Development of Doped Nanoporous Carbons for Hydrogen Storage

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PENNSTATE
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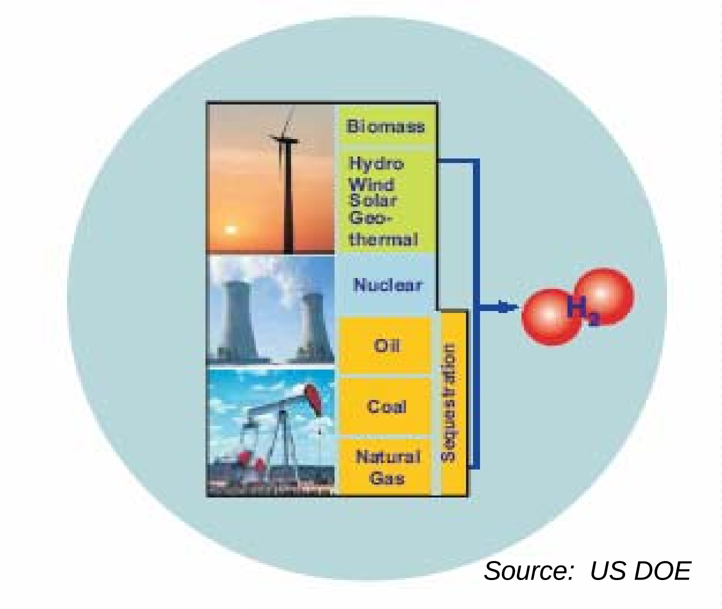
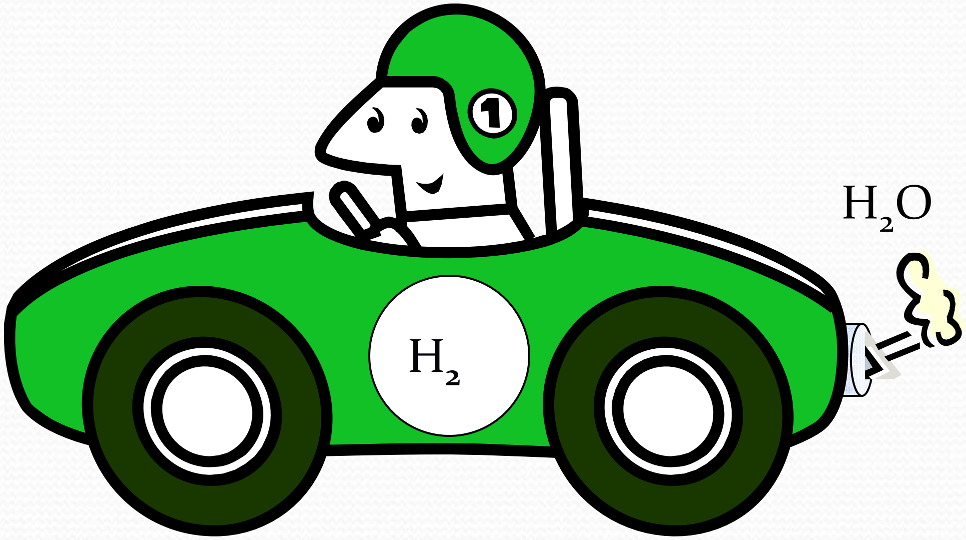
Hydrogen,

A brief introduction.



Source: US DOE

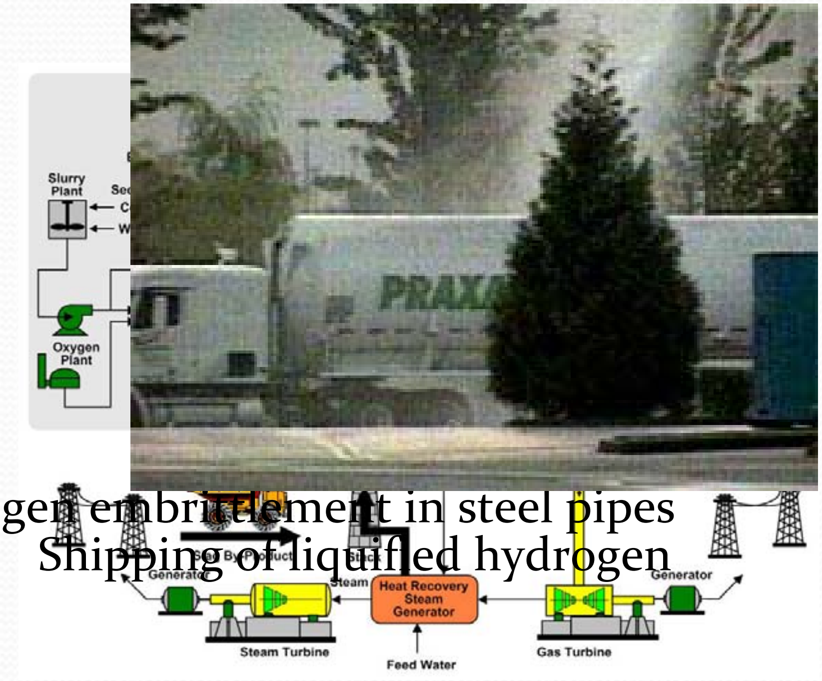


Hydrogen easily combines with other elements, and is found naturally as a part of other compounds such as coal, oil, natural gas, plant material, and water.

