

NREL Activities in DOE Carbon-based Materials Center of Excellence

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May 25, 2005

This presentation contains no proprietary information

Overview: Timeline and Budget

Timeline

- Work at NREL since FY93
- Center of Excellence start date: FY05
- Center of Excellence end date: FY09
- Percent complete: 10%

Budget

- Project funding
 - \$27.5 M for five-year Center of Excellence
 - \$2.5 M Contractor share (20% of Contractor budget)
 - \$2 M in FY04 for NREL
 - \$2 M in FY05 for NREL

Overview: Barriers & Targets

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.
- O. Test Protocols and Evaluation Facilities.

Crosscutting Relevance

Compressed Gas Systems Barrier H: Sufficient Fuel Storage for Acceptable Vehicle Range.

Off-Board Hydrogen Storage Barriers S & T: Cost and Efficiency

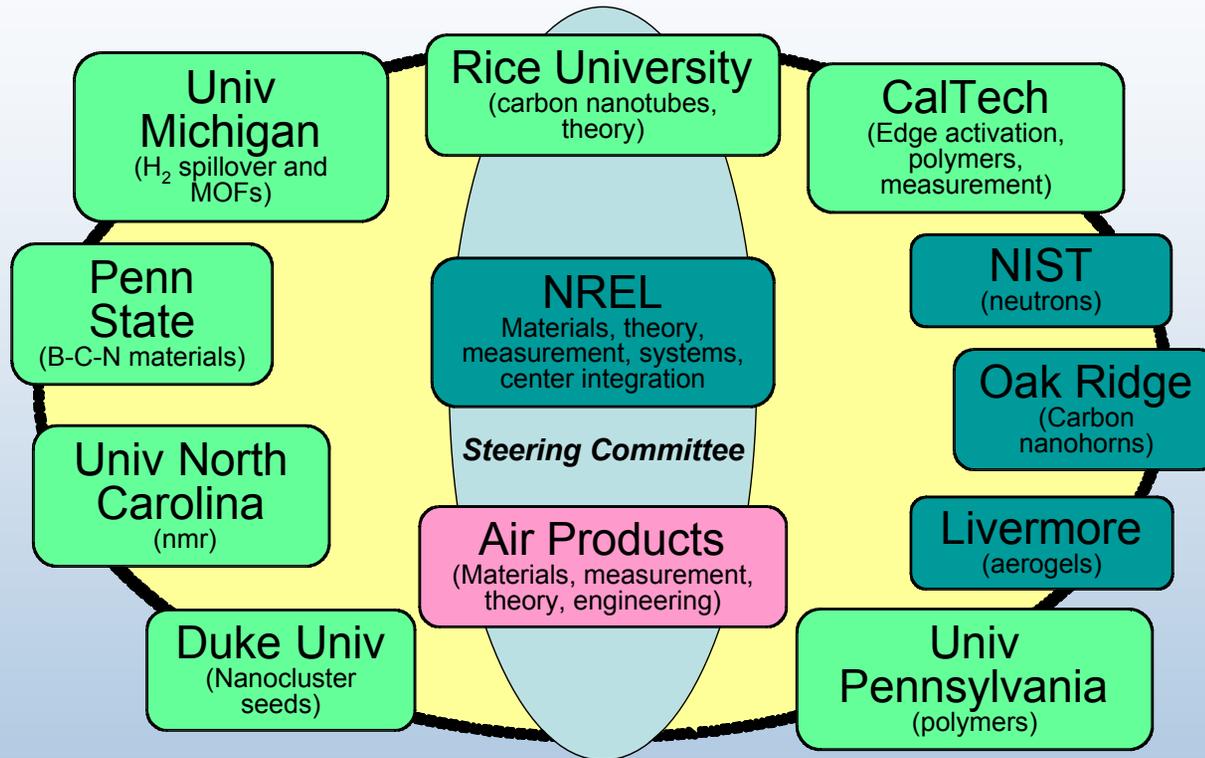
DOE 2010 Technical Targets for Storage System

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

Overview:

CoE Interactions & Collaborations

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



Also: IEA Annex 17 (R. Chahine, K. Ross), SwRI, Stanford GCEP, U. Minn. IREE, NIST, NASA, Virginia Commonwealth U. (G. Glaspell), Chinese Academy of Sciences (H.-M. Cheng), Argonne National Lab (R. Ahluwalia), synergy with two BES projects at NREL

Organization of Conferences: IPHE (Lucca, 6/'05), MRS (Fall '04, Fall '05, and Spring '05)

Objectives

Themes of CbHS Center of Excellence

- Develop conducting and boron/carbon polymers, MOFs, carbon nanohorns, nanotubes and aerogels, and carbon-metal hybrid 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)

Continuum of H Binding Energies

and three Centers of Excellence

CbHS CoE

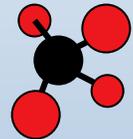
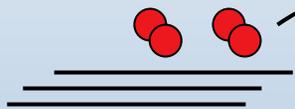
**Binding energies of interest:
10 - 50 kJ/mol**

**Metal hydrides
50 - 100 kJ/mol**

**Chemical hydrides
> 100 kJ/mol**

graphite-H₂
physisorption
(4 kJ/mol)

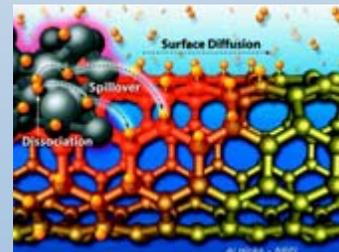
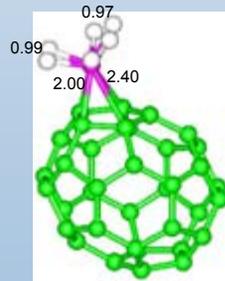
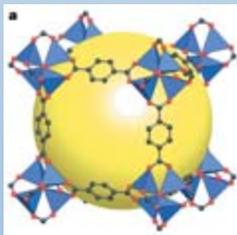
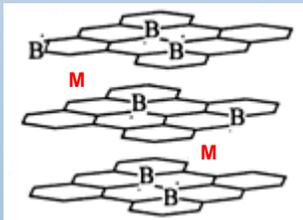
Methane
(~ 400 kJ/mol)



"Kubas" binding

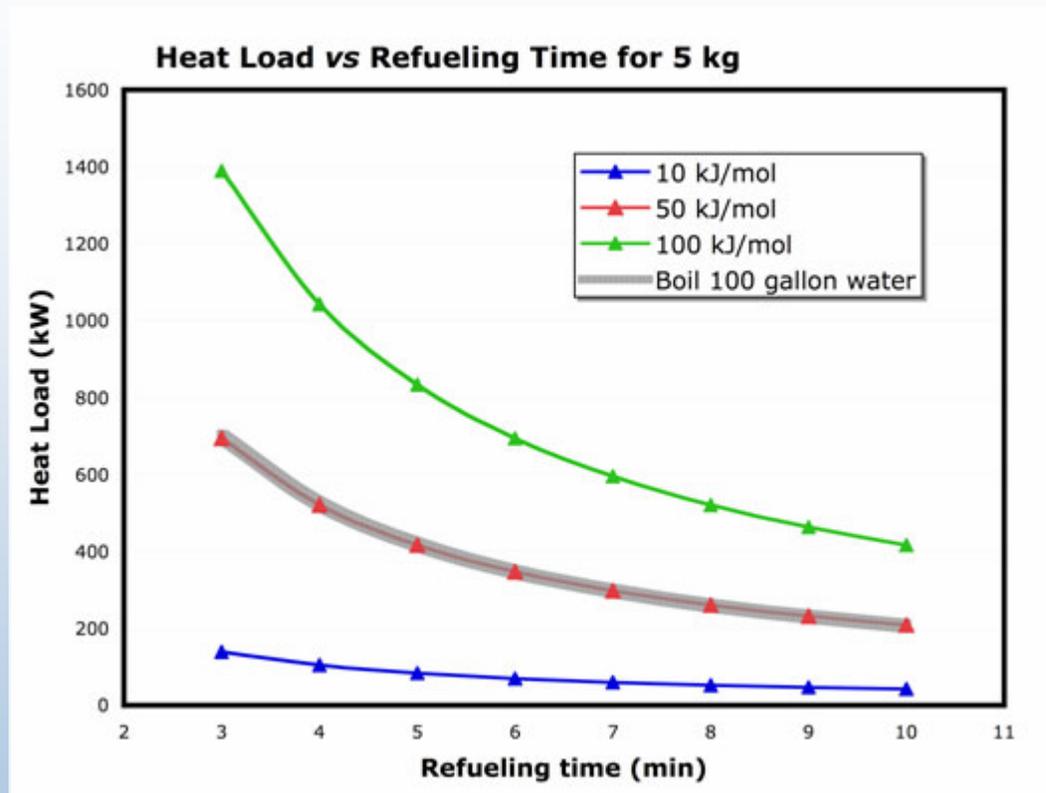
"spillover"

Enhanced physisorption



CbHS CoE: Nanostructural design of electronic & bond strain effects

Binding Energy Impacts System Design

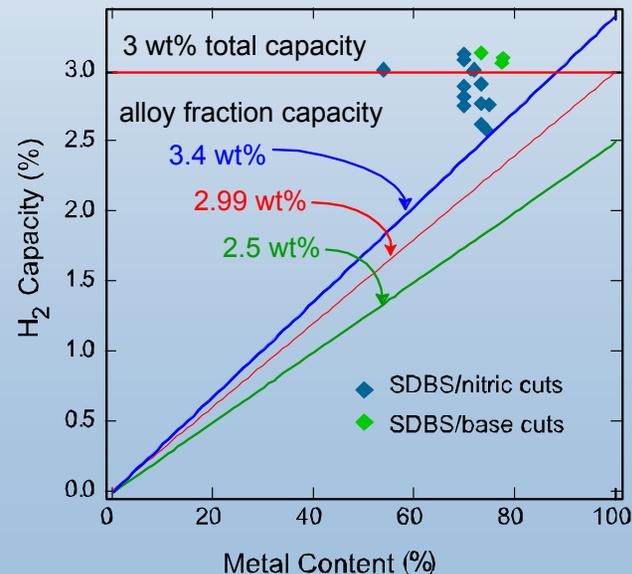
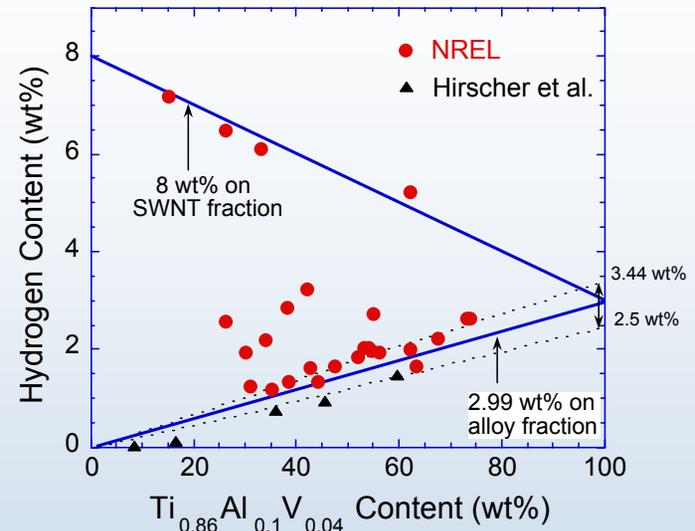


A large binding energy will lead to energy penalties during charge & discharge, prohibit on-board recharging, and reduce system capacities (heat exchangers)

Approach: Reproducible Activation

- Probe-sonicated SWNT/alloy hybrid data was scattered
- Up to 8 wt% H on tube fraction
- Contribution of alloy measured to be 2.5 wt% H
- Maximum on alloy 2.99 wt% (literature) or 3.4 wt% (TiH_2 fraction @ 4 wt%)

