Enhanced Hydrogen Dipole Physisorption

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California Institute of Technology
with DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

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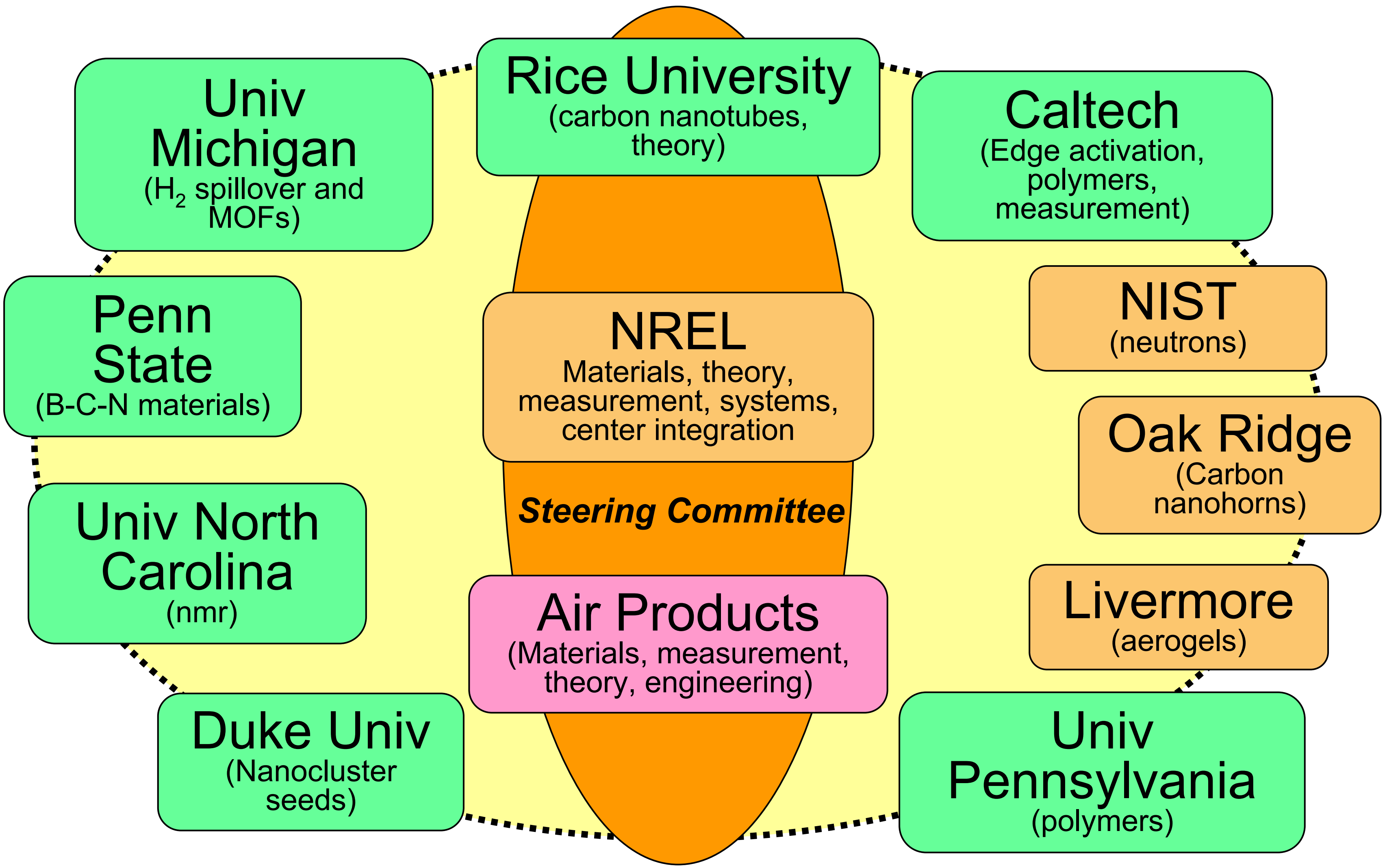
Project ID # STP34 AHN

Caltech role with CbHS Center of Excellence Partners



Overview

Timeline

- Project start date: October 1, 2004
- Project end date: September 30, 2009

On board hydrogen storage Barriers and Targets

(B) Weight and volume of on board hydrogen storage systems

(N) Low temperatures that physisorption based systems typically need to work in order to store high hydrogen densities.