The 9 million tons of hydrogen currently used per year in the U.S. is enough energy for 20-30 million H_2 cars or 5-8 million homes.
This hydrogen is produced through reforming or gasification.

2: The challenges.

Centralized H_2 production methods require storage for distribution



Hydrogen embrittlement in steel pipes

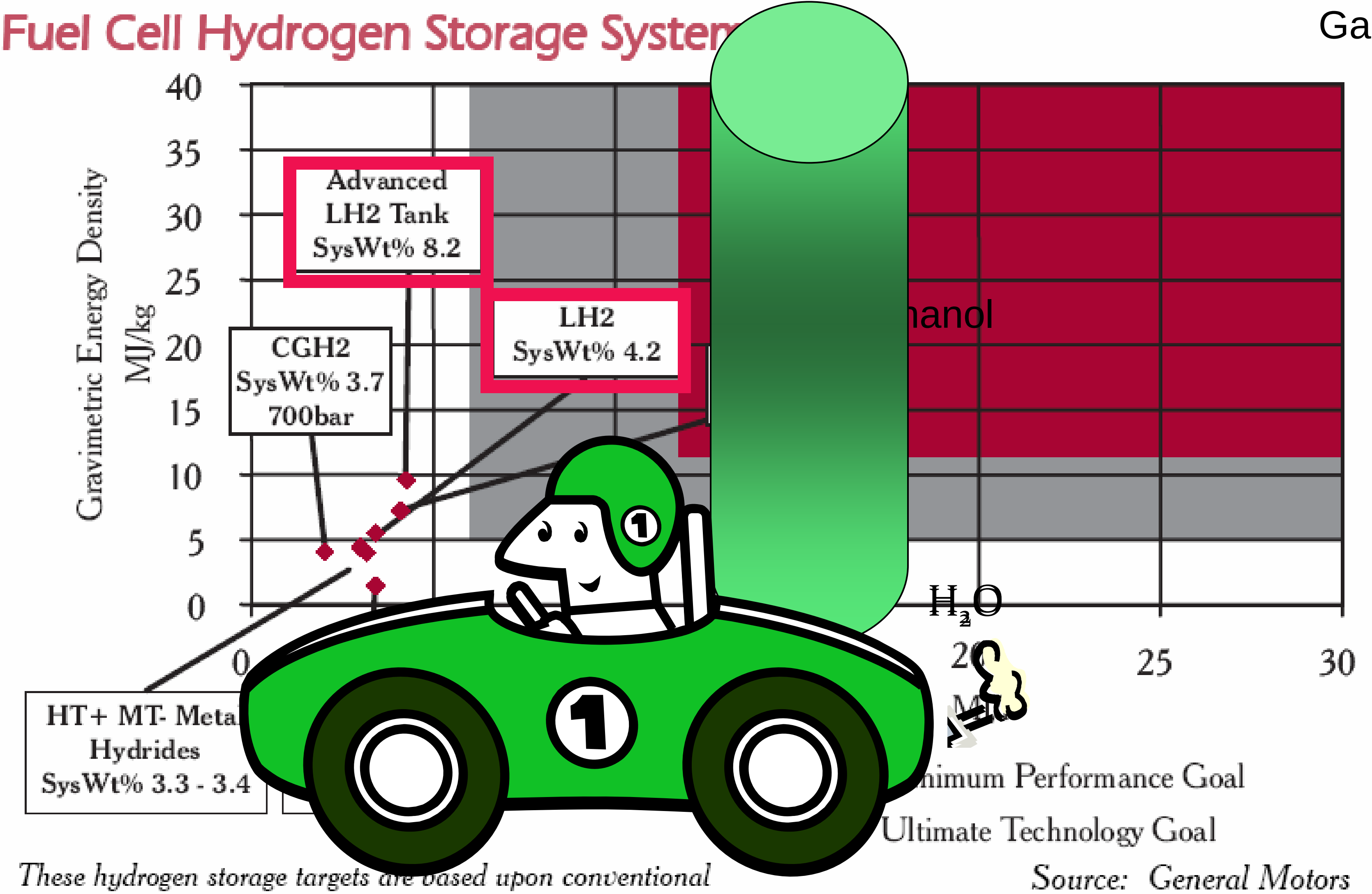
Shipping of liquified hydrogen

Coal gasification to produce H2 on large scale

Compared to gasoline, H_2 would cost four times as much at the pump—if the infrastructure existed to get it there.

Gravimetric Energy Density vs. Volumetric Energy Density of Fuel Cell Hydrogen Storage System