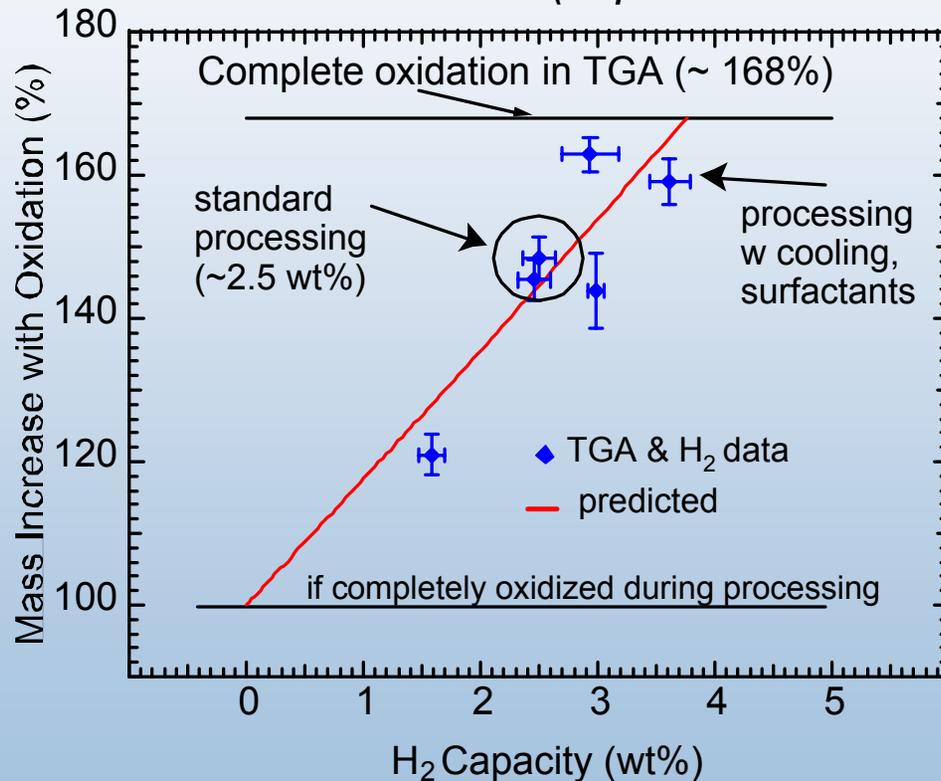
- Generated 3 wt% samples consistently with optimization
- Employed surfactants and cooling during sonication
- XRD reveals lack of alloy oxides
- Unoxidized alloy fraction adsorbs ~3.8 wt% H (Feb. 05 milestone)
- No significant uptake on tubes



Accomplishment: Measured Uptake of Alloy/Alloy Oxide vs Processing

- Oxide coating on alloy particles is a function of processing
- 3.8 wt% on pure alloy measured for the first time

(importance to nuclear industry)

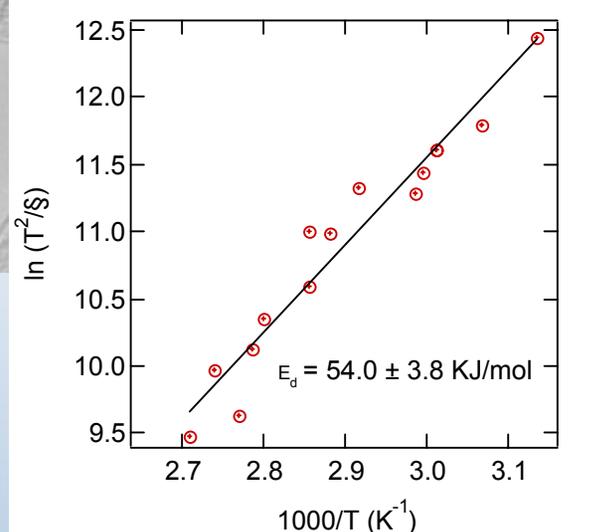
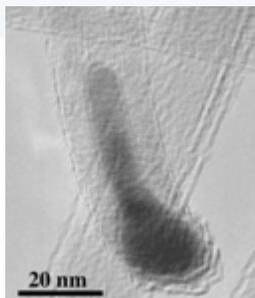
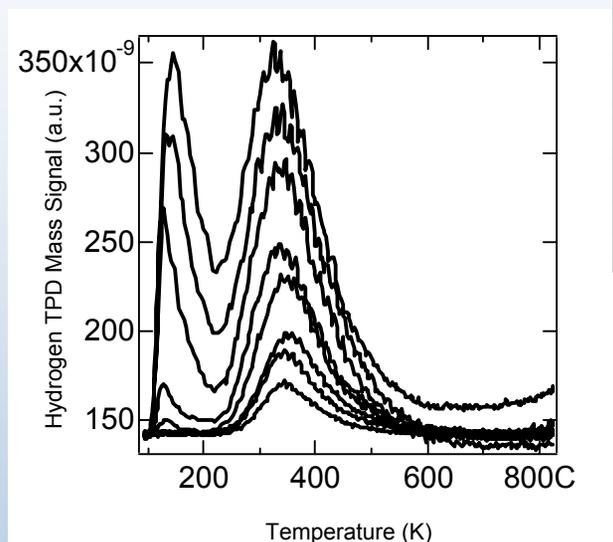


4 wt% H milestone will likely not be met with this approach (EOFY05)

Approach: Reproducible Activation

MWNTs by hot-wire CVD (A. Dillon et al.)

- Fe is in intimate contact with aromatic carbon



Peak desorption temperature does not shift with coverage:

- first order desorption - adsorbed molecular H₂

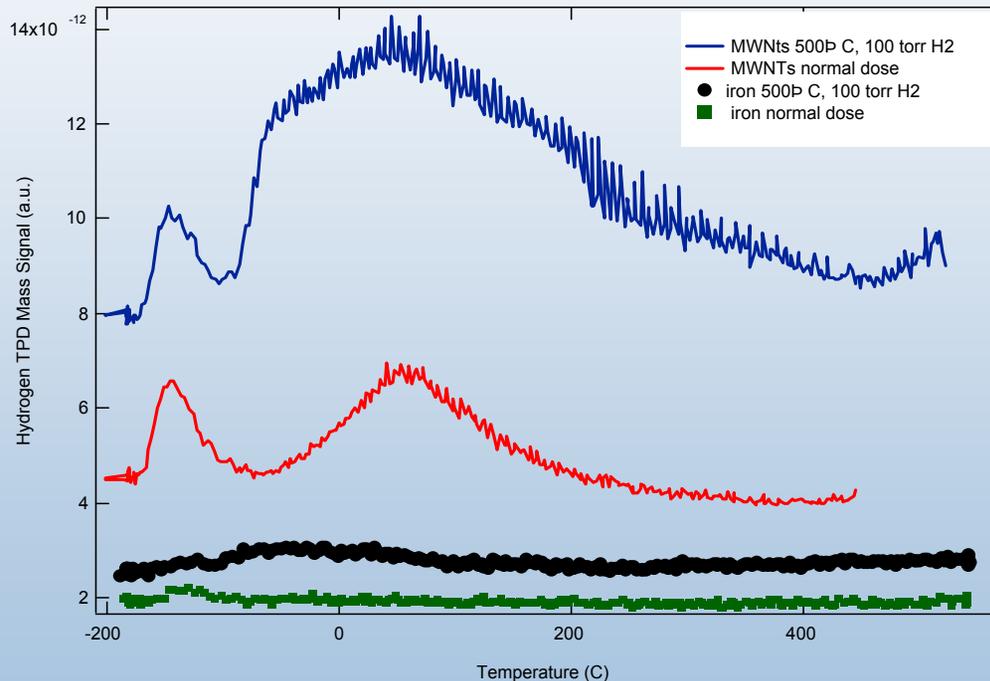
Desorption activation energy:

$$\ln(T_m^2/\beta) = E_d/RT_m$$

- binding energy of ~54 kJ/mol.

Activation without Metal-Hydride Incorporation

As-synthesized MWNTs vs Fe powder control
Fe is not a known metal hydride

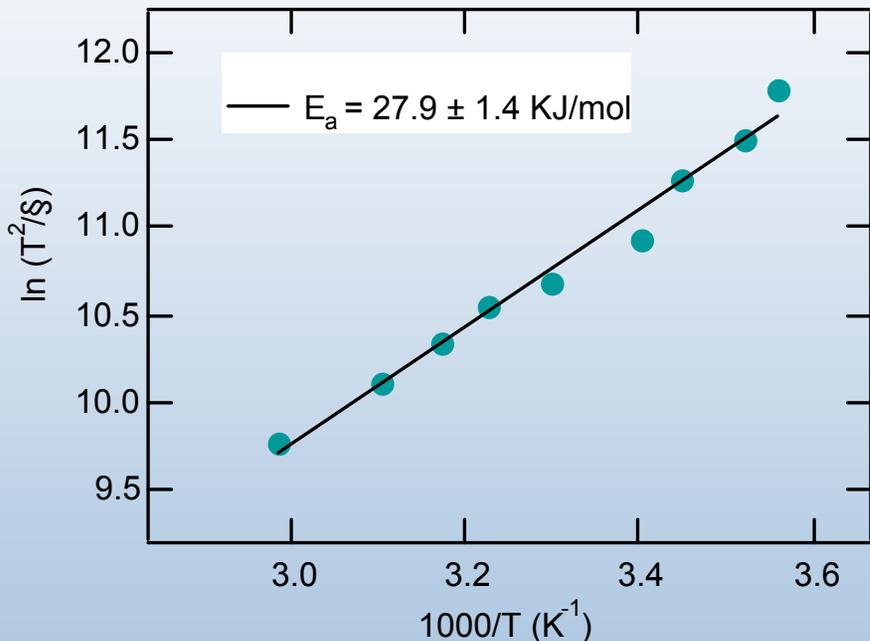


Normal Dose: Degas 825 K in vacuum, 500 Torr H₂ at room temperature

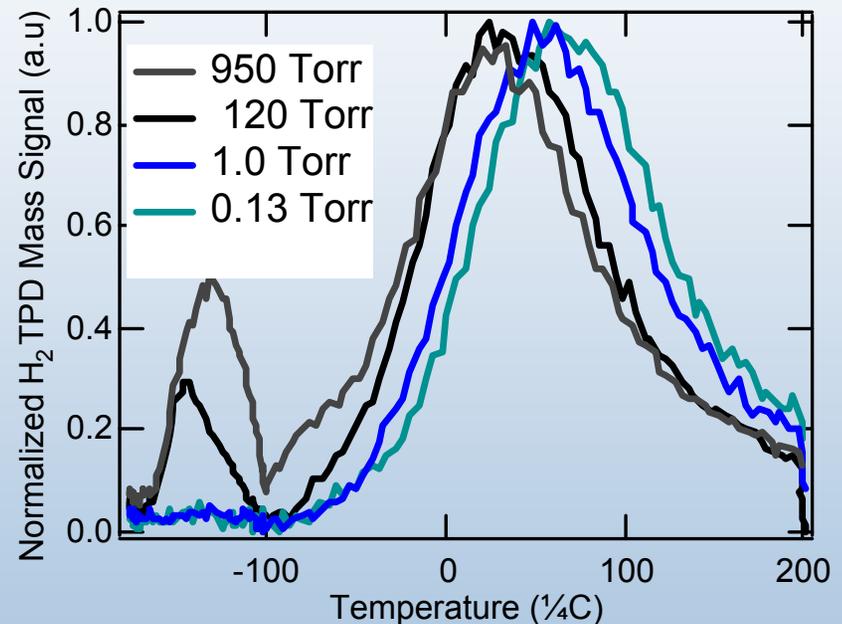
Reduction: Anneal to 775 K in 100 Torr H₂ for 10 min., Degas 825 K in vacuum, 500 Torr H₂ at room temperature. **Increase capacity to ~ 0.035 wt%.**

Organometallic, Solution Phase Synthesis

UV photolysis of Co_2CO_8 w SWNTs



500 Torr H_2 at room temperature

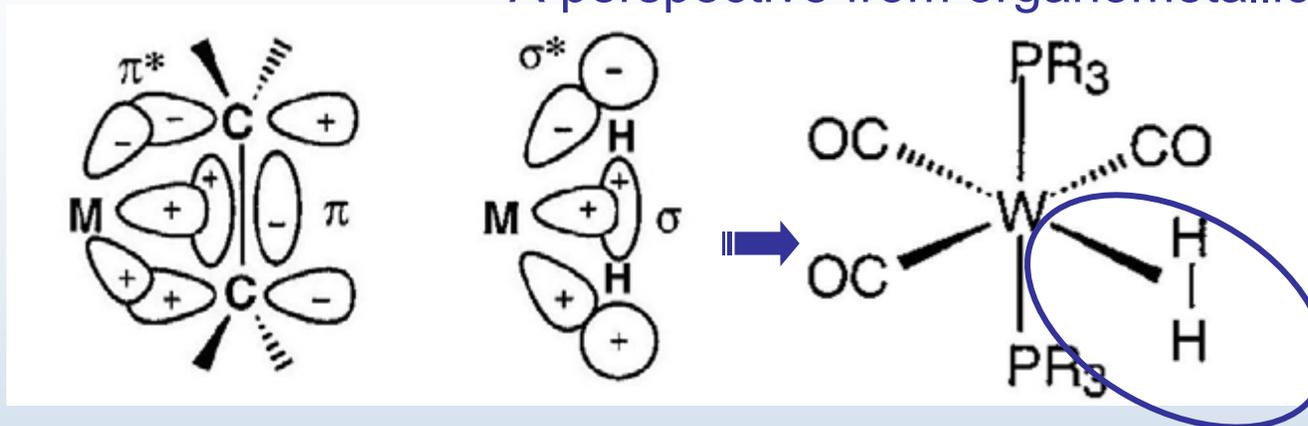


Shift to higher peak desorption temperature at low coverage.