Budget

- Total project funding
  - DOE share $1M (5 yrs)
  - Contractor share $250k (5 yrs)
- Funding for FY05
  - DOE share $200k
  - Contractor share $50k

Partners

Interactions/collaborations:

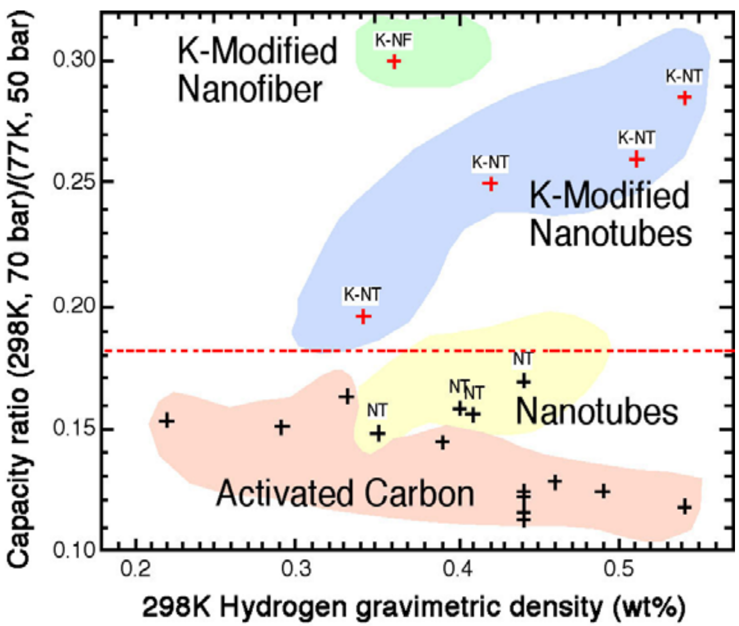
National Renewable Energy Lab. (M. Heben)
CNRS, Grenoble, France (R. Yazami)
UNC (Yue Wu)
NIST (Dan Neumann)
Univ. Michigan (O. Yaghi)
Univ. Pittsburgh (J. Karl Johnson)
LLNL (J. Herberg)

Objectives

- To enhance site potentials from 10's to 100's of meV in order to promote stronger physisorption effects that will increase gravimetric densities of non-dissociative based hydrogen storage systems at temperatures greater than 77K.
- Enhancement of physisorption enthalpies to be achieved by manipulation of site potentials through the use of local charge states and pKa-adjusted edge sites.

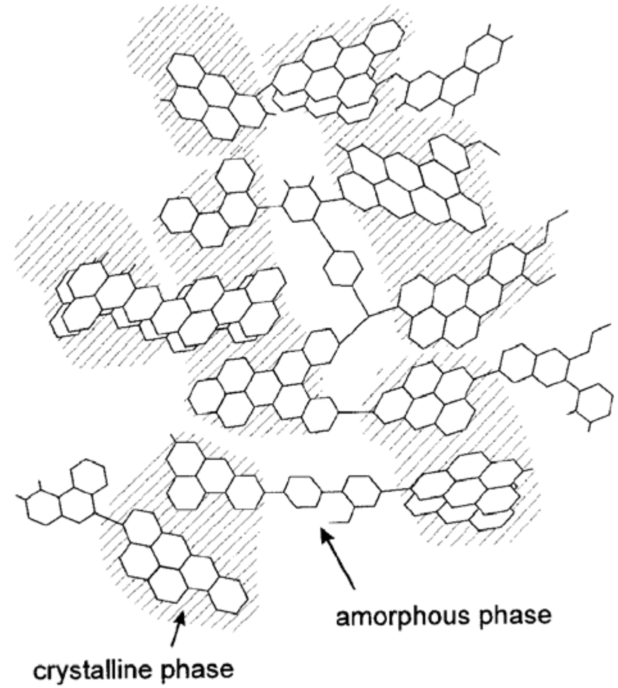
Approach

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.