Gasoline

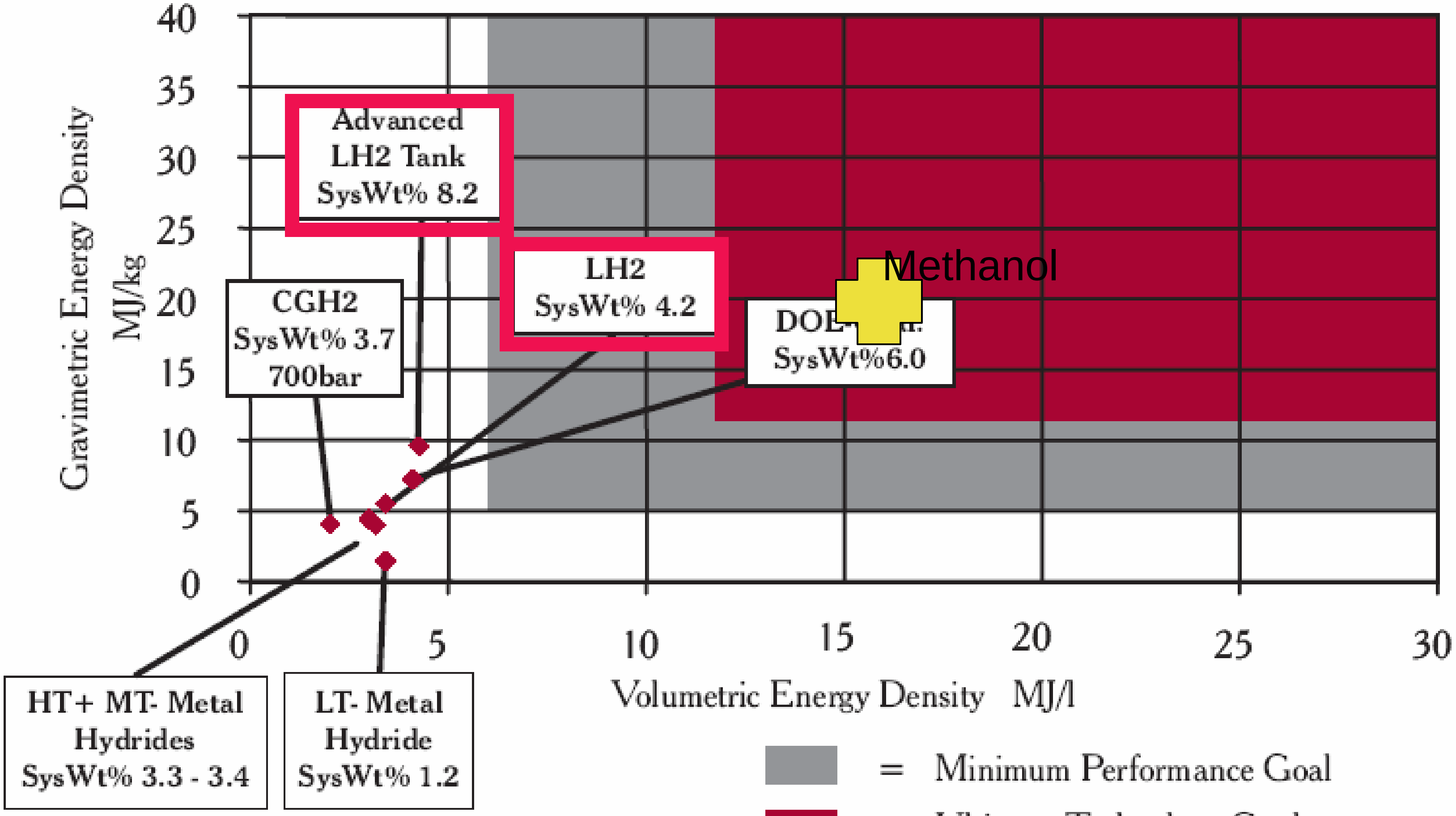


Source: *General Motors*

These hydrogen storage targets are based upon conventional vehicle architectures and vehicle performance requirements.

Source: U.S. DOE

Gravimetric Energy Density vs. Volumetric Energy Density of Fuel Cell Hydrogen Storage Systems



These hydrogen storage targets are based upon conventional vehicle architectures and vehicle performance requirements.

