Enhanced Hydrogen Dipole Physisorption

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with DOE Hydrogen Sorption Center of Excellence

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This presentation does not contain any proprietary or confidential information

Project ID # STP7

Overview

Timeline

- Project start date: October 1, 2004
- Project end date: January 31, 2010

On board hydrogen storage Barriers and Targets

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

(N) Low temperatures that sorbent-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 FY06
  - DOE share $175k
  - Contractor share $43.5k
- Funding for FY07
  - DOE share $175k
  - Contractor share $43.5k

Partners

Interactions/collaborations:

Jet Propulsion Laboratory (R. C. Bowman, Jr.)

LLNL (T. Baumann, J. Satcher, Jr., J. Herberg)

ORNL (D. Geohegan, H. Hu)

National Renewable Energy Lab. (M. Heben)

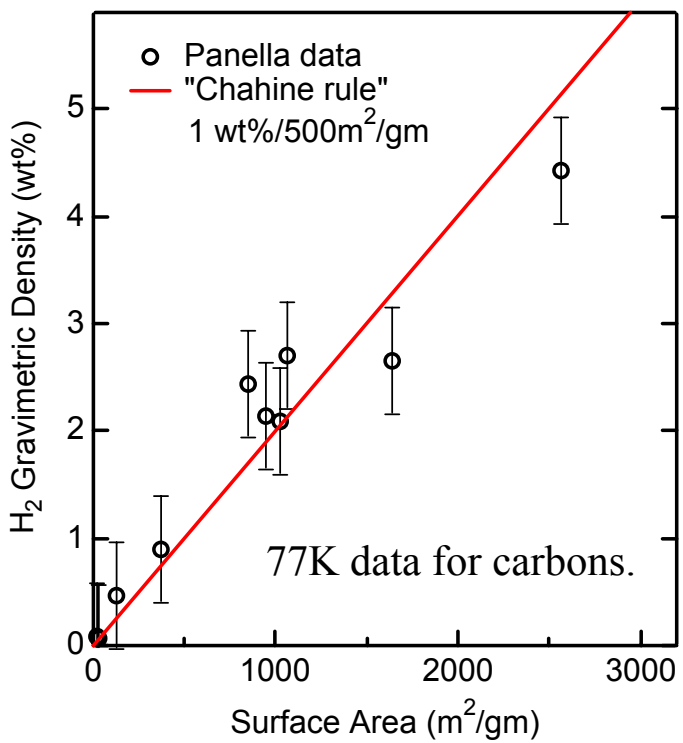
NIST (Dan Neumann)

Objectives

- High surface areas will be necessary for physisorbents for non-dissociative H_2 storage. Materials such as activated carbons and carbon aerogels and metal organic frameworks have proven to be effective, if not optimized, candidate materials as they presently work best at 77K temperature and pressures of 30 to 40 bar.
- Further enhancement of surface area needs to be accomplished in order to improve gravimetric density (from our work, presently at 5.4wt% at 77K for a 2447m^2/gm surface area activated carbon).
- Tailoring pore size needs to be addressed to maximize volumetric density (presently ~38gm/liter at 77K). Optimal pore size should be ~1.1 nm in order to maximize volumetric density.
- Sorption enthalpies beyond the 4 to 8 kJ/mole range typical of current materials needs to be increased so that sorbents can work at ambient temperatures.

Approach:

Gravimetric density observed to scale with surface area in physisorbents as shown below, in most materials so maximizing surface area in physisorbents our initial criterion for these materials.



from "Hydrogen adsorption in different carbon nano-structures," B. Panella, et al, Carbon, 43, 2209, (2005)

A) Adsorption/desorption evaluation with volumetric Sieverts apparatus capable of measurements of samples at 77, 87, 195, and 298K temperatures.

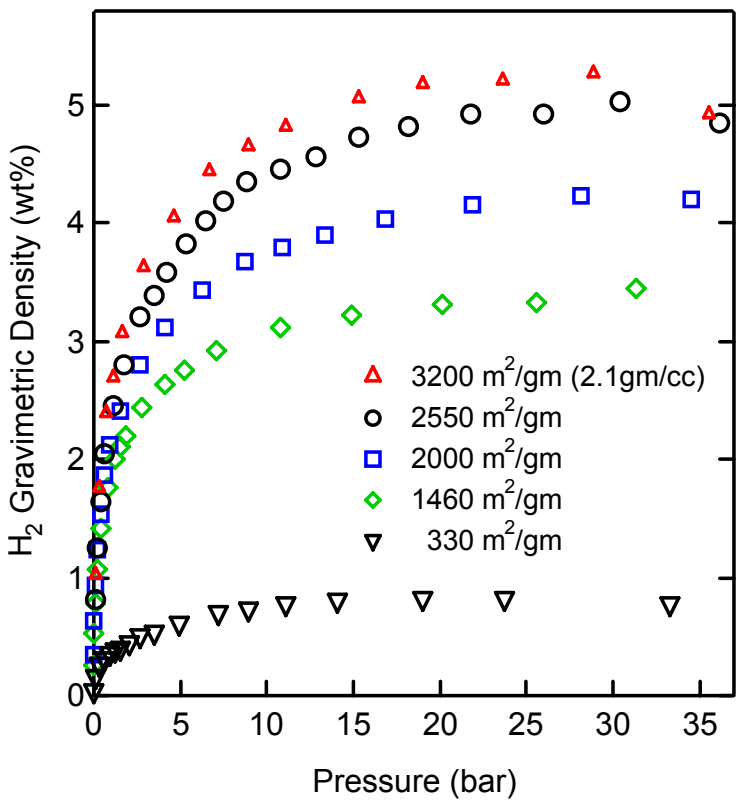
B) Differential enthalpy of adsorption measurements at zero coverage in order to identify adsorption "heats" based on Henry's law region of isotherm. Isosteric enthalpy of adsorption also critical.

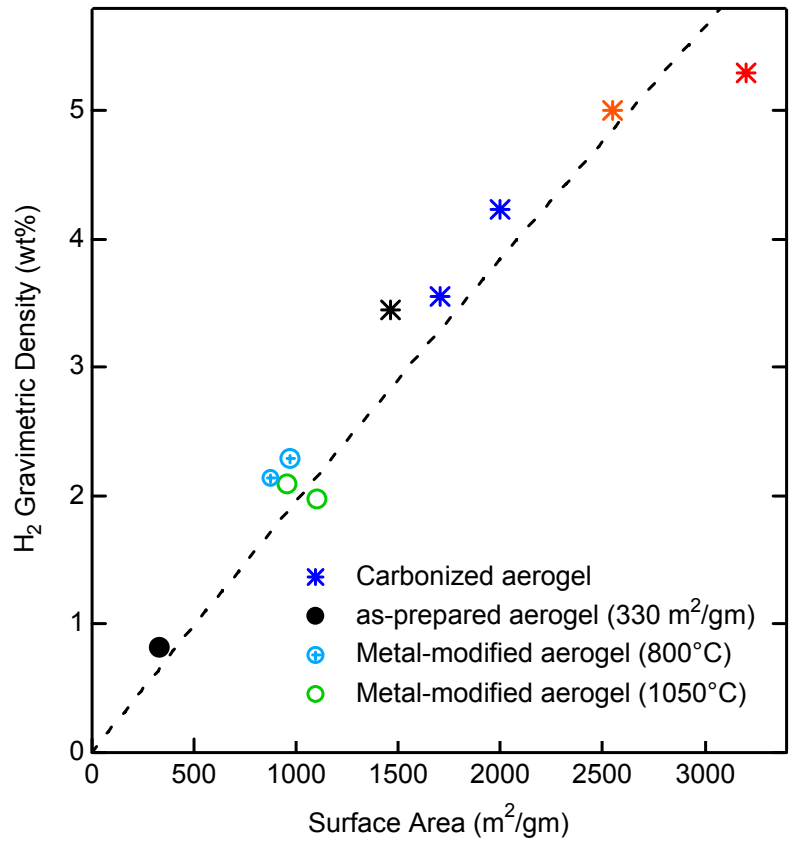
C) Synthesis of framework structures by normal solvo-thermal routes.

We have over 10 years experience with volumetric hydrogen sorption measurements.

Technical accomplishments: Isotherm analysis (surface area)

For carbon aerogels synthesized by HS CoE partner T. Baumann (Lawrence Livermore National Lab.), we note that gravimetric density scales with surface area as seen previously in activated carbons. 77K isotherms traces for several surface area aerogels are shown below and an increase in surface excess gravimetric density is seen to vary with surface area*.



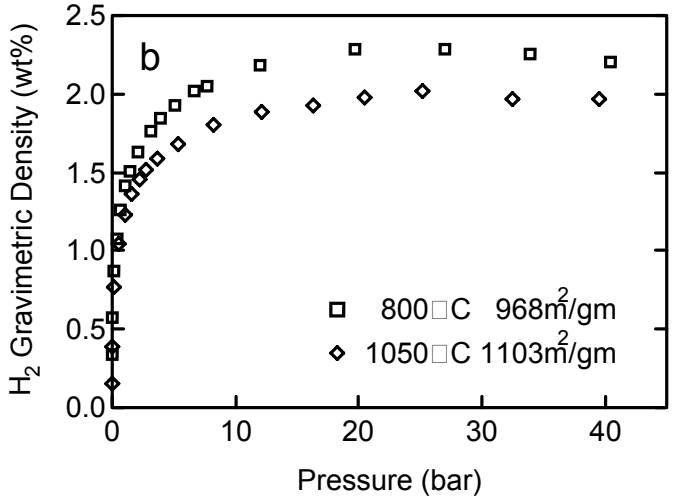


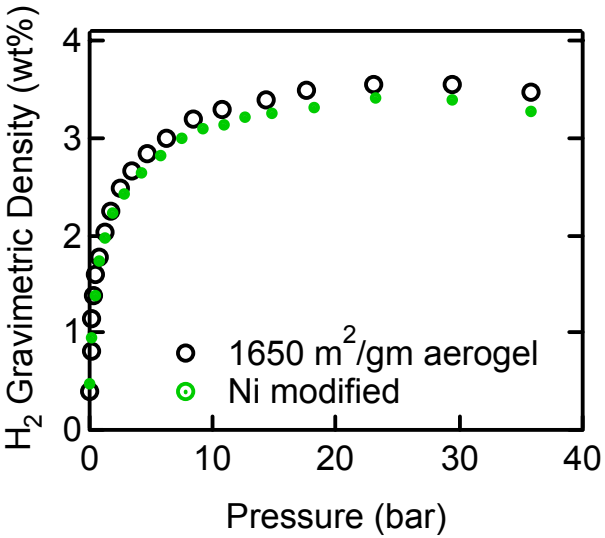
Surface area dependence on gravimetric density density in wt% is shown above for LLNL aerogels at 77K. The 3200 m^2/gm aerogel synthesized at LLNL is the highest known surface area made of a material of this type.

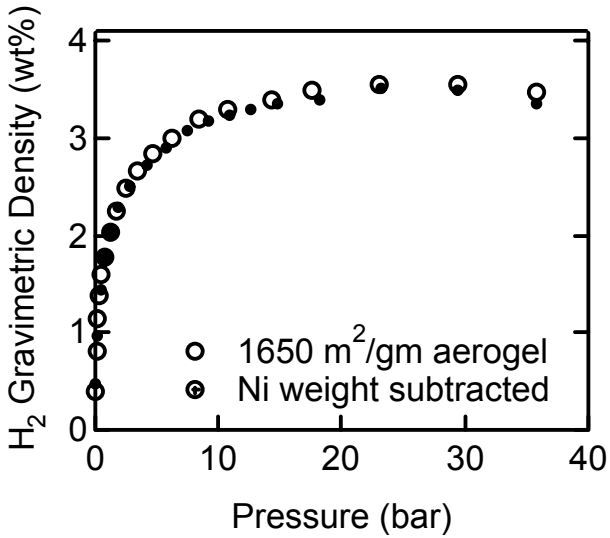
*``Toward New Candidates for Hydrogen Storage: High-Surface-Area Carbon Aerogels," Houria Kabbour, Theodore F. Baumann, Joe H. Satcher, Jr., Angelique Saulnier and Channing C. Ahn, Chem. Mater. 18 (26), 6085 (Dec. 2006).

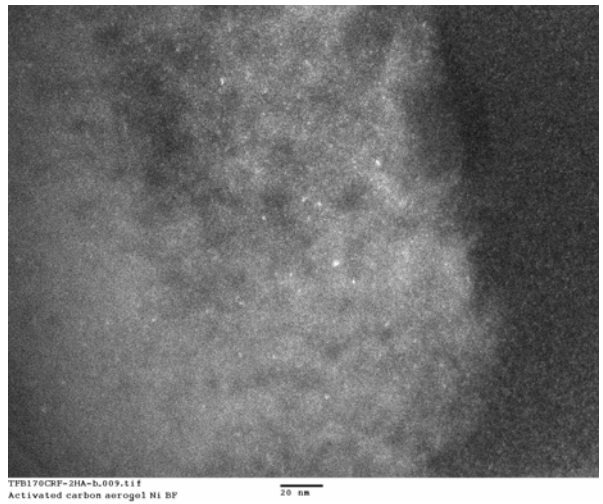
Technical accomplishments: Isotherm analysis (Ni catalytic additions)

- Previous work at right showed that catalytic additions have been shown to enhance sorption over that of similar surface area materials*.
- Plot at left compares 77K isotherms of lower surface area catalytically active (Ni catalyst has clean surfaces) aerogel with that of a higher surface area non-catalytically active aerogel (Ni catalyst particles are encased in graphitic carbon, rendering them inactive) .
- Attempts at post aerogel activation Ni salt impregnation and reduction have not as yet improved sorption behavior as seen in isotherms below. Dark Field micrograph shows typical Ni catalyst microstructure from our impregnation processing.



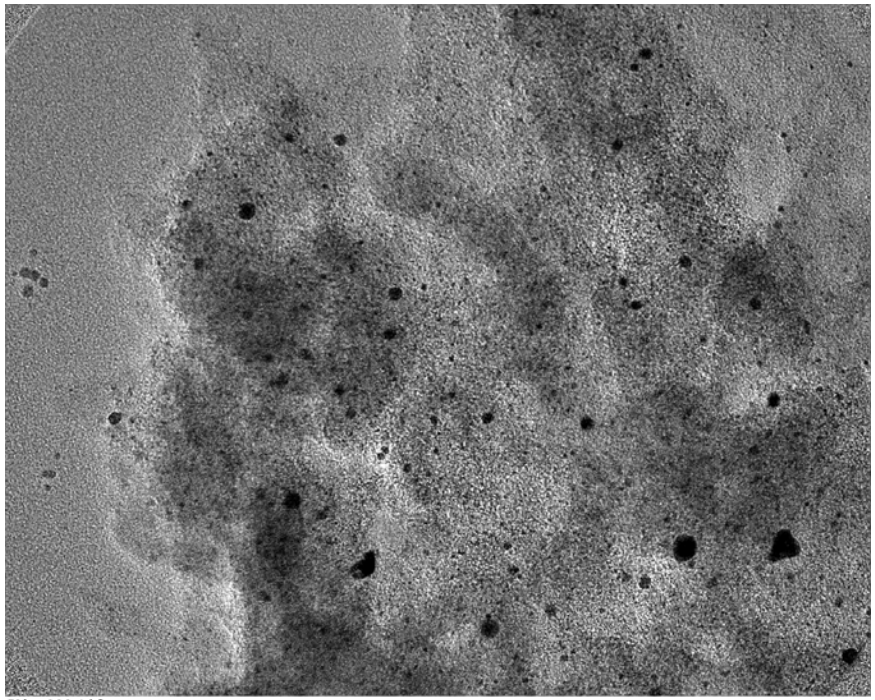






*Effect related to work of J. Schwarz of Syracuse, “Metal assisted cold storage of hydrogen,” U.S. patent 4,716,736.

Technical accomplishments: Isotherm analysis (Pt catalytic additions)



CAhn_002.tif
Pt TFB206
sample 1
Print Mag: 360000x @ 7.0 in
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TEM Mode: Imaging

20 nm
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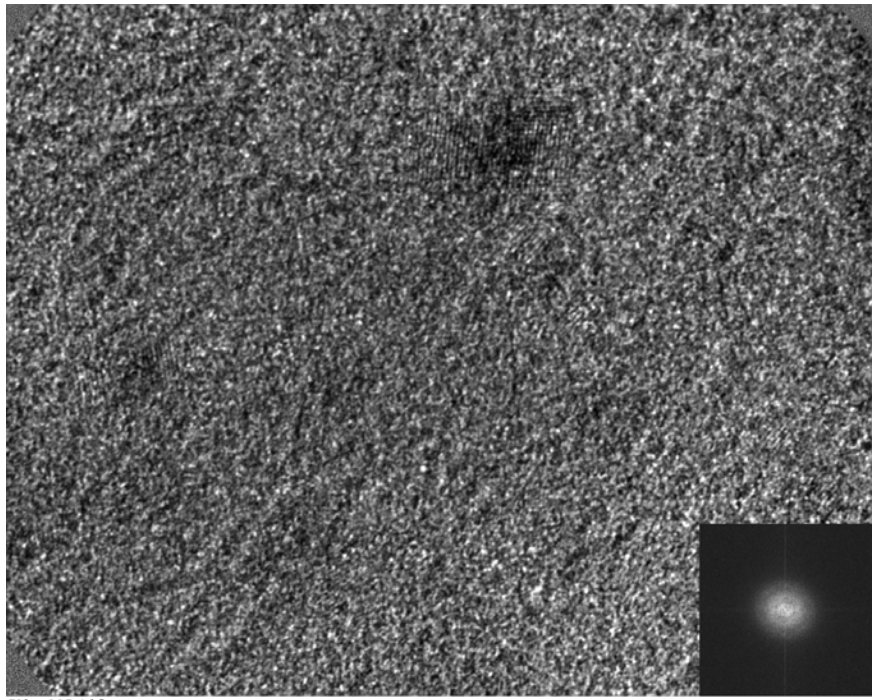
Direct Mag: 259000x
TF30U



CAhn_005.tif
Pt TFB206
Sample 1
Print Mag: 4350000x @ 7.0 in
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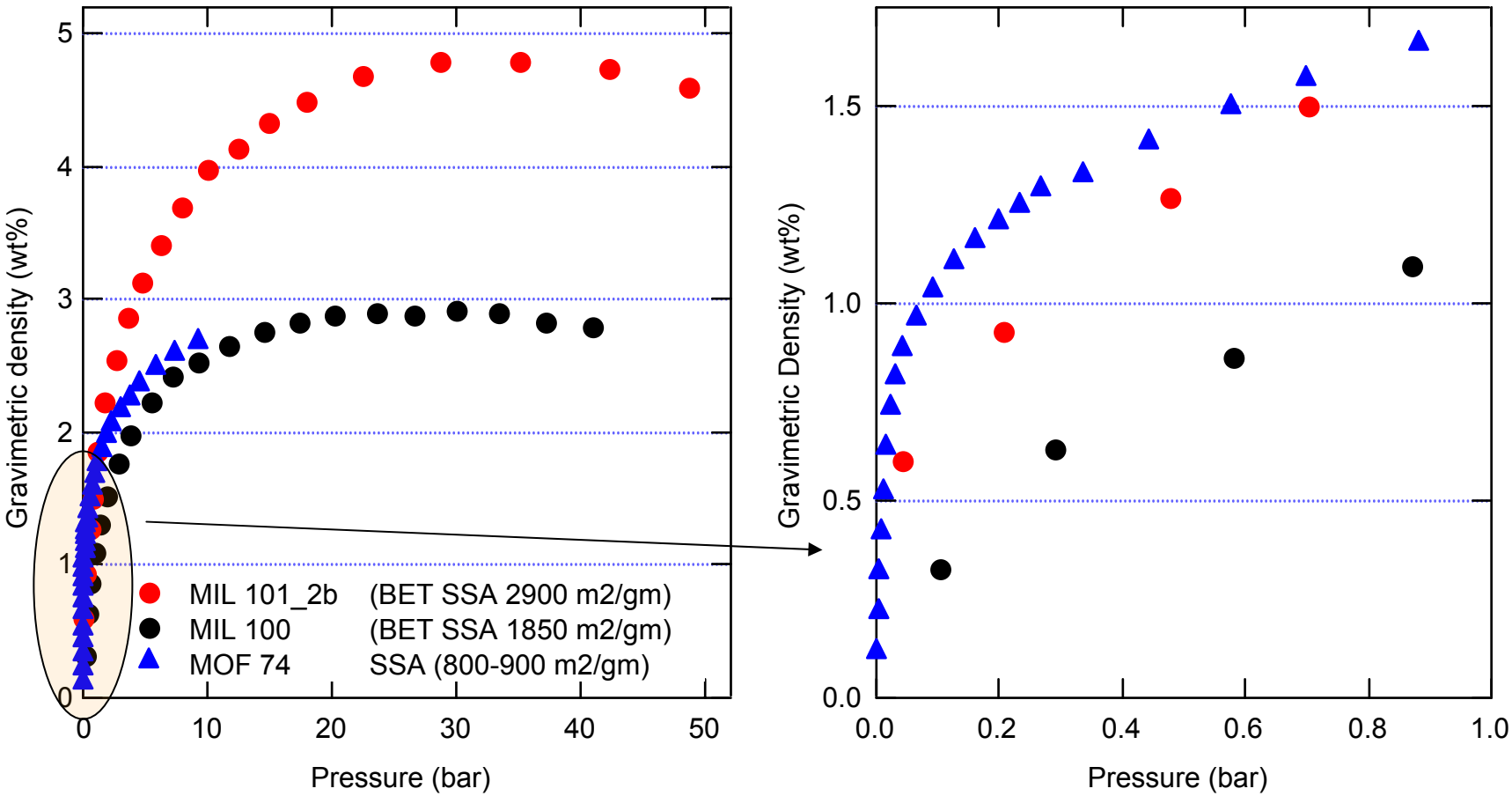
TEM Mode: Imaging

5 nm
HV=300kV
Direct Mag: 3135000x
TF30U

- Pt salt reduction in carbon aerogel work is continuing and low temperature reduction (350°C) results are shown above in a Bright Field image on the left and a high resolution image on the right.
- Reduction and crystallization of the Pt have occurred but other processing conditions that will promote particle faceting to maximize dissociation are presently being carried out.

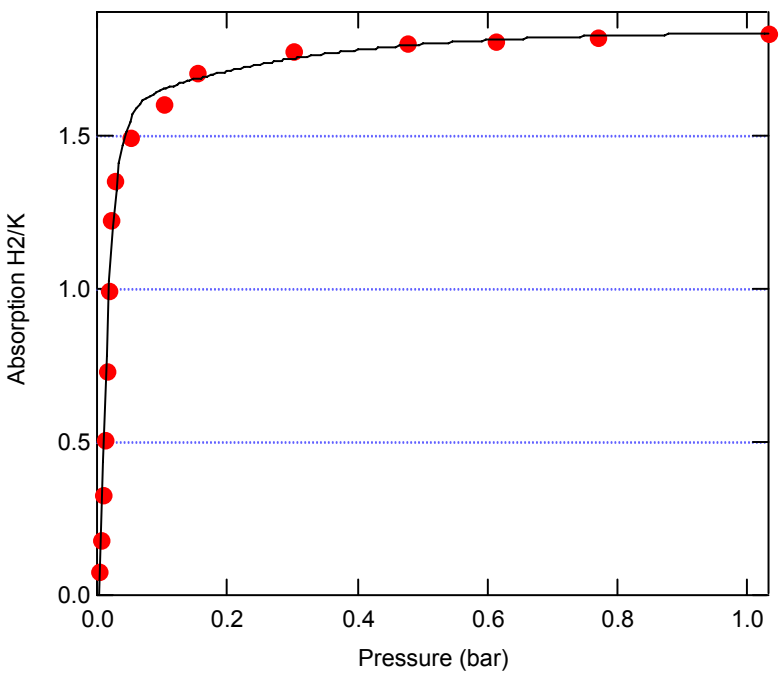
Technical accomplishments: MIL-100, MIL101 and MOF74 synthesis, isotherms and analysis



- Work being continued on high surface area framework structures and our reproducible synthesis and isotherm behavior in have been achieved in MIL-100 and MIL-101 structures. BET surface area and 77K isotherm data are shown on the left.
- Right plot shows an enlargement of the low pressure regime. Higher slopes in this regime are an indication of higher Henry's law regime, differential enthalpy of adsorption at zero coverage. This material is being evaluated at NIST to determine the high enthalpy sorption sites.

Technical Accomplishments: High ΔH analysis

The paradigm for desired isotherm behavior are still intercalated graphites. Shown below is our isotherm (Langmuir behavior typical) for KC24 which shows complete uptake at 77K at under 1 bar pressure. Note the sharp "knee" in the isotherm at below 0.2 bar pressure.



While a 10 to 12 kJ/mole system, the layered geometry of this system can still provide insights into sorption behavior for technologically relevant systems.

In this case, the maximum uptake we can expect is 1.2 wt%.

Planned Work for FY2006/FY2007

- Continued collaboration with LLNL on aerogel analysis including:
  - Further incorporation of catalysts in higher surface area aerogels to improve gravimetric densities over the 5.6wt% presently achievable.
  - Continued synthesis and activation of MIL (Material Institut Lavoisier) and other high surface area structures to improve gravimetric densities.
- Optimization of pore size/volume in order to maximize volumetric density. An ideal graphitic structure with a 1.1 nm pore size can accommodate as much as 7.7 wt% gravimetric and, from 44 to 58 gm/liter volumetric density.
- Continuation of evaluation of thermodynamic properties (isosteric enthalpy of adsorption and differential enthalpy of adsorption at zero coverage).

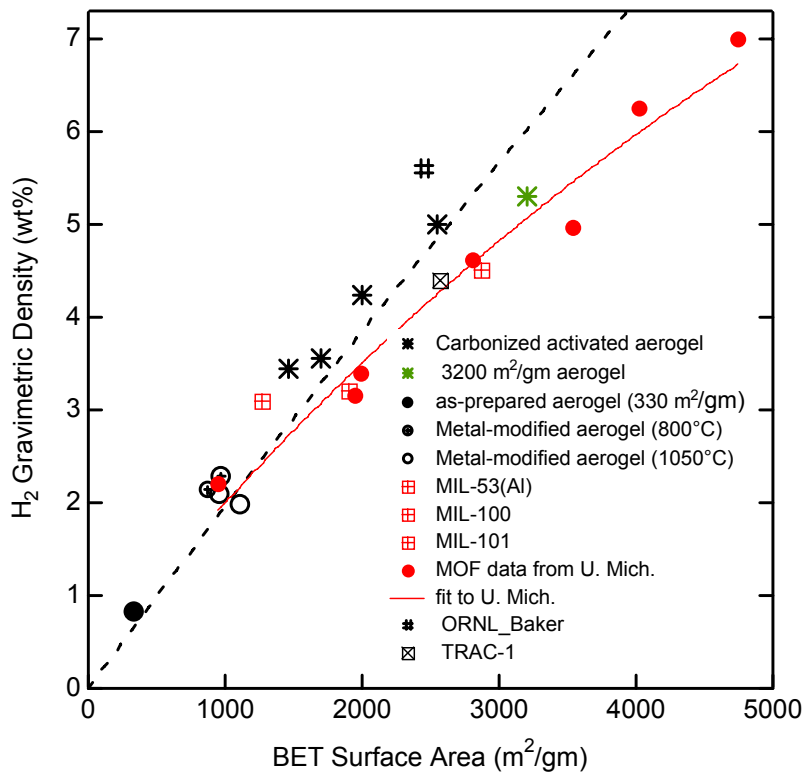
Project Summary

- Relevance: Physiorbents for non-dissociative hydrogen storage offers higher storage densities than compressed gas storage.

- Approach: Synthesis of high surface area physisorbents (in order to achieve gravimetric densities of 7.7wt%) with tailored pore size (to reach volumetric densities of 58 gm/liter) and high adsorption enthalpies (ambient temperature operation) our key goal.

- Technical accomplishments and progress: Study of large range of carbon based materials including activated carbon, aerogels and metal organic frameworks to show that gravimetric densities scale with surface area and that these materials have sorption enthalpies of 4-8 kJ/mole.

- Collaborations: JPL, LLNL, ORNL, NREL, NIST



Shown above is a summary of the materials we have measured and/or synthesized compared with literature data, showing the trend of gravimetric density vs BET surface area.

Project Summary

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)				
Storage Parameter	**Units**	**2010 System Target**	**FY07 materials****	
Specific Energy	kWh/kg (wt. % H2)	2.0 (6 wt.%)	1.91 5.6 wt% at 77K	
Volumetric Energy Capacity	kWh/L	1.5	1.28	