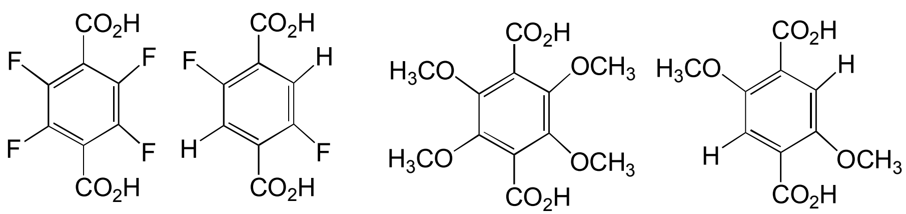
B. Polarization at heterogeneities (activated carbons, graphites)



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.

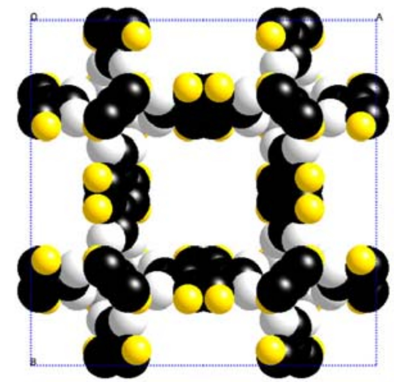
Approach, cont'd

C. Modification of metal organic framework electron structures

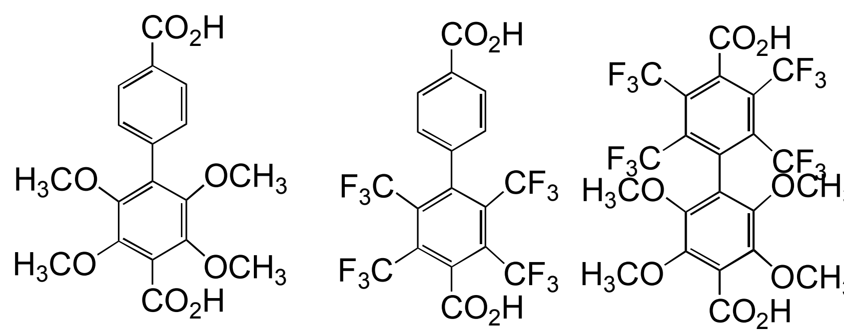


A B C D

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

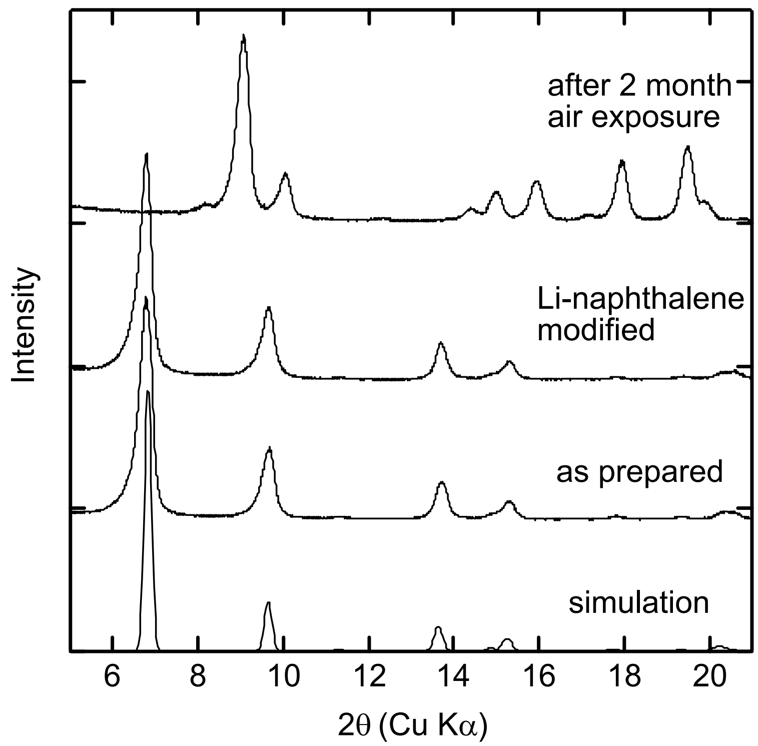


Above are asymmetric polarization structures that will be used to verify hydrogen sorption properties

Sorption analysis by volumetric Sieverts apparatus

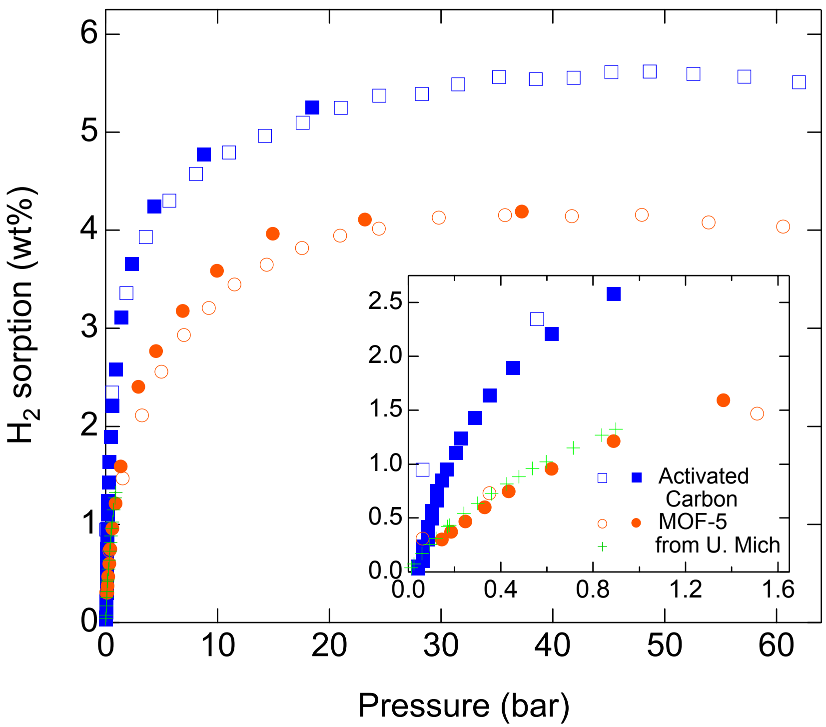
- We have extensive experience with volumetric hydrogen sorption measurements.
- Computer controlled unit is 3rd generation Sieverts, built at JPL from unit originally built at Caltech.

Progress/Initial Results from MOF synthesis



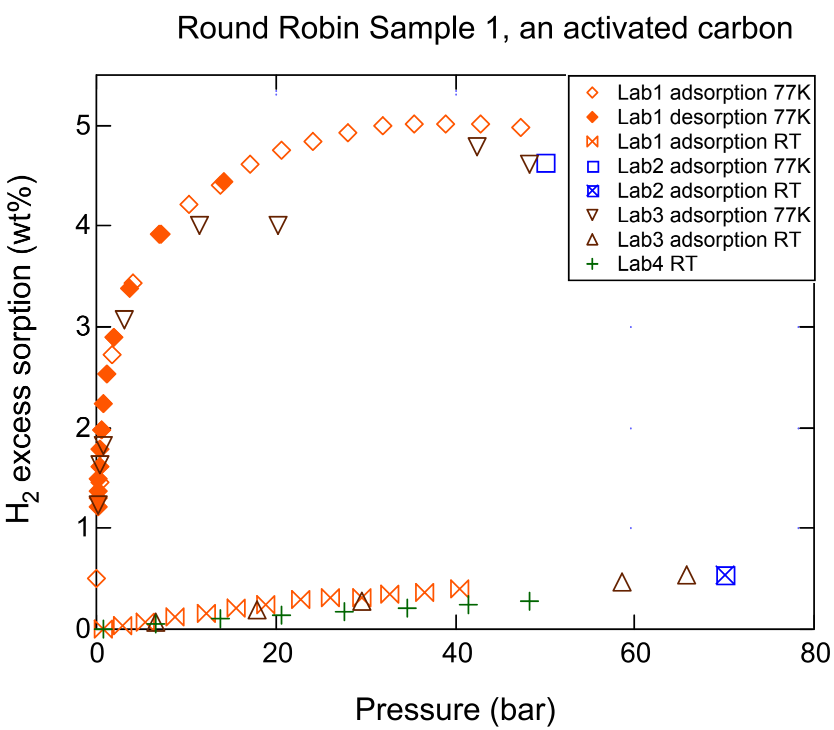
- Successful synthesis and activation of MOF-5 structure as verified by x-ray diffraction.
- Structure matches simulation and density measurements confirm 80% void space of structure.

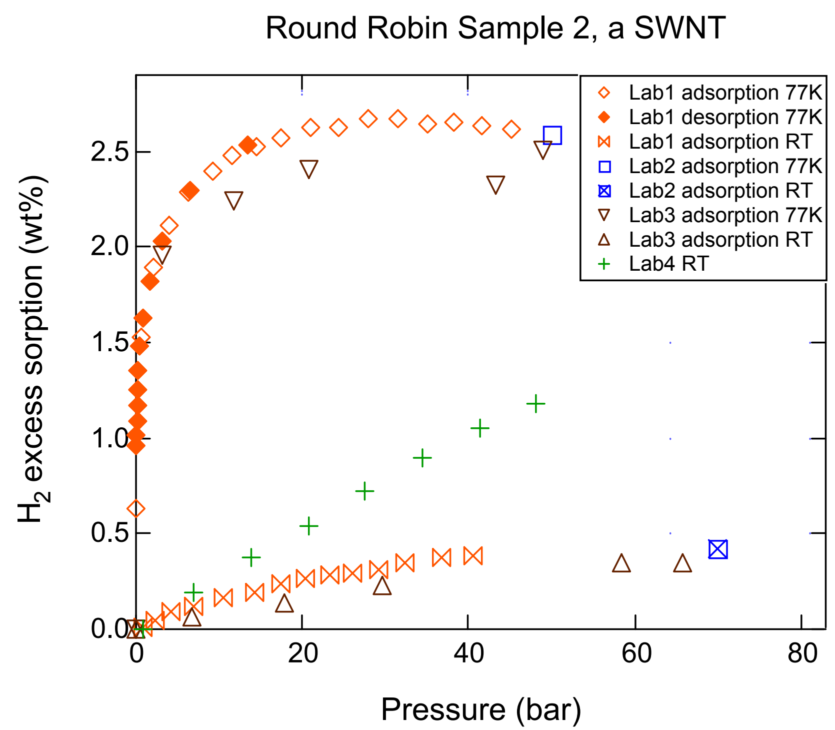
Progress/Initial Results from MOF storage capacity studies



- Sieverts volumetric sorption at 77K and 60 bar range shows up to ~4.5 wt%
- Low bar range comparable to U. Mich. gravimetric data.
- Wood based activated carbon shows highest sorption at ~5.4 wt% at 77K.

Validation of sorption measurement techniques





We have been an active participant in test measurement validation studies. Data from two different carbons is shown above and shows excellent agreement in the determination of sorption behavior in comparison to other labs.

Future Work for FY2005

- Commencement of other synthesis and material modifications including:
  - **Mechanical attrition of graphites**
  - **MOF linker syntheses**
  - **Intercalation studies pending nanotube availability**
- Evaluation of thermodynamic properties (isosteric heats)

Key Milestones and Activities

- Year 1:
  - Synthesis and reproducible measurement of hydrogen storage capacity for at least 2 SWNT K intercalated materials (4Q Year 1).
- Year 2:
  - Determine volumetric and gravimetric limits of performance for both diacid modified MOFs and K intercalated SWNT material relative to 6 wt%, 4.5 gH_2/L system
- Year 3:
  - Deliver sample exhibiting material performance characteristics that can meet FY10 system targets to DOE-specified facility.
- Year 4:
  - Scale up of synthesis and materials modifications techniques (2Q Year 4).
- Year 5:
  - Complete development of 1 kg system with Center partners (2Q Year 5).
  - Deliver 1 kg active material that meets system goals (4Q Year 5)

- ***Go/No-Go Decisions***
  - Determine volumetric and gravimetric limits of performance for both diacid modified MOFs and K intercalated SWNT material relative to 6 wt%, 4.5 gH_2/L system (Go/No Go: 4Q Year 2).
  - Deliver sample exhibiting material performance characteristics that can meet FY10 system targets to DOE-specified facility (Go/No Go: 4Q Year 3).

Tasks and Milestones