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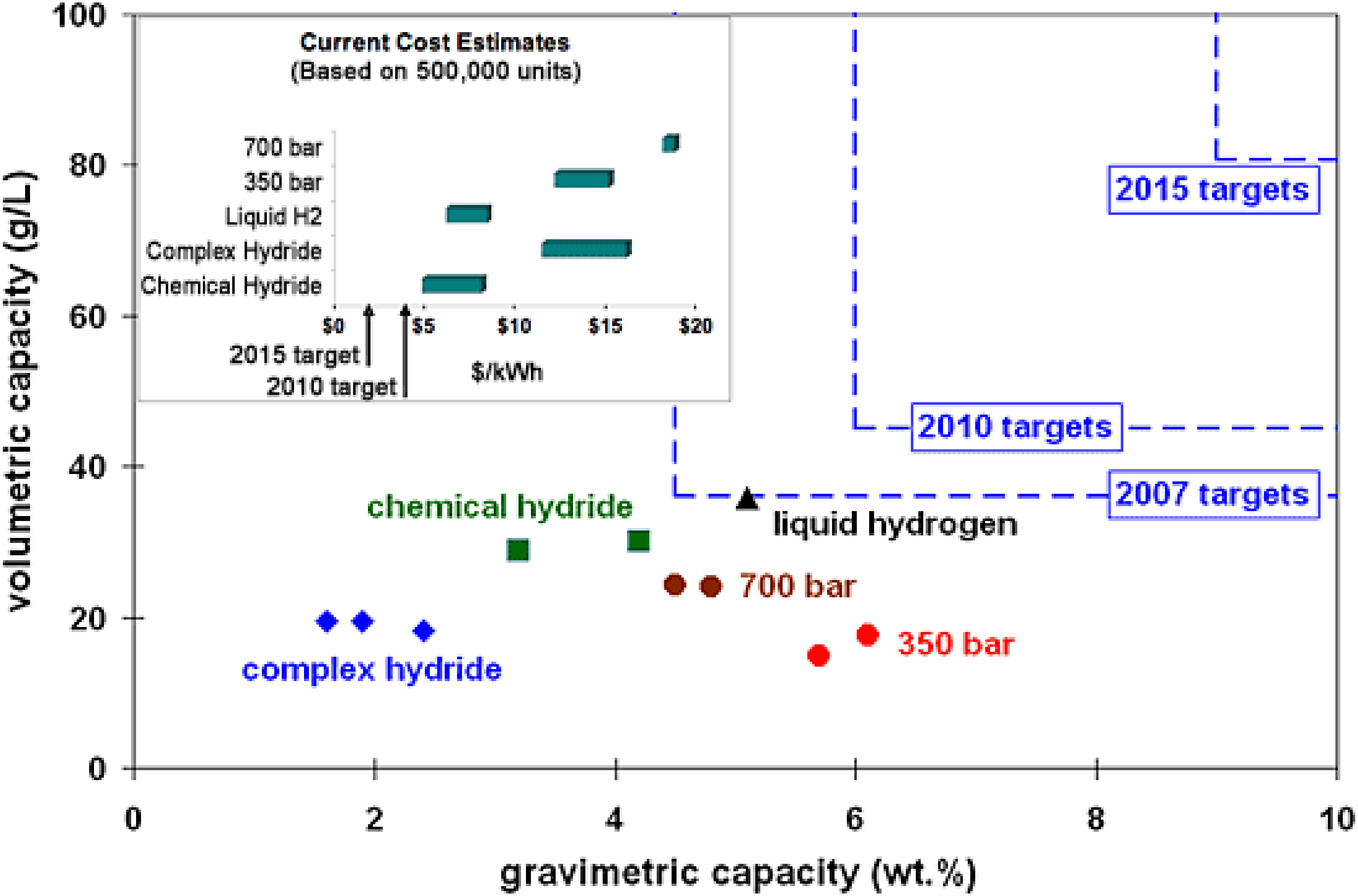
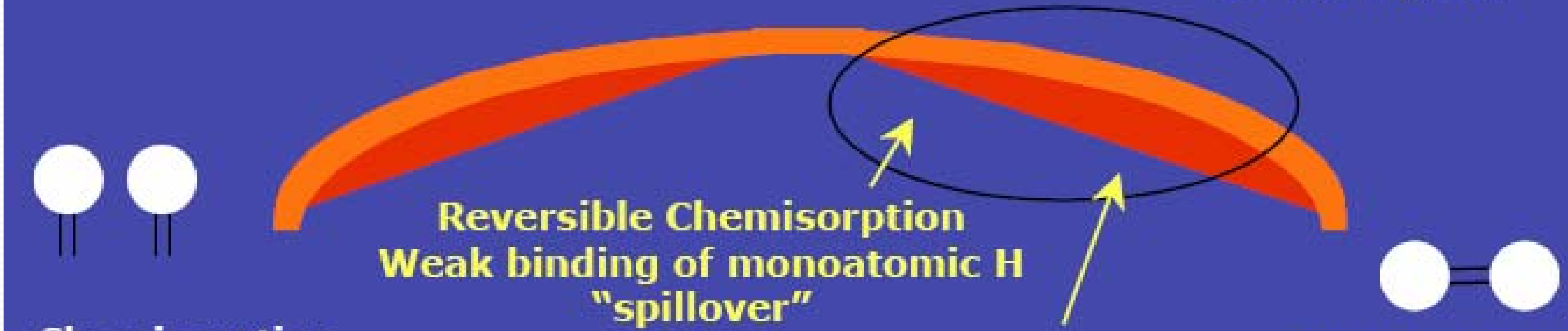


Source: U.S. DOE

Continuum of Hydrogen Binding Energies

Affects of bond strain & electronic properties

Desired Energy Range
20-60 kJ/mol

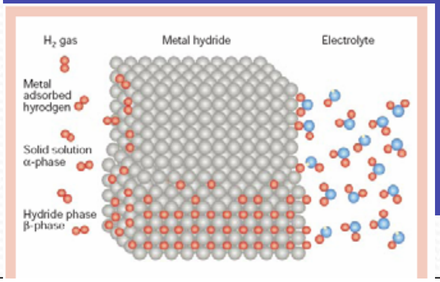


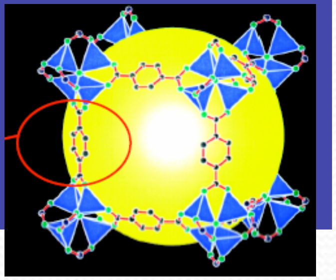
Reversible Chemisorption
Weak binding of monoatomic H
"spillover"

Chemisorption
C-H bond
200-400 kJ/mol

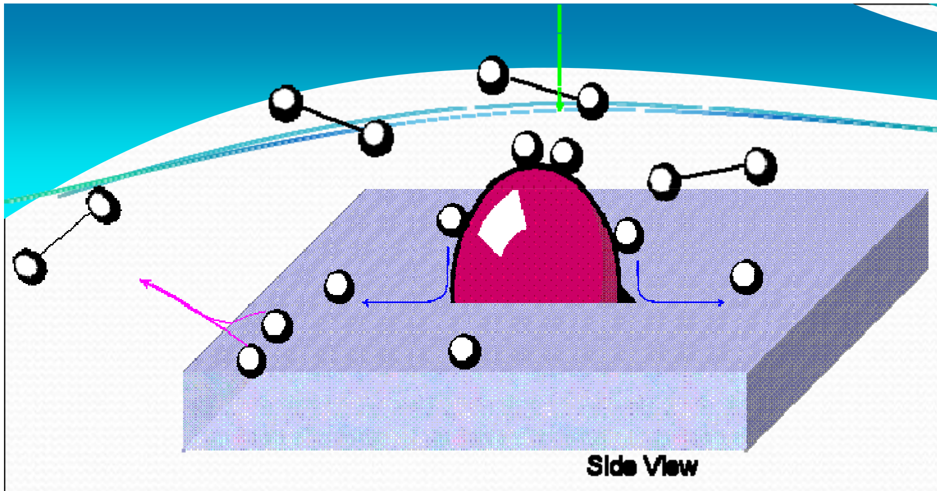
Partial Charge Transfer
Strong "physisorption" of dihydrogen
Organometallic Complexes
"Kubas-type compounds"

Physisorption
Planar graphite H_2
4 kJ/mol





Source: NREL



● Hydrogen atom

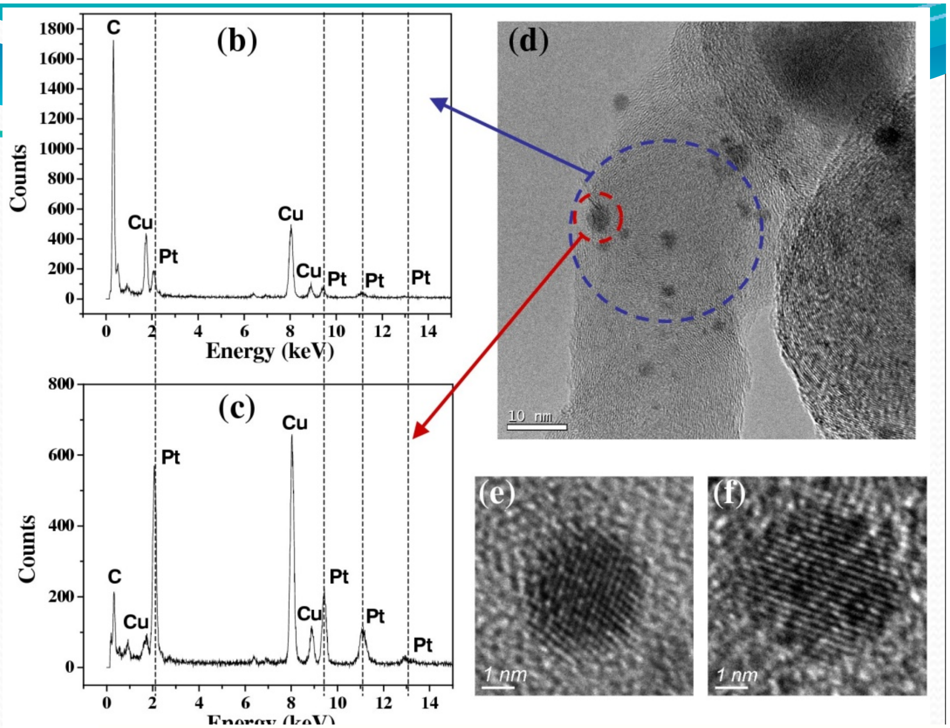
Metal

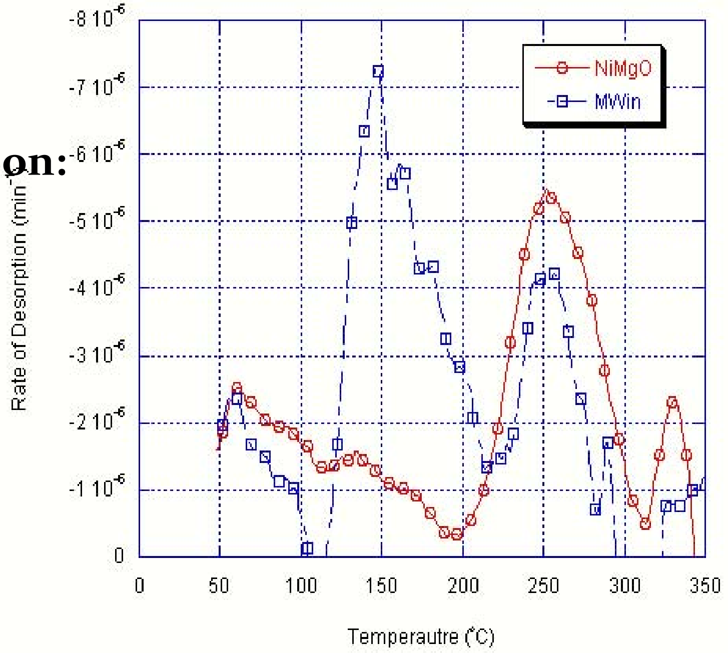
▭ Support

→ Dissociation of H_2 on metal

→ Surface Diffusion of H atoms to support

→ Desorption of H atoms from support as H_2





Hydrogen Storage via Spillover in Metal-assisted Carbon:

(Lueking's work at Michigan)

Lueking & Yang, Appl.Catal. A, 265, 259, 2004.

*Lueking & Yang, AIChE J, **49**, 1556, 2003*

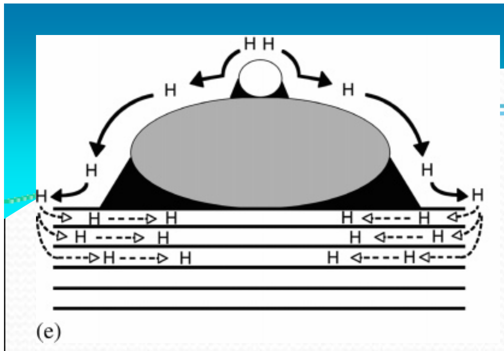
*Lueking & Yang, J. Catal. **206**, 165, 2002*

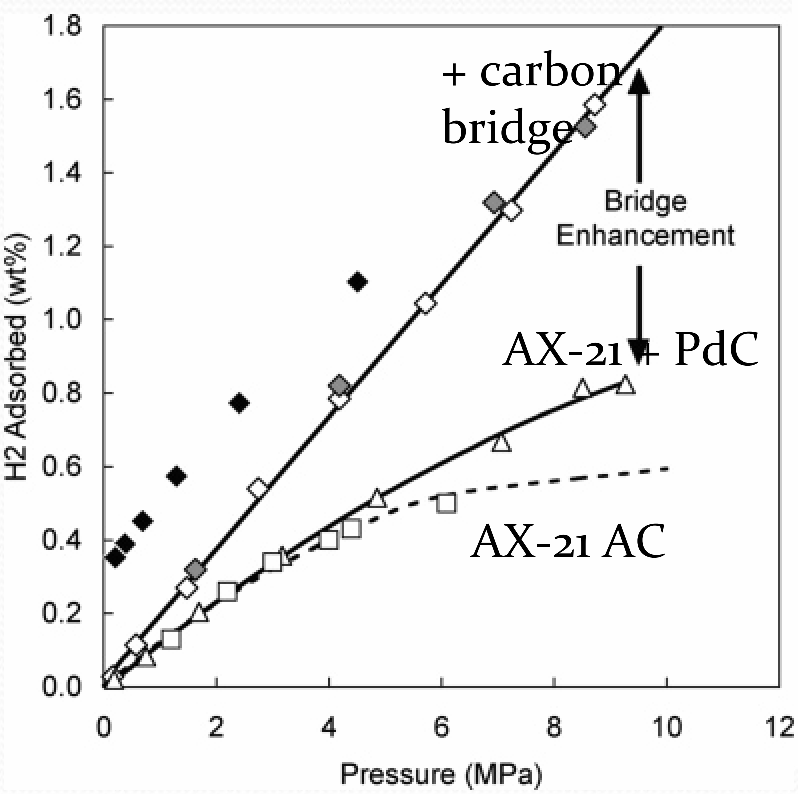
(Lueking's work at Penn State)

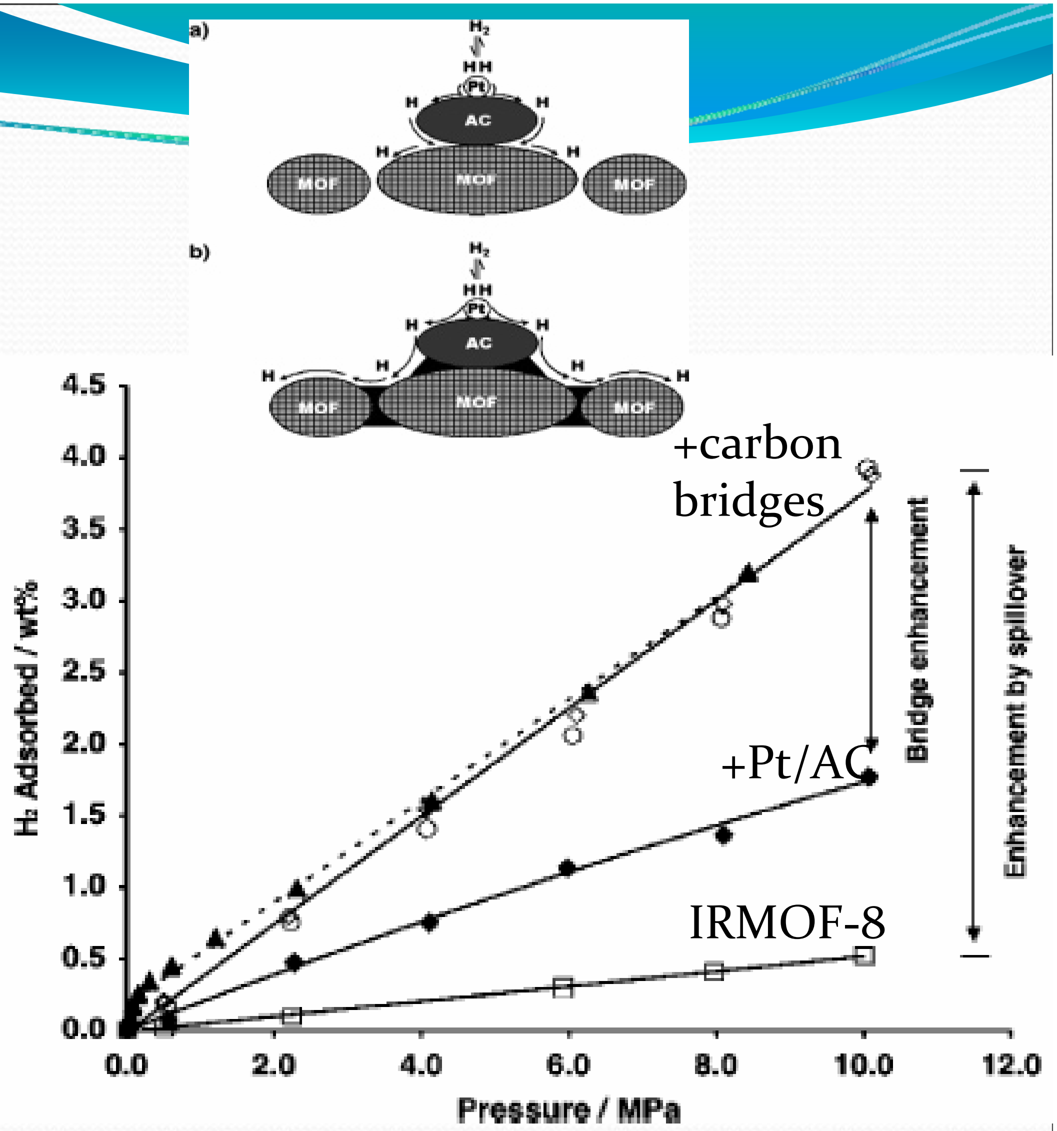
Jain & Lueking, J. Phys. Chem. C. 111, 1788, 2007.

Li, Badding, & Lueking, In Progress

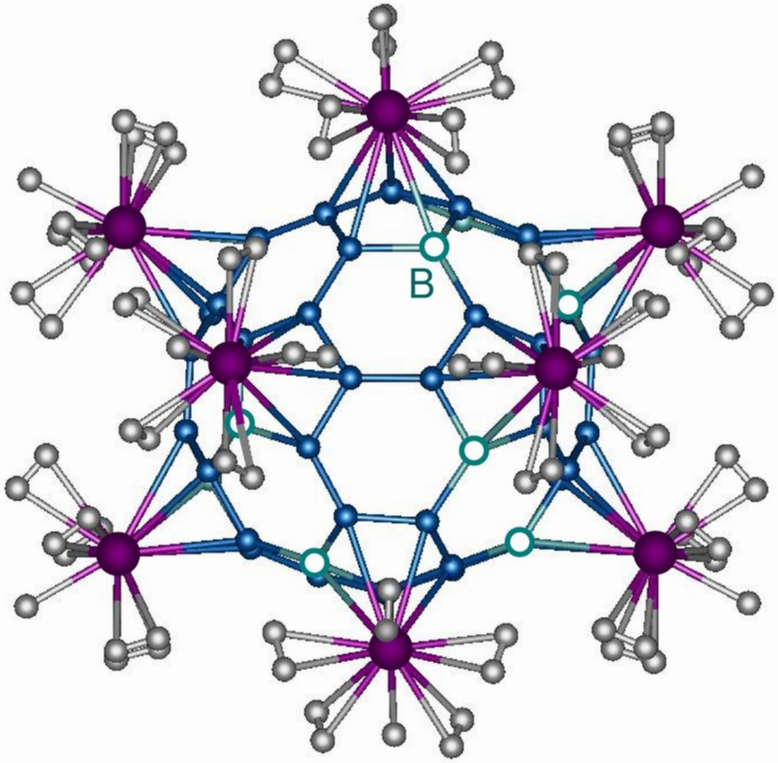
Adu & Lueking, In Progress







Lachawiec et al., Langmuir, 2005
Li & Yang, JACS, 2006
Yang et al., J. Phys. Chem. B, 2006



7.7 wt% for $Ti_{14}C_{13}$

0.17-0.89 eV/H_2

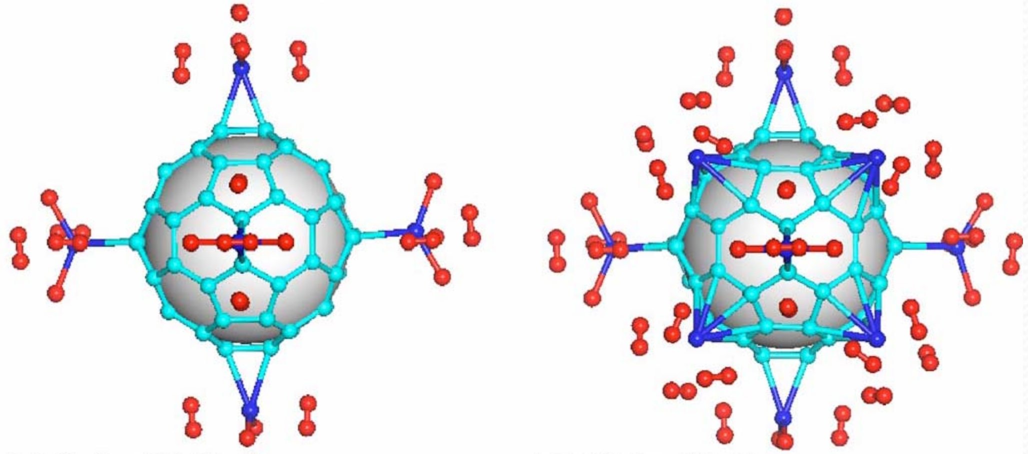
9wt% for $C_{48}B_{12}[ScH(H_2)_5]_{12}$

0.3 eV/H_2

Y. F. Zhao, et al., Phys Rev Lett 94, 155504 (2005)
Zhao, et al., Chem Phys Lett 425, 273-277 (2006).

7.5 wt% for Ti – C_{60}

Yildrim et al., PRB 2005
Dag et al., PRB 2005 (Pt + SWNT)



4.6 (3.4) wt% H_2 E_B= 2.368 eV/H_2-3H_2 (2.235 eV)

7.5 (6.7) wt% H_2 E_B= 2.089 eV/4H_2 (2.021 eV)

Objectives

Primary

- To understand the active adsorption sites in carbon materials that have been activated with nanocatalysts, such that synergistic effects create new adsorption sites and activate the carbon nanomaterials for adsorption at ambient temperatures

Objectives, continued

- To understand, identify, and optimize specific adsorption sites, *in situ* high-pressure analytical techniques are needed to fully characterize these sites at the pressures of interest.
  - Multi-wavelength resonance Raman,
  - Infrared spectroscopy (IR),
  - X-ray diffraction
  - Temperature programmed desorption (TPD)

  - Combined with measurements of overall adsorption uptake and energetics

At 100 bar

Prof. John Badding,
Co-PI

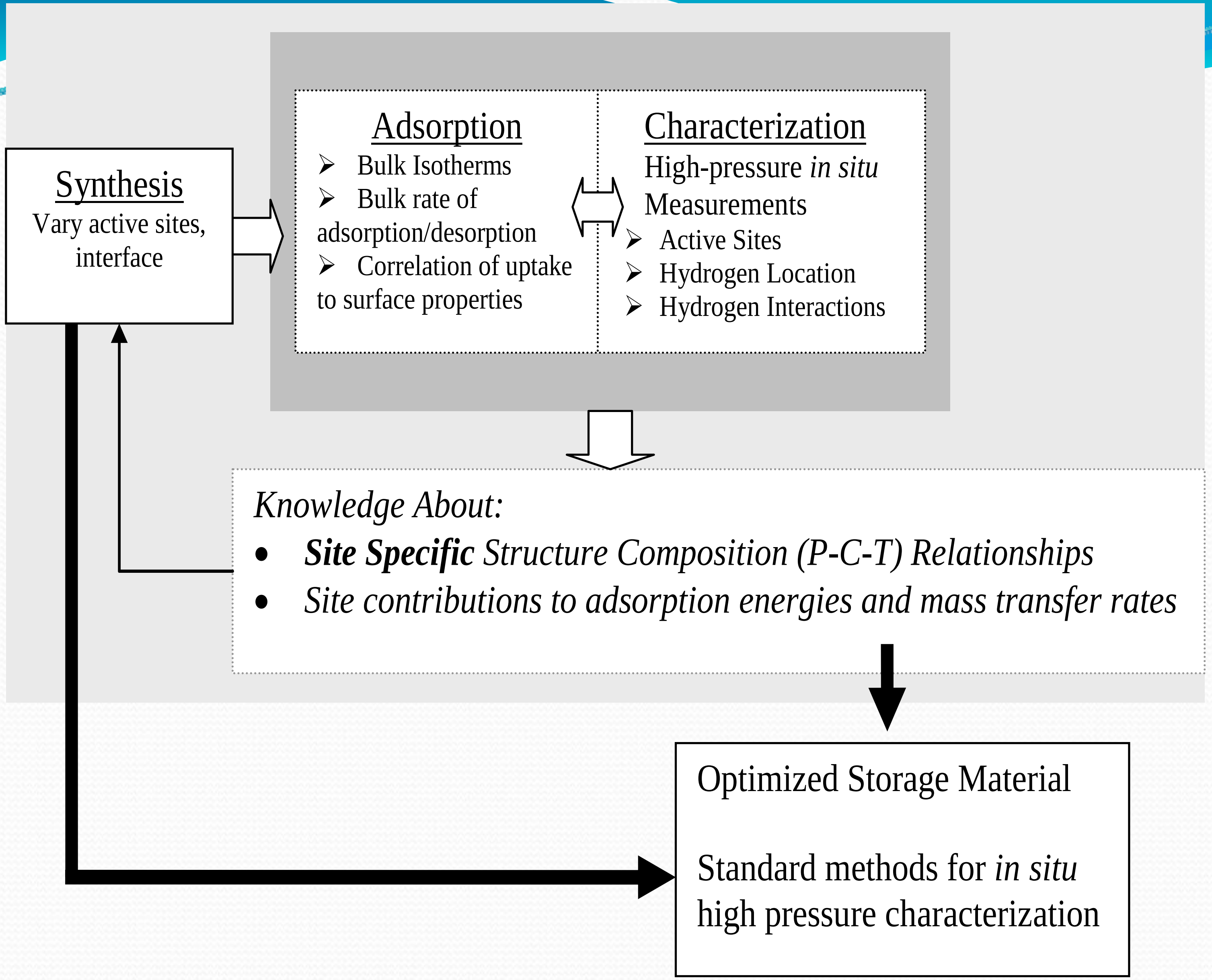
Project Goals

- Delineation of surface sites:
  - Hybridization state
  - Potential to (reversibly) rehybridize upon application of pressure
  - Chemical functional groups
  - Local bonding environment
  - Nature of binding between surface sites and hydrogen

↓

Site specific structure composition relationships and optimