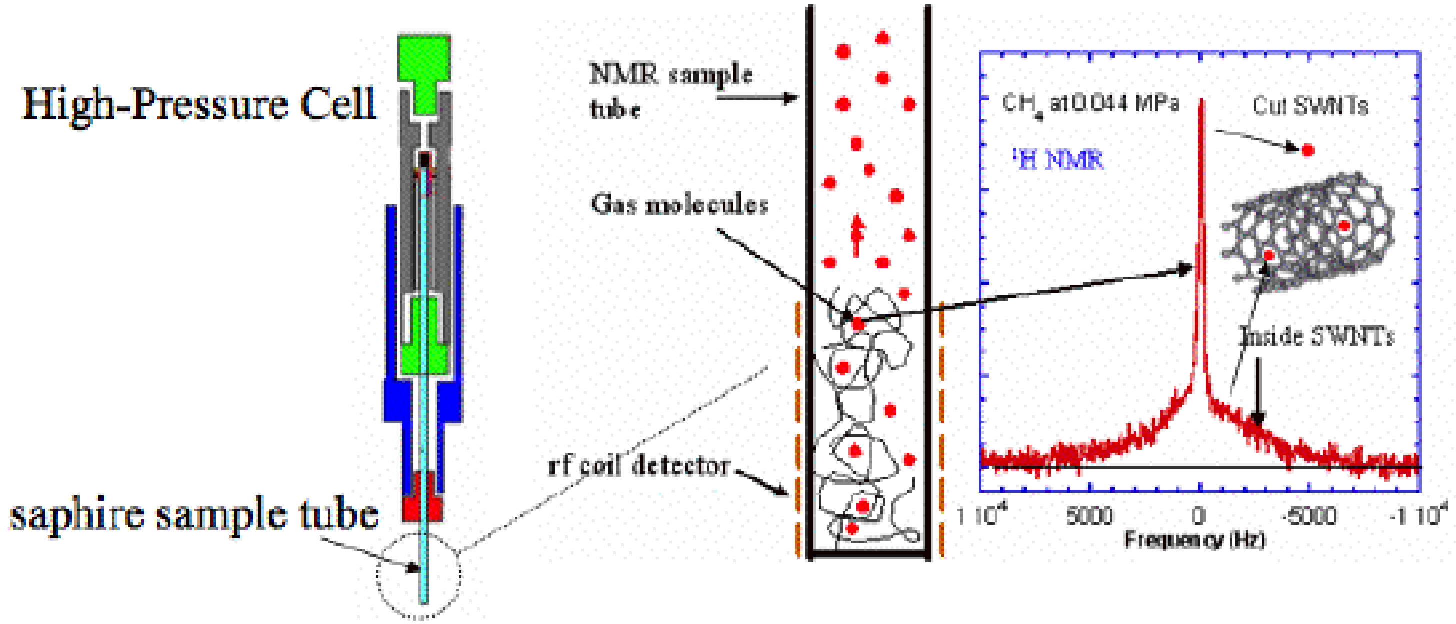
This presentation does not contain any proprietary or confidential information

Project ID # STP41

Technical Accomplishments/ Progress/Results

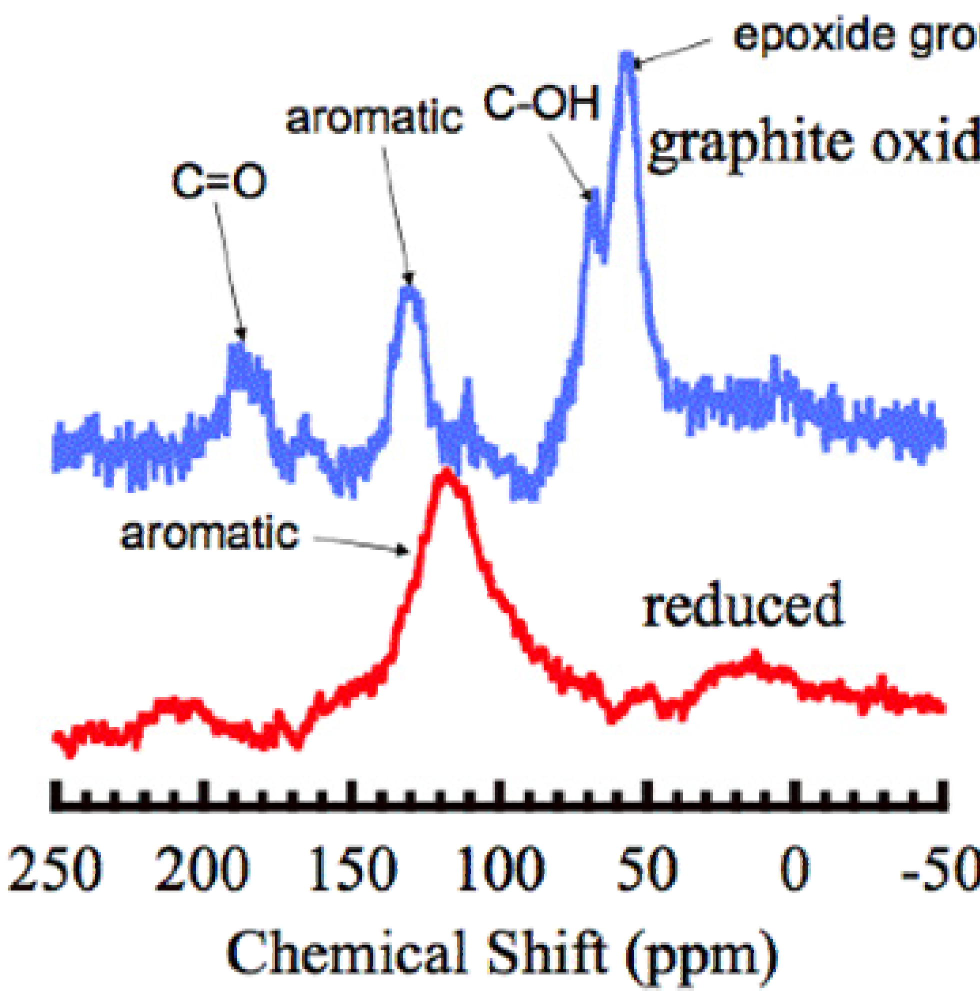
High-Pressure NMR Probe

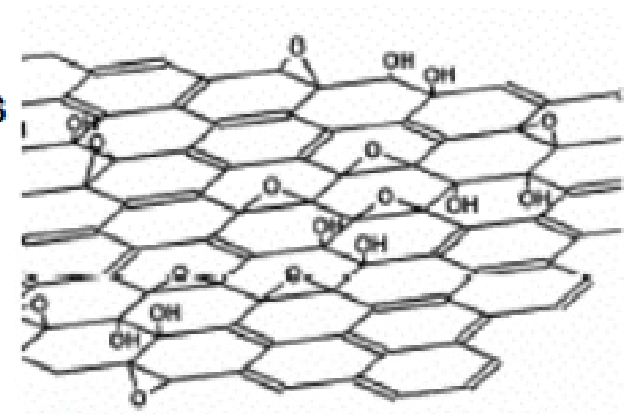
H_2 pressure ranging from 1-100 atmospheres is required for evaluating hydrogen adsorption in carbon-based materials. Therefore, we need to carry out NMR measurements under H_2 pressure up to 100 atm. A saphire-based high-pressure cell was built and tested successfully up to 100 atm. The high-pressure cell is incorporated in an NMR probe for high-pressure NMR measurements.



Proton NMR signal revealing both adsorbed (broad peak) and free gas (narrow peak) molecules in single-walled carbon nanotubes.

Technical Accomplishments/ Progress/Results





The ^{13}C NMR spectrum of graphite oxide reveals the details of the functional groups in this material. The ^{13}C NMR spectrum of the reduced material shows clearly the return to a graphitic structure. This demonstrates that ^{13}C NMR could be used to analyze the structure of high surface area carbon-based absorbents and understand the interactions with hydrogen. This could provide crucial information on hydrogen adsorption mechanisms.

Neutron Characterization of Carbon-Based Materials

carried out in the

DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

Craig Brown

Dan Neumann

NIST

National Institute of Standards and Technology

Technology Administration, U.S. Department of Commerce

(NCNR)

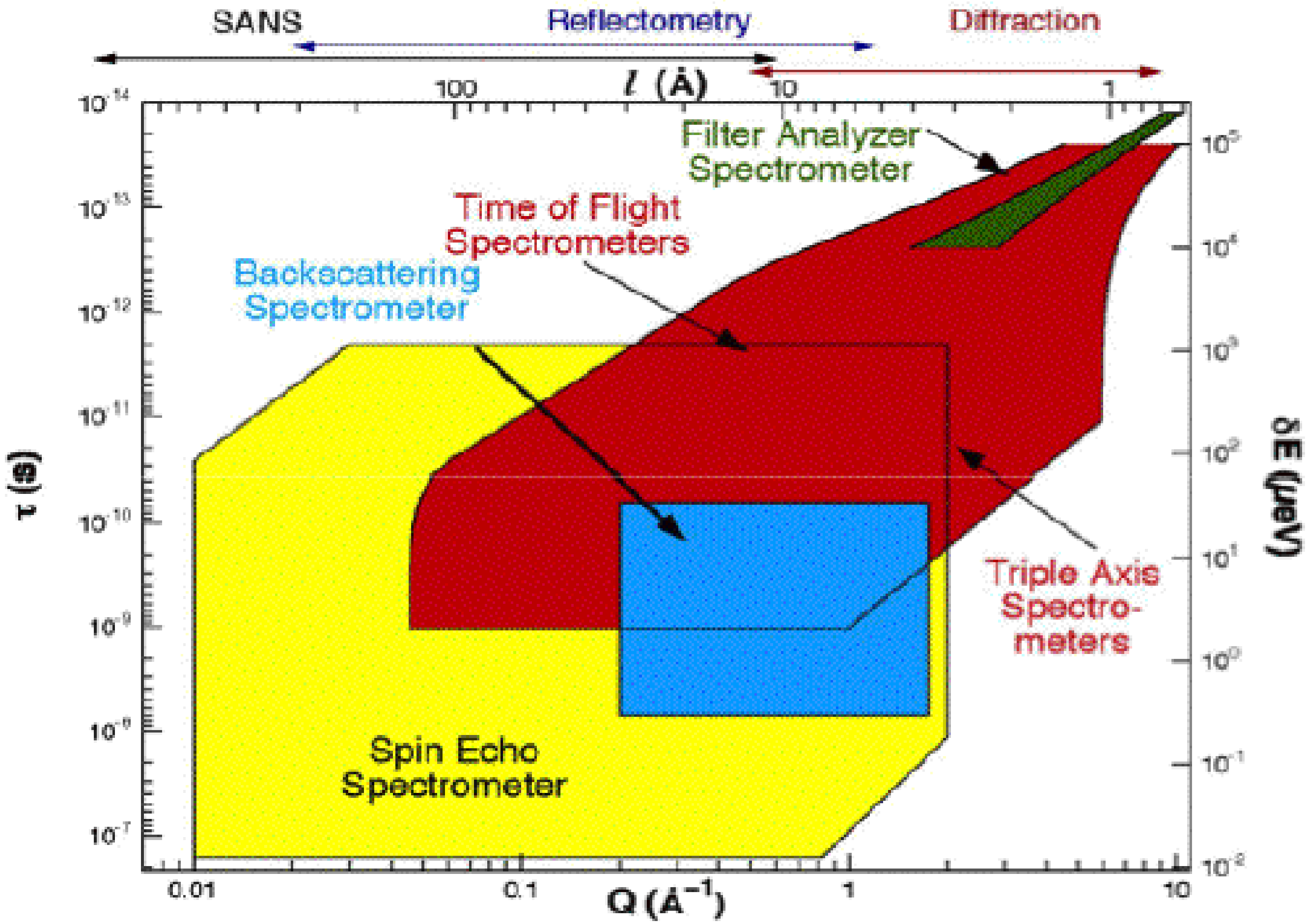
May 23th 2005

This presentation does not contain any proprietary or confidential information STP33

Approach

- neutron scattering will be used to address the following questions:
- **Where is the hydrogen?**
- **Is the hydrogen atomic or molecularly adsorbed?**
- **Can we identify adsorption sites and activation barriers?**
- **What are the diffusion mechanisms?**
- **How is the substrate influenced upon adsorption?**
- **Do sorption processes change as the system lengthscale decreases to the nanoscale?**
- **Does manipulating the host electronic structure change these processes?**

Approach


SANS
Reflectometry
Diffraction
l (Å)
100
10
1
Filter Analyzer Spectrometer
Time of Flight Spectrometers
Backscattering Spectrometer
Triple Axis Spectro-meters
Spin Echo Spectrometer
τ (s)
δE (μeV)
Q (Å⁻¹)
0.01
0.1
1
10

State of the Center of Excellence

- Detailed work statements for each partner with Go/No-Go decision points 24 months from start
- Project flow matches Grand Challenge time table
- All contracts are now in place
- Collaboration in earnest is beginning
- Center Safety plan reviewed by S. Weiner and colleagues - recommendations implemented
- Partner safety plans are being prepared
- Website and ftp site are operational
- Steering Committee has met and plans to meet regularly (Rice, Air Products and Chemicals, NREL)
- Center technical workshop this afternoon