Low capacity, but proof of concept

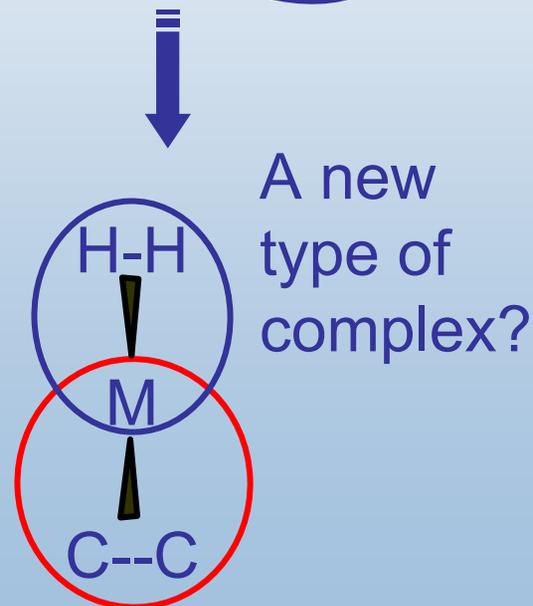
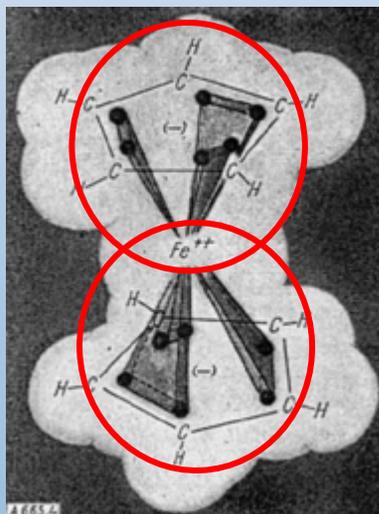
Approach: Rational Design of Adsorbents

-- A perspective from organometallic chemistry



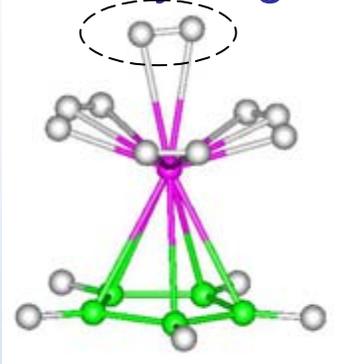
Kubas, *J. Organometallic Chem.* **635**, 37 (2001)

Fischer and Jira,
J. Organomet Chem.
637, 7 (2001).



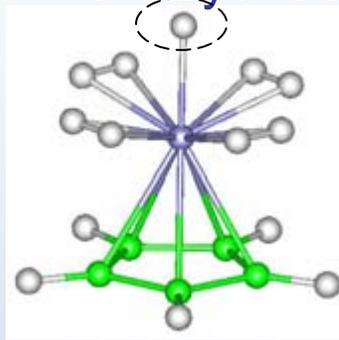
Calculated Structures of Hydrogen Saturated Cyclopentadiene (Cp) - [MHx] Complexes

Dihydrogen



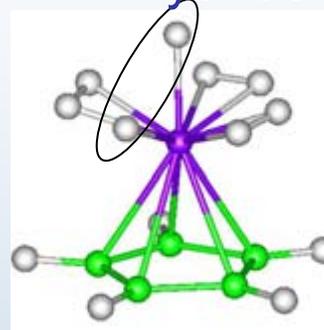
Sc

Monohydride

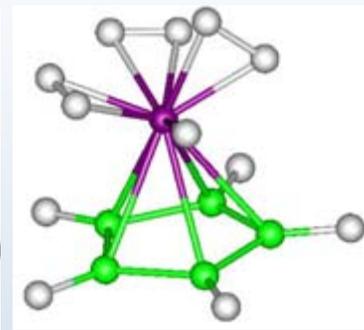


Ti

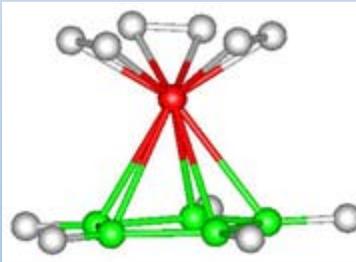
Dihydride



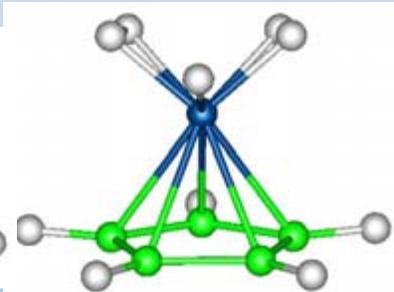
V



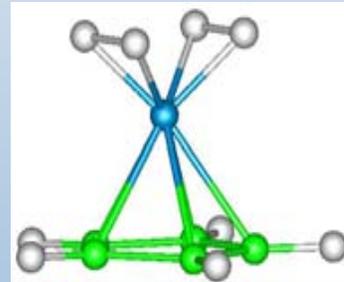
Cr



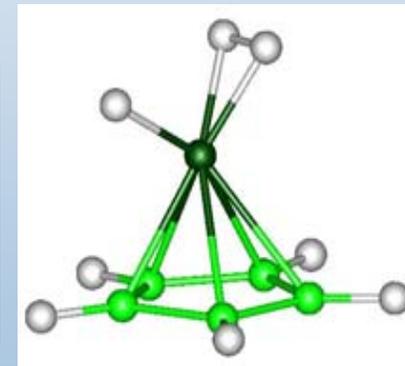
Mn



Fe



Co



Ni

Different H capacities for the different first row transition metals

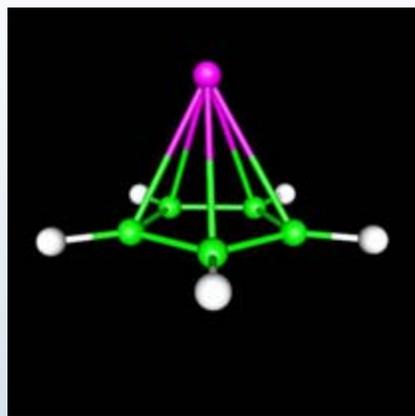
18-e Rule and Cp-TM Binding

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
n_v	3	4	5	6	7	8	9	10
N_H	10	9	8	7	6	5	4	3
$E_b(kJ)$	360	371	333	221	258	285	314	389

- 18-e rule: $n_v + N_H + 5 = 18$
 n_v : number of valence electron in metal atom;
 N_H : number of hydrogen atoms bound;
5: number of π electrons in the Cp ring.
- Sc binding to Cp: second largest E_b .

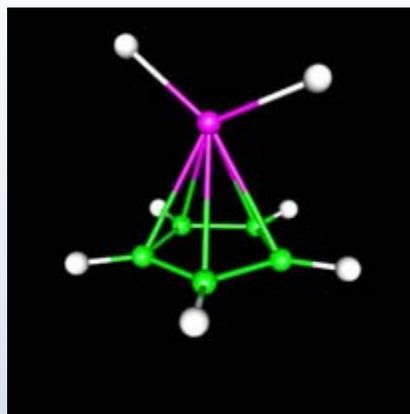
Reversible 6.7 wt% Storage

Stable "host" material



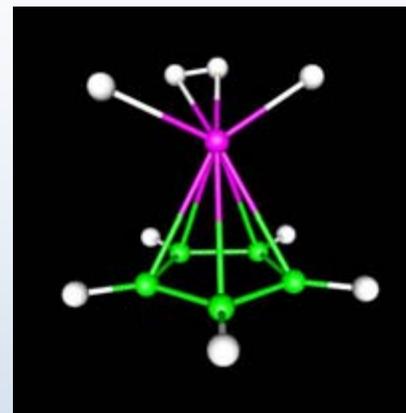
CpSc

+ H₂
124 kJ



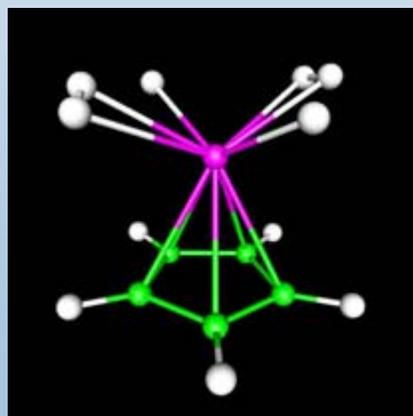
Cp[ScH₂]

+ H₂
30 kJ



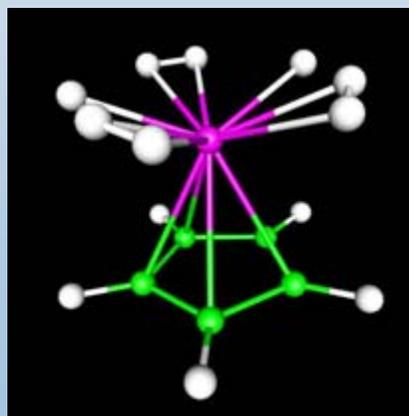
Cp[ScH₂(H₂)]

+ H₂
27 kJ



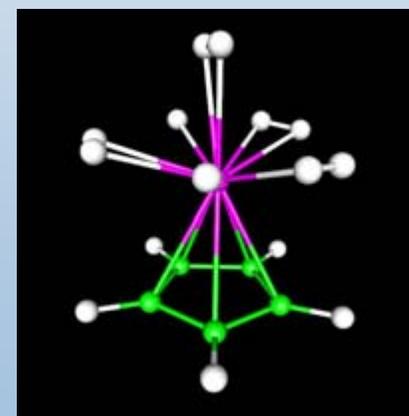
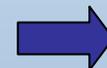
Cp[ScH₂(H₂)₂]

+ H₂
44 kJ



Cp[ScH₂(H₂)₃]

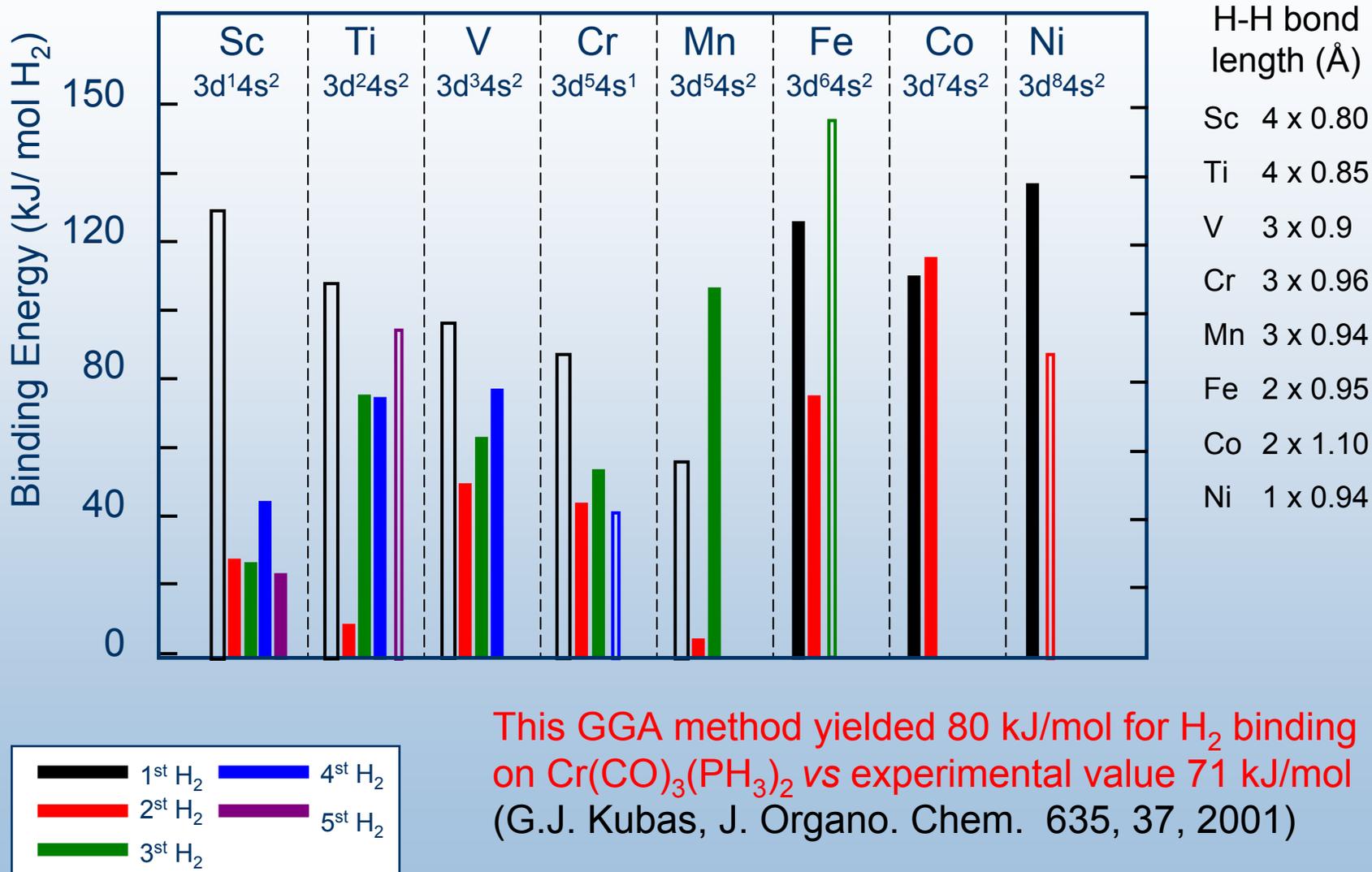
+ H₂
22 kJ



Cp[ScH₂(H₂)₄]

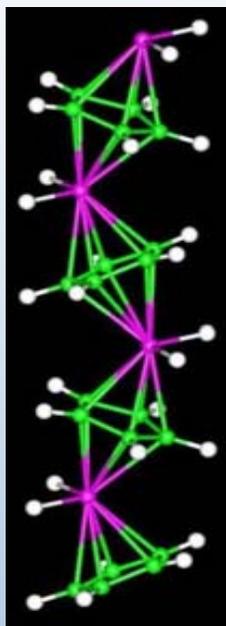
16

Energetics of Cp:TM-H₂ Binding



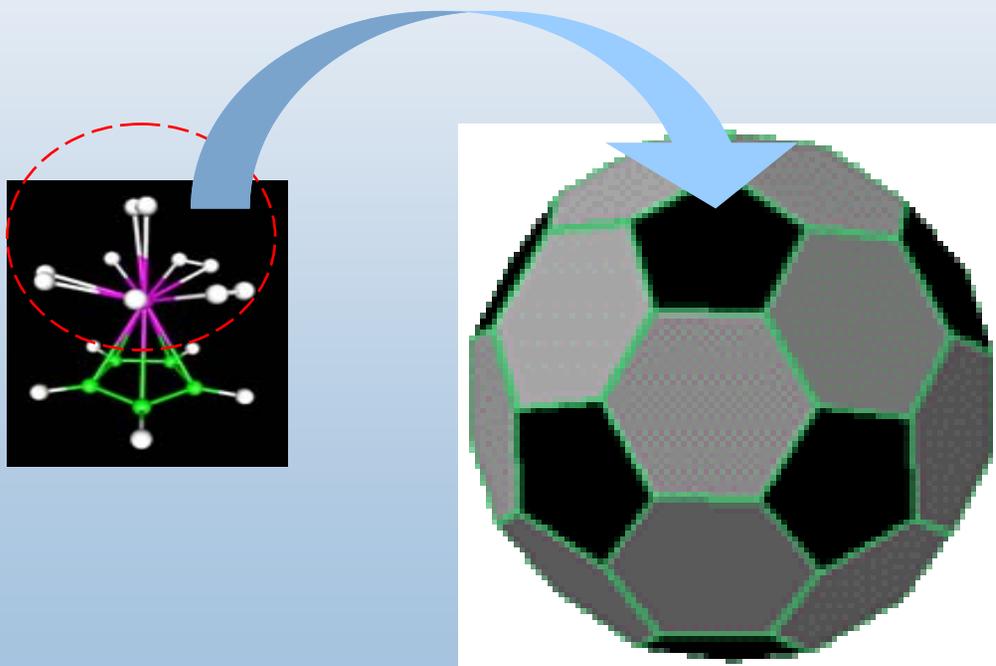
Integration with Carbon Frameworks

To avoid polymerization.....



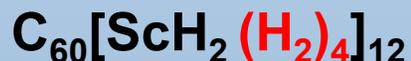
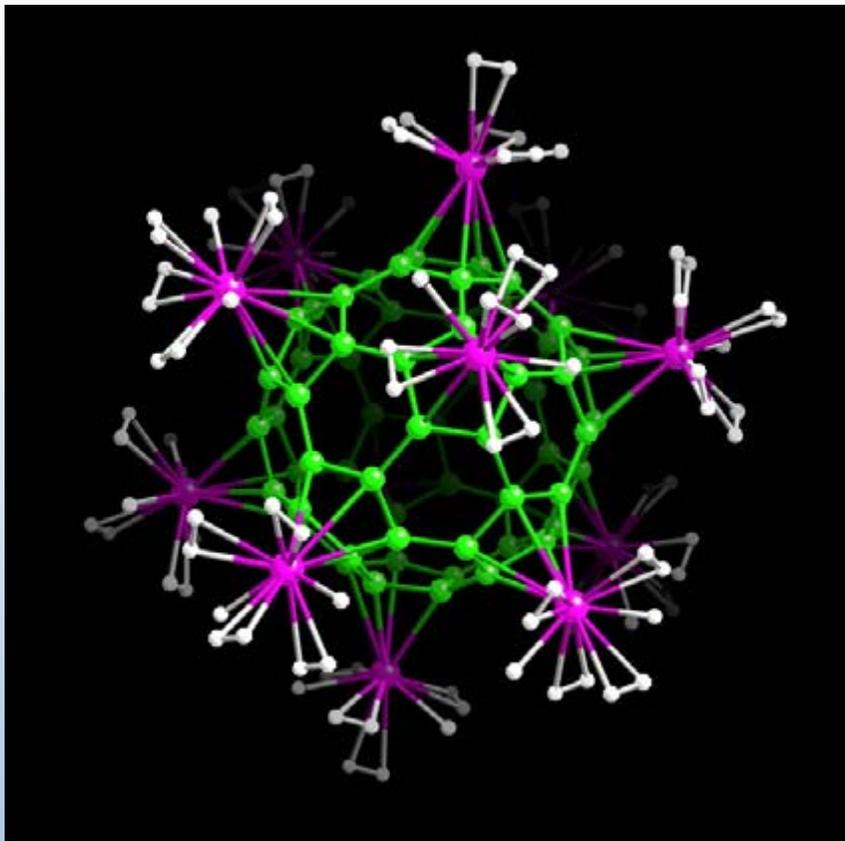
$\text{Cp}[\text{ScH}_2]_{\text{chain}}$

...transfer TM:H cluster to carbon framework (i.e. the pentagons of C_{60})



Route to 7 wt% Reversible Storage with Carbon-based Adsorbents

Metal-coated Fullerenes



Stable Scandium organo-metallic complex represents a compound that stores a total amount of hydrogen at 8.7 wt%, 7.0 wt% reversibly.

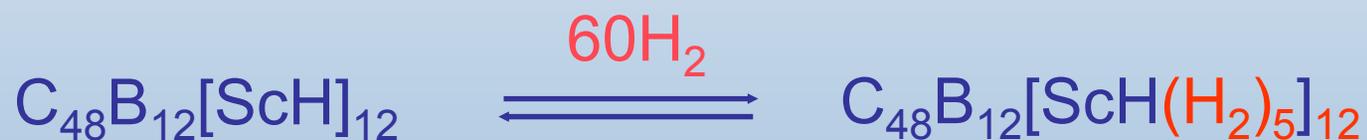
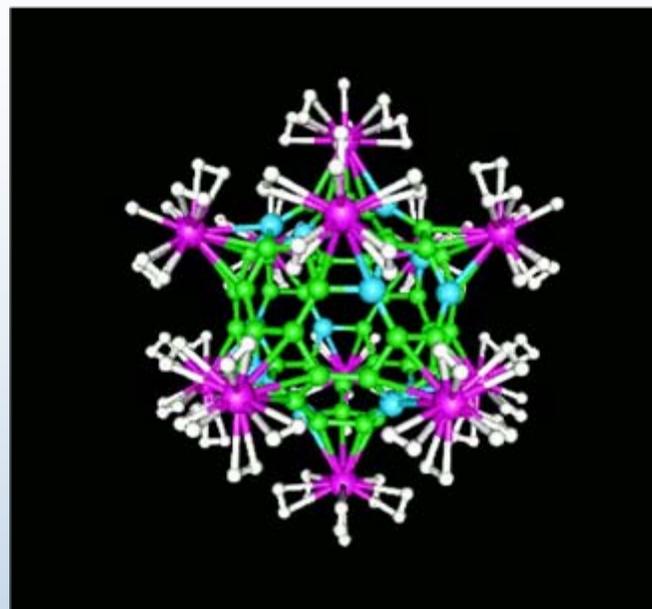
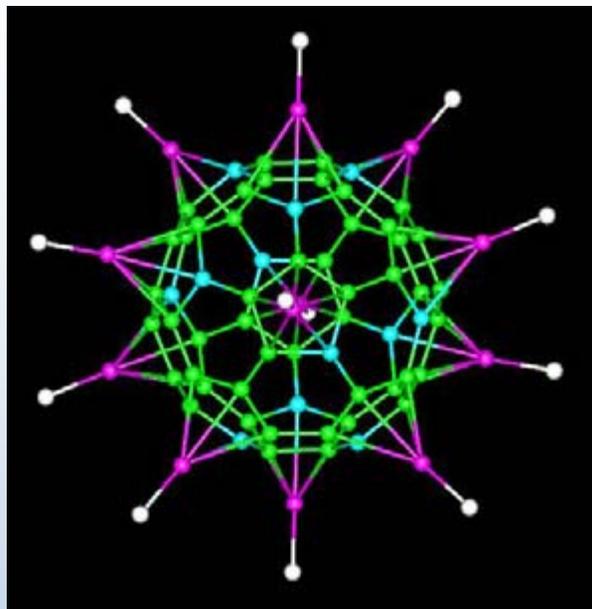
Minimum Energy Structure with regions around the 5-membered rings that have aromatic character.

Without TMs, C_{60} has aromatic character around the 6-membered rings.

J. Poater, M. Duran and M. Sola Int. J. Quant. Chem. 98 (2004) 361

Y. Zhao, Y.-H. Kim, A.C. Dillon, M.J. Heben, and S.B. Zhang, PRL **94**, 155504 (2005)

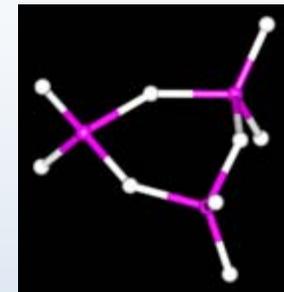
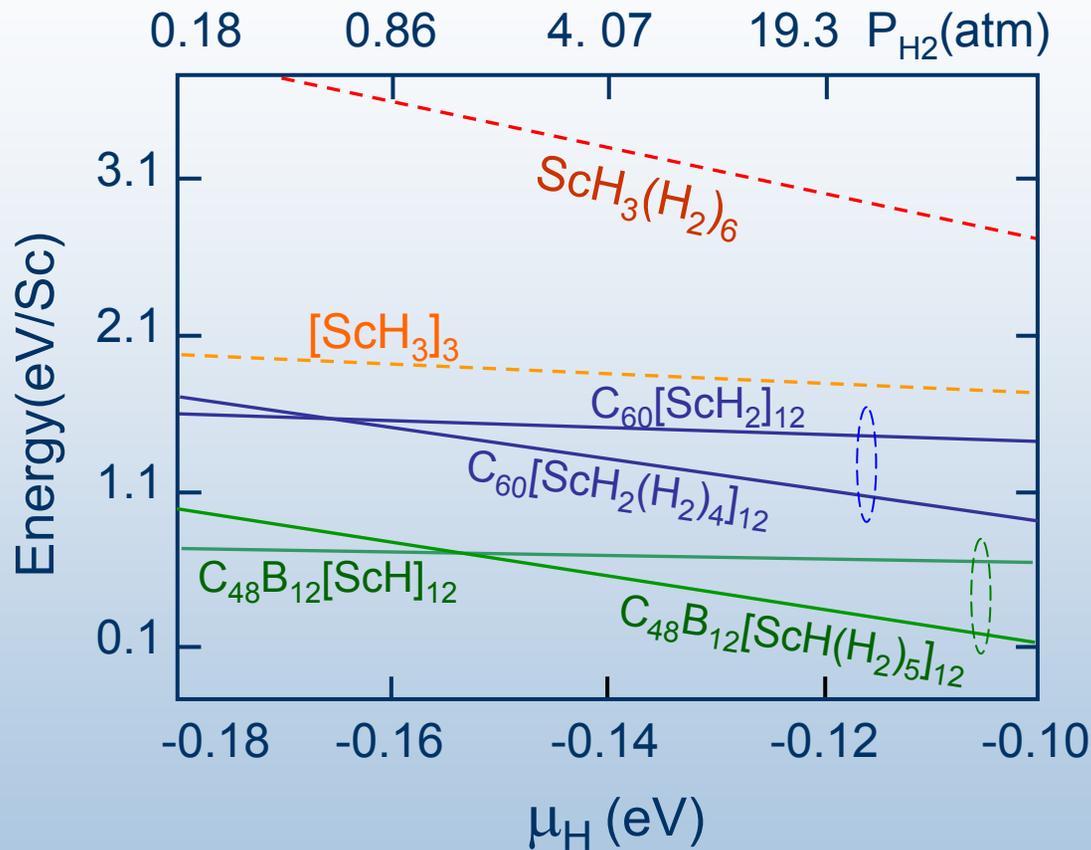
Route to 8.8 wt% Reversible Storage with B-doped C₆₀



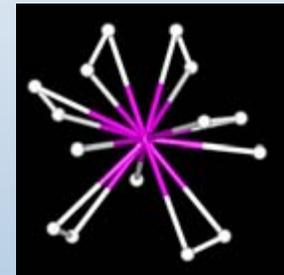
One more electron transferred from a Sc to the pentagon

- a) Enhanced Sc-C₆₀ binding;
- b) Increased capacity;
- c) 43 kg H₂/m³ without efficient packing (conformal)

Reversible Storage at Room Temperature



$Sc[H_3(H_2)_6]$

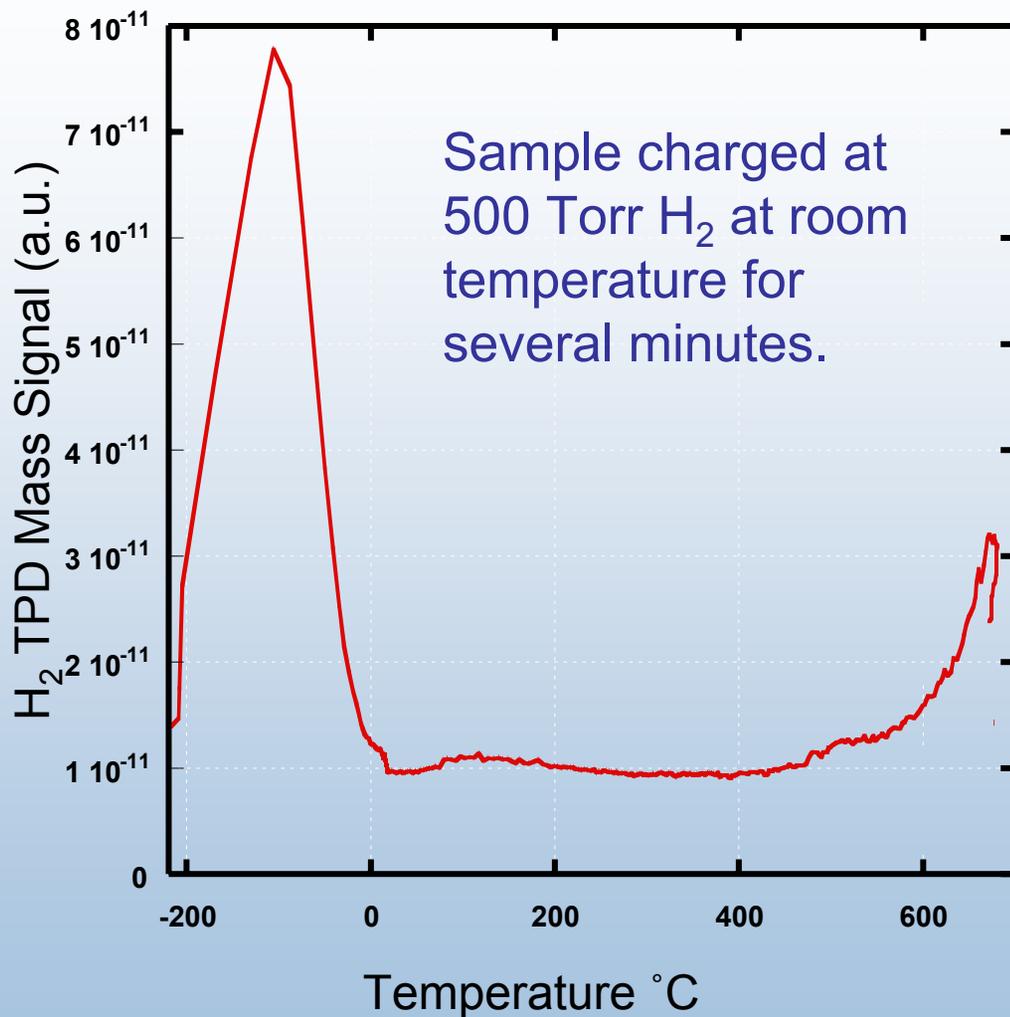


$[ScH_3]_3$

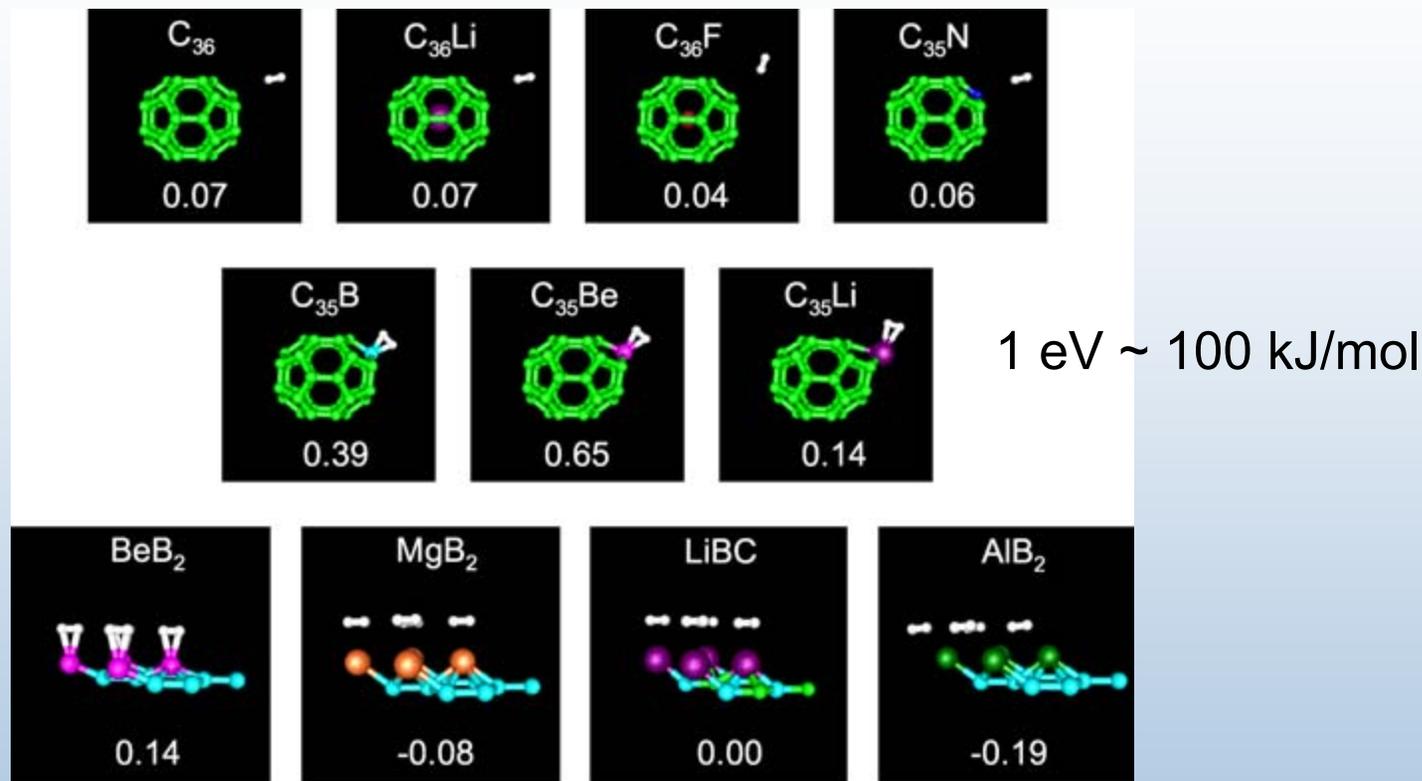
- Charge/release is switched at ~ 1 atm, $T=300K$;
- Storage materials are stable

Preliminary Data on an Sc / Carbon System

- Laser vaporization of graphite target doped with Cp_3Sc
- Enhanced low temperature adsorption peak
- Capacity must be evaluated with overpressure



Substitutional Doping: DFT within Local Density Approximation



- LDA typically overbinds, whereas GGA typically under binds
- MP2 study showed LDA results are significantly closer¹
- State-of-the-art fixed node, diffusion quantum Monte Carlo (QMC) calculations, performed by A. Williamson (LLNL), agrees

¹Y. Okamoto et al., J. Phys. Chem. B 105, 3470 (2001).

Synthesizing Boron-doped Nanostructures

CVD

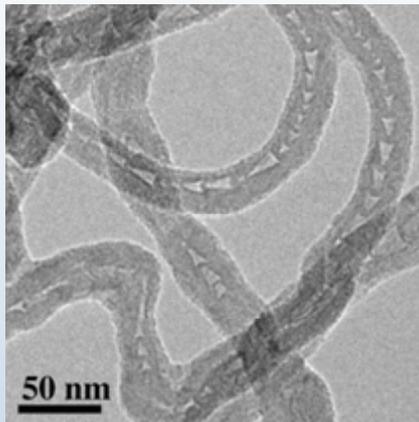
- Sources
 - $(C_6H_5)_3B$
 - $(CH_3)_3N \cdot BH_3$
 - $(CH_3)_3B_3O_3$
- HWCVD
 - Decomp. Of B source and ferrocene
- CVD
 - Decomp. Of B source over Fe-Mo catalysts

Laser and Arc

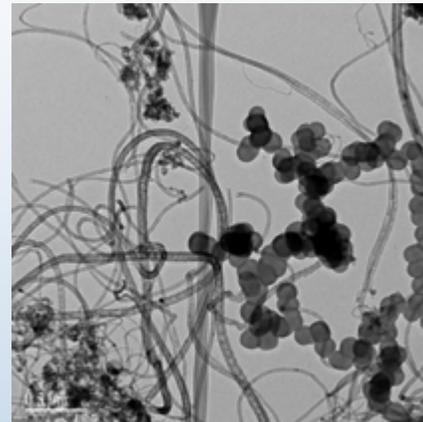
- Laser ablation dopants
 - B: low yield NTs
 - BN: low yield NTs
 - B_4C : low yield NTs
 - Gas phase dopants: onions and MW cages
 - high yield SWNTs with certain catalysts
- Arc dopants
 - High yield SWNTs with certain catalysts

Adsorption on B-doped Nanostructures

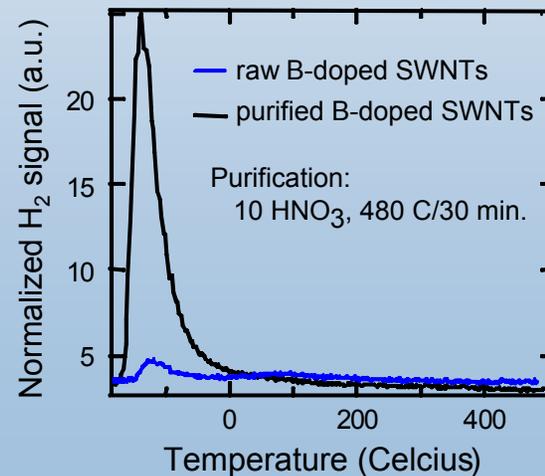
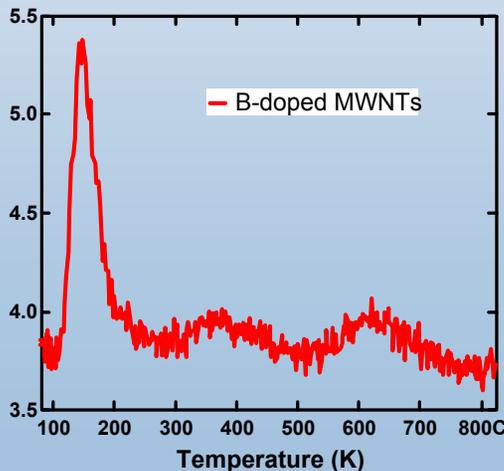
Bamboo-like MWNTs
from HWCVD



Conventional CVD using
 $(\text{CH}_3)_3\text{N}\cdot\text{BH}_3$



TPD
spectrum
shows two
high energy
binding sites
on MWNTs
in addition to
low-T
adsorption

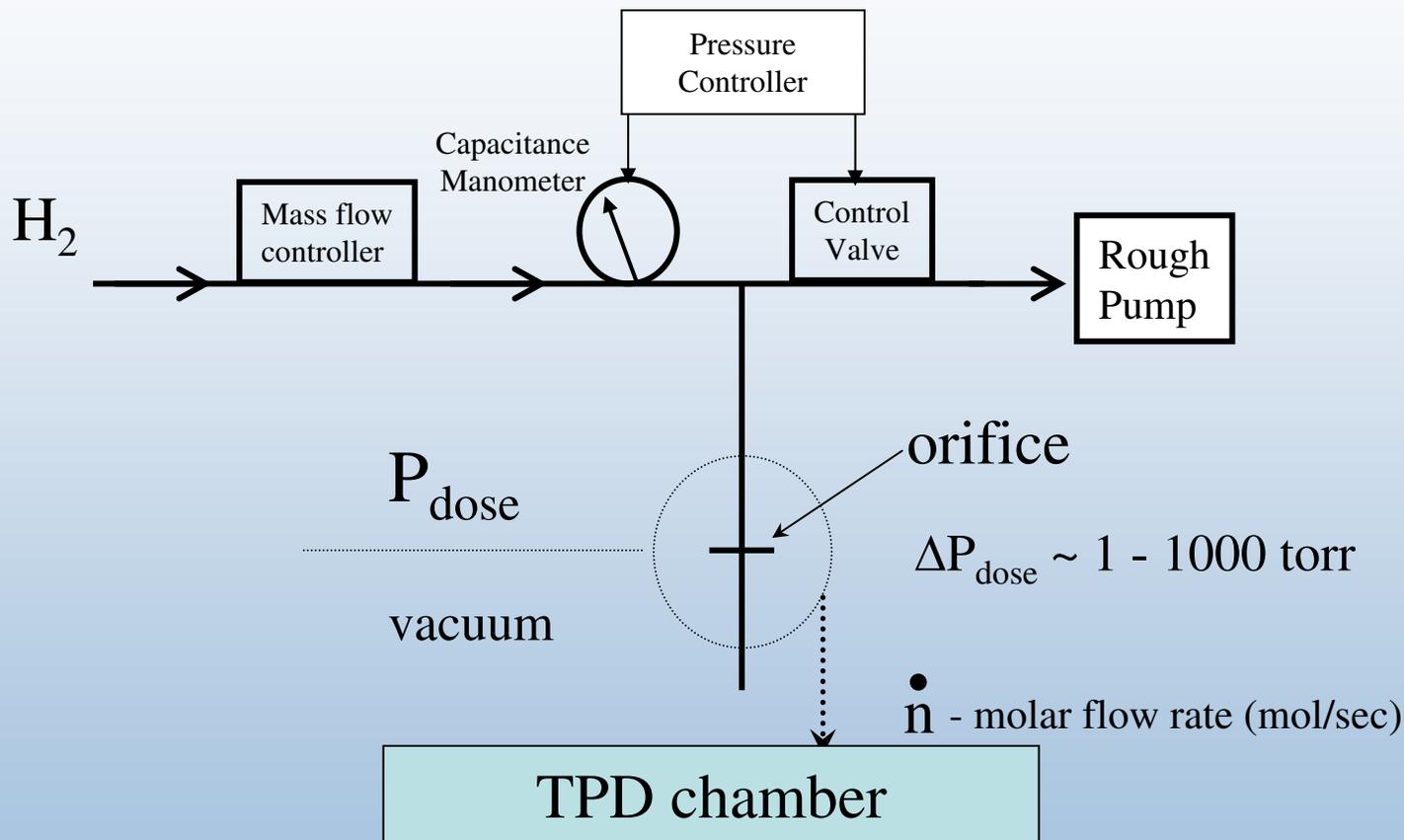


Increase in
low-T
adsorption in
purified B-
doped SWNTs

Capacity
increase must
be evaluated
with
overpressure.

Advances in Measurement Techniques

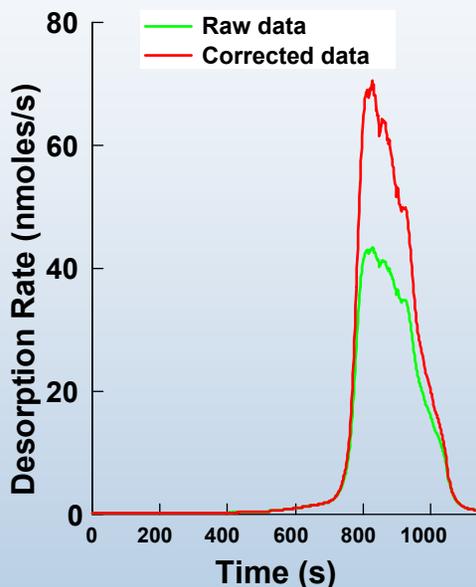
Variable Calibrated Leak for High Throughput, Quantitative TPD



Permits direct measurement of detector response as a function of molar flow rate \rightarrow accurate, *in situ* calibration

Using TiH₂ to Test Calibration

From SwRI/U. Penn review of NREL techniques

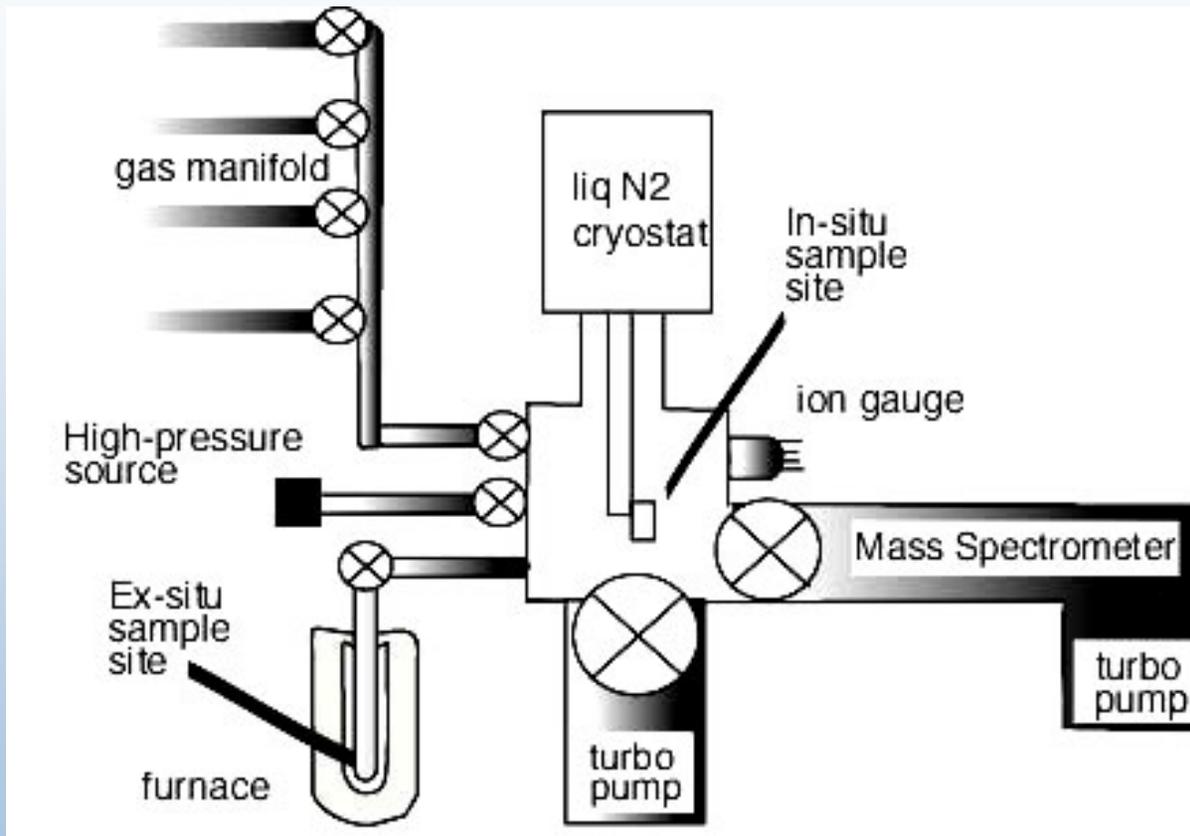


- Extends operation of detector into non-linear regime
- Accounts for detector aging
- 1 hr vs. several days
- Highly accurate
- Excellent agreement with volumetric measurements

Blind experiments showed calculation of the correct weight of TiH₂ with < 2% error

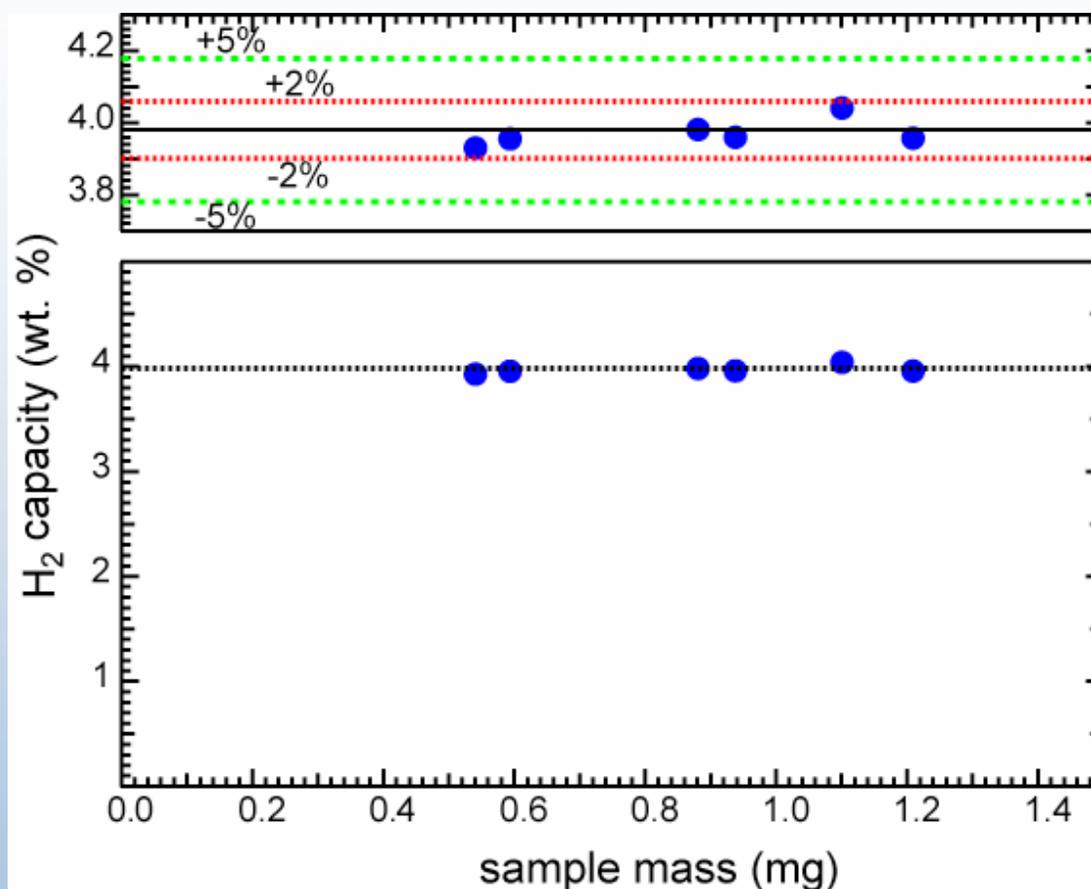
<u>Loaded amount of TiH₂</u>	<u>Calculated Amount</u>	<u>Error</u>
1.56 mg	1.54 mg	1.3 %
1.76 mg	1.73 mg	1.7 %

High Throughput Analysis with External Sample Cell



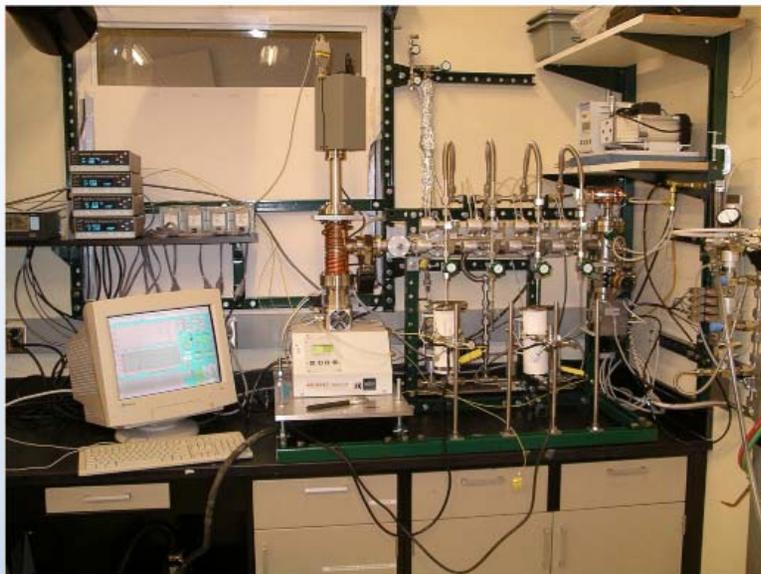
Multiple external cells can be connected to one manifold, with one mass spectrometer, for multi-sample, high throughput measurement

High Throughput, Accurate H₂ Measurement



*Six samples of TiH₂ measured within 2% accuracy in 6 hours
Meets milestone (6 samples, within 5%, in 24 hrs)*

High Throughput, Multi-station Apparatus

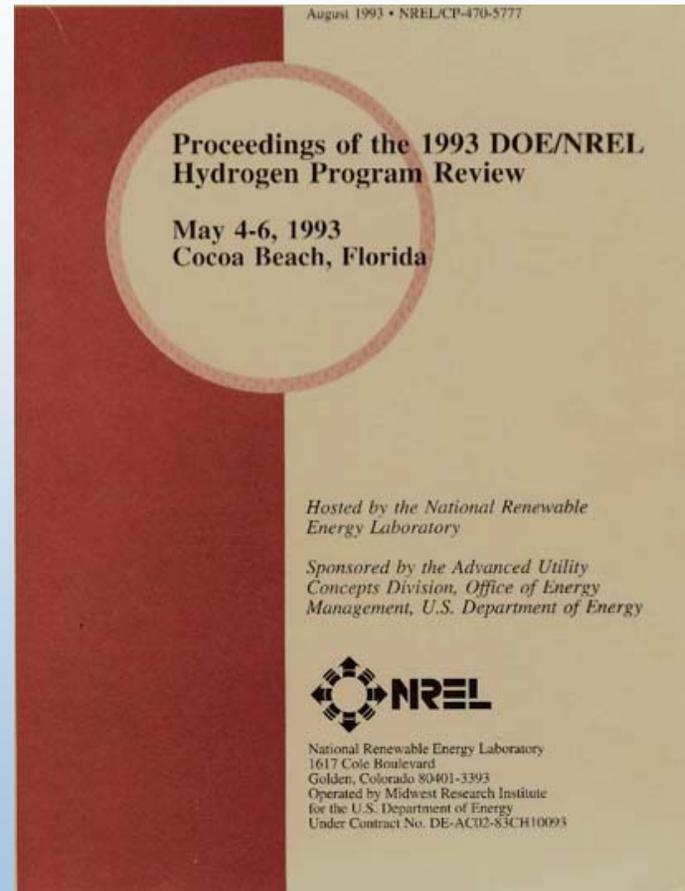


- *Current set-up has four stations and is expandable*
- *Will operate 24 hrs/day when fully automated*
- *Offers measurement support to Center partners*

Re-visiting Low T, Moderate P (< 100 bar) Adsorption Storage

“Activated carbon materials have been projected to meet and exceed density targets... if concurrent increases in hydrogen storage capacity and carbon density can be achieved. These two goals are in conflict for conventional porous materials such as activated carbons. However, the desired results may be obtained if the void spaces....can be organized ... The synthesis of carbon nanotubules indicate that such organization is possible.”

in Proceedings of the 1993 DOE/NREL Hydrogen Program Review, pg 79.



Re-visiting Low T, Moderate P (< 100 bar) Adsorption Storage

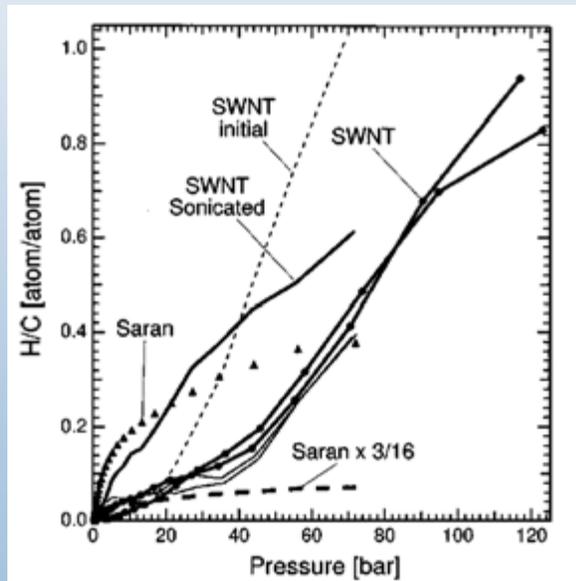
Seeking the “holy grail” for adsorbents:

Meeting DOE goals at ambient T and a few atmospheres

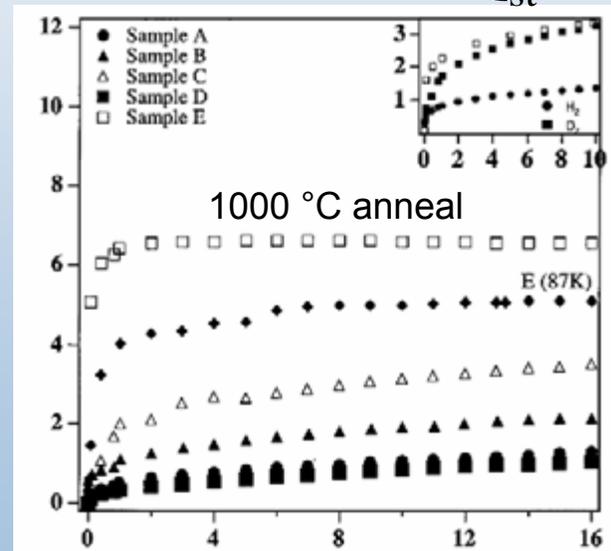
However:

Recent progress suggests that relaxing one (P or T) requirement can allow 2005 goals to be met

$$Q_{st} \sim 0.12 \text{ eV}$$

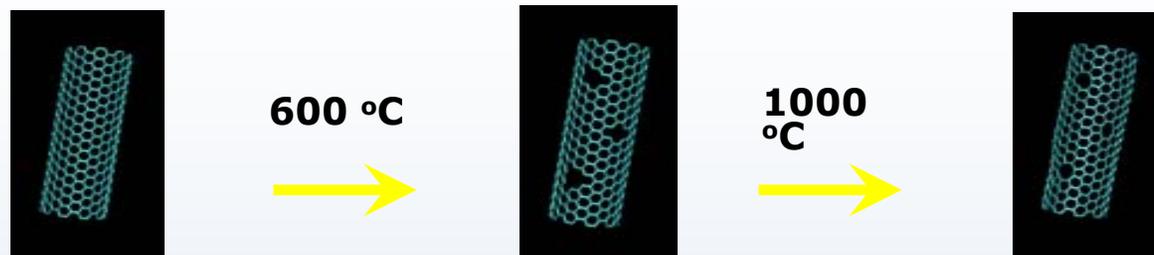


8 wt% on SWNTs at 80K, 100 bar
Ye, et al., APL 74, 2307 (1999)



6 wt% on SWNTs at 77K, 2 bar
Pradhan, et al., JMR 17, 2209 (2002)

Hydrogen storage on SWNTs at 77 K and 1 bar



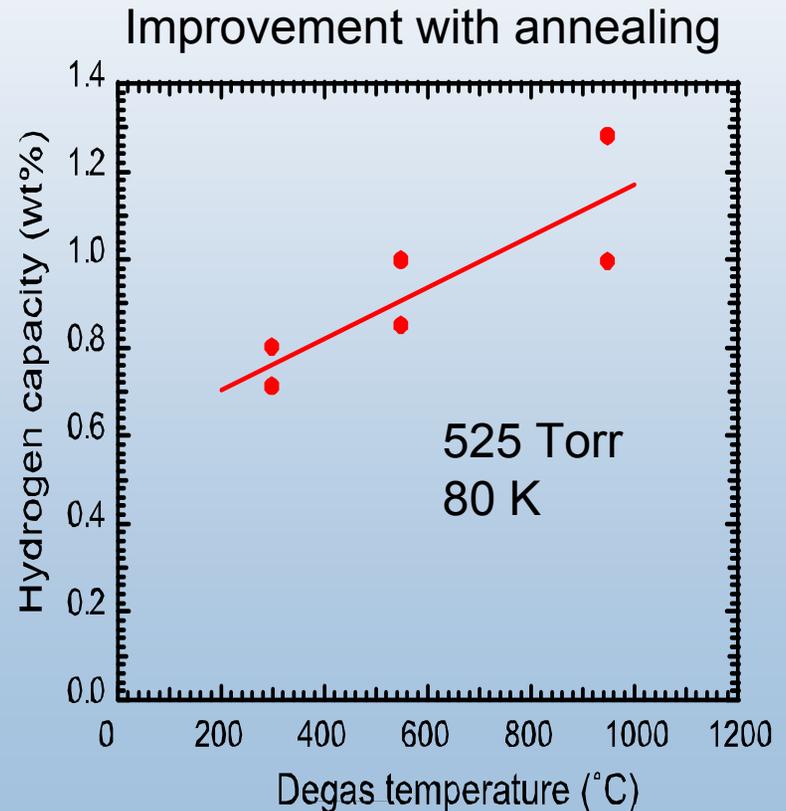
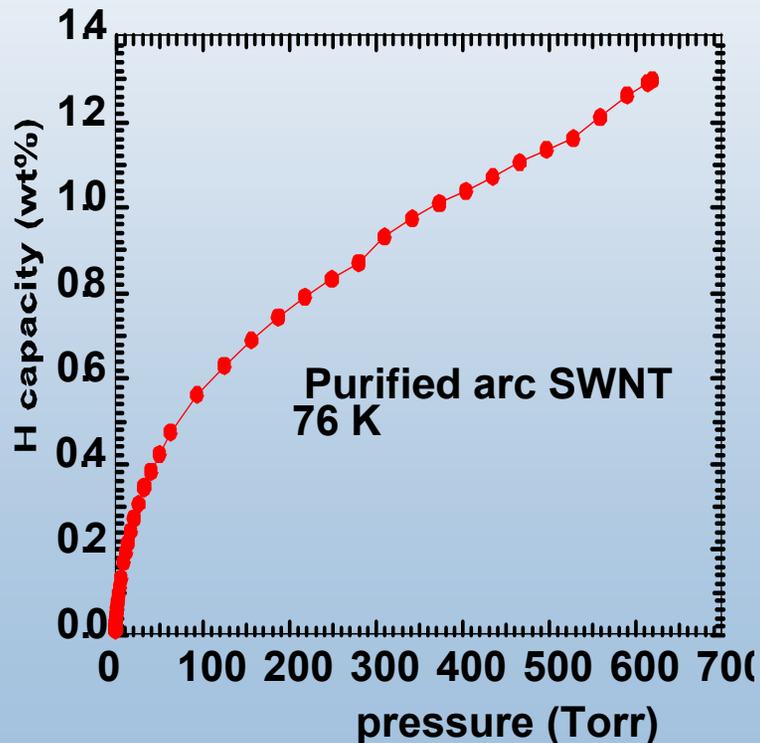
Acid	S_{spec} m^2/g	H_2 ads wt. %	S_{spec} m^2/g	H_2 ads wt. %	S_{spec} m^2/g	H_2 ads wt. %
HF	635	1,07	1555	4,6	806	1,73
HCl	878	1,55	1047	3,15	829	2,11
H_2SO_4	690	1,93	1084	1,38	430	1,12
HNO_3	40	1,04	375	0,98	193	1,22

- Both chemical and heat treatments result in an increase in the number and size of pores.

NREL Measurements at Low T, Low P

Purified arc-generated SWNTs

- *Isotherms with Quantochrome BET apparatus*
- *Single-point measurements in home-built volumetric*
- *Un-optimized materials*

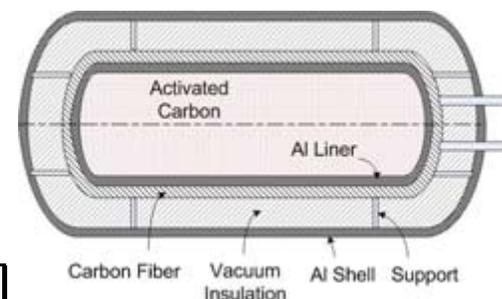


May have Potential to Meet 2005 System Targets

Preliminary System Analysis by Ramesh Ahluwalia, Argonne

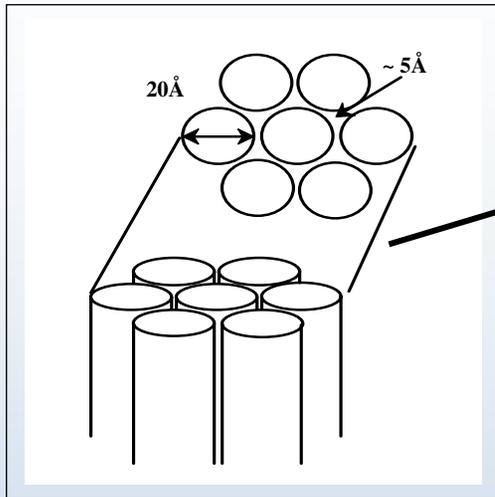
Engineered AC to Meet DOE-2005 Goals

- AX-21: Commercially available AC, 300 kg/m³ bulk density
- Densified AX-21: 700 kg/m³ bulk density
- EAC-05: Hypothetical AC engineered with physical properties to meet 2005 targets of 4.5 wt% and 36 kg/m³.
- Development effort: 1 < 2 < 3 < 4 < 5 < 6.

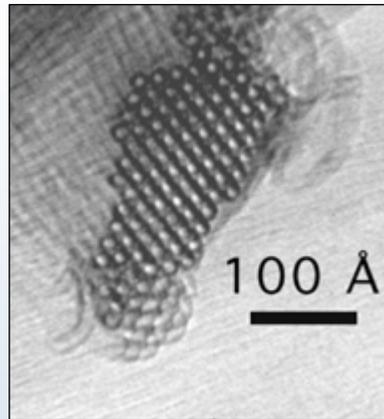


T (K)	P (bar)	ΔT (K)	AX-21		Densified AX-21		EAC-05	
			wt% H ₂	kg/m ³	wt% H ₂	kg/m ³	wt% H ₂	kg/m ³
77	50	0	3.2	11.6	1.6	10.6		
77	50	50	5.0	19.5	3.2	23.0	4.5 ²	36
77	100	0	5.4	21.7	2.5	17.4		
77	100	50	7.1	29.6	4.1	29.9	4.5 ¹	36
150	50	0	2.3	8.1	1.4	9.4	4.5 ⁶	36
150	50	50	2.8	10.0	1.8	12.4	4.5 ⁵	36
150	100	0	3.9	14.9	2.2	15.8	4.5 ⁴	36
150	100	50	4.3	16.8	2.6	18.8	4.5 ³	36

High Material Density SWNT Arrays



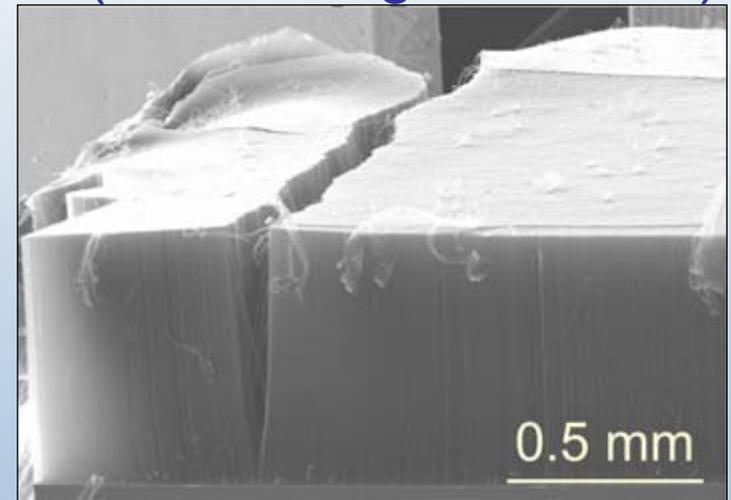
Concept in 1993



TEM in 2000



Macroscopic, vertically aligned arrays in 2005 (D. Geohegan, ORNL)



Cost analysis by
M. Ringer (NREL) in FY06

Can we achieve 6 - 8 wt% (80 K & 10 atm), with a bulk density approaching 1000 kg/m^3 (1 g/cc) ?

Potential winning technology

Comments from Last Year's Review

- 4 wt% capacity as a target is inadequate - should be revised to at least 8 wt% for any chance of success.
 - Interim target (FY2006) is 6 wt%
 - Developed rational approach to 8 wt% adsorbents
- Try to get industry involvement in collaborations.
 - Air Products and Chemicals, Inc., is leader in hydrogen technologies
 - Carbon Nanotechnologies, Inc., is leader in carbon nanomaterials
 - Connection through NREL's vehicle group connects the Center to numerous vehicle and vehicle component manufacturers
- Scope should be refocused beyond carbon nanotubes.
 - Scope now includes a wide variety of carbon-based materials

Comments from Review (cont.)

- Need to list what a system based on carbon materials would contain (including masses and volumes).
 - Work has begun to scope-out system from a thermal/fluid/mechanical & packaging point of view
 - Working with Vehicle Group at NREL and R. Ahluwalia at Argonne
- Cost needs to be assessed.
 - Analysis effort planned with M. Mann & M. Ringer at NREL
 - Will be active with TiAx effort
 - Will build from cost estimate of scale-up of SWNT production previously done by NREL using input from industry (APCI, CNL and others)
- Focus totally on making a sample others can measure 4% storage in.
 - This *is* the main focus
- Cryo work is an appropriate addition.
 - Have expanded work in this area.

Future Work

FY05:

- Support integration of and provide technical guidance to DOE's Carbon-based Hydrogen Storage Center of Excellence
- Develop methods for reproducible sample preparation of carbon hybrid materials
- Investigate low T, moderate P approaches
- Key milestone is 4 wt% at external lab (SwRI) by Oct. 2005

FY06:

- Work with Center Partners to develop carbon materials solutions to meet FY2010 DOE storage goals
- Key milestone is 6 wt% at external lab (SwRI) by Oct. 2006

NREL Publications

1. "Non-dissociative adsorption of H₂ molecules in light-element doped fullerenes", Y.-H. Kim, Y. Zhao, A. Williamson, M.J. Heben, and S. B. Zhang, submitted to *Physical Review Letters*.
2. "Hydrogen storage in novel organometallic bucky balls", Y. Zhao, Y.-H. Kim, A.C. Dillon, M.J. Heben, and S. B. Zhang, PRL **94**, 155504 (2005).
3. "Experimental Gibbs free energy considerations in the nucleation and growth of single walled carbon nanotubes", L.M. Wagg, G.L. Hornyak, L. Grigorian, A.C. Dillon, K.M. Jones, J.L. Blackburn, P.A. Parilla and M.J. Heben, to appear in *J. Phys. Chem. B*
4. "Systematic inclusion of defects in pure carbon single-wall nanotubes and their effect on the Raman D-band" A.C. Dillon, P.A. Parilla, J.L. Alleman, T. Gennett, K.M. Jones & M.J. Heben. *Chemical Physics Letters* 401, 522-528 (2005).
5. "Generalized Kubas complexes as a novel means for room temperature molecular hydrogen storage", Y.-H. Kim, Y. Zhao, M. J. Heben, and S. B. Zhang, to be published in Hydrogen Storage Materials (Materials Research Society Symposium Proceedings).
6. "Discovering the mechanism of hydrogen adsorption on aromatic carbon nanostructures to develop adsorbents for vehicular applications", Y. Zhao, Y.-H. Kim, S. B. Zhang, J.L. Blackburn, A.C. Dillon, P.A. Parilla, A.H. Mahan, J.L. Alleman, K. M. Jones, T. Gennett, K.E.H. Gilbert, Y-W. Lee, B.M. Clemens and M.J. Heben, to be published in Hydrogen Storage Materials (Materials Research Society Symposium Proceedings).
7. "Hydrogen adsorption properties of single wall carbon nanotube-organometallic hybrid materials", T. Gennett, C. Curtis, J.L. Blackburn, K.M. Jones, J.L. Alleman, A.C. Dillon, M.J. Heben, to be published in Hydrogen Storage Materials (Materials Research Society Symposium Proceedings).
8. "Employing Raman spectroscopy to qualitatively evaluate the purity of carbon single-wall nanotube materials" A.C. Dillon, M. Yudasaka & M.S. Dresselhaus. *Journal of Nanoscience and Nanotechnology* 4, 691-703 (2004).
9. "High yield nanotube synthesis in a hot-zone arc-discharge apparatus", T. Gennett, C. Engtrakul, J. Blackburn, K. Franz, J. Alleman, K. Jones, A. Dillon, M. Heben, manuscript in preparation.
10. "Rapid, accurate, *in situ*, calibration of a mass spectrometer for temperature programmed desorption studies", K.E.H. Gilbert, P.A. Parilla, J.L. Blackburn, T. Gennett, A.C. Dillon, and M.J. Heben, manuscript in preparation.
11. "Competitive adsorption between carbon dioxide and methane on carbon nanotube materials" K.E.H. Gilbert, P.A. Parilla, J.L. Blackburn, T. Gennett, A.C. Dillon, and M.J. Heben, manuscript in preparation.
12. "Reaction intermediates in chemical vapor deposition growth of single-wall nanotubes", L.M. Wagg, J.L. Blackburn, A.C. Dillon, K.M. Jones, , P.A. Parilla and M.J. Heben, manuscript in preparation.
13. "Formation of nanooctahedra in molybdenum disulfide and molybdenum diselenide using pulsed laser vaporization", P.A. Parilla, A.C. Dillon, B.A. Parkinson, K.M. Jones, J. Alleman, G. Riker, D.S. Ginley & M.J. Heben. *Journal of Physical Chemistry B* 108, 6197-6207 (2004).
14. "High-energy, rechargeable Li-ion battery based on carbon nanotube technology", R.S. Morris, B.G. Dixon, T. Gennett, R. Raffaele & M.J. Heben. *Journal of Power Sources* 138, 277-280 (2004).
15. "Development and characterization of single wall carbon nanotube Nafion actuators", B.J. Landi, R.P. Raffaele, M.J. Heben, J.L. Alleman, W. VanDerveer & T. Gennett. to appear in *Materials Science and Engineering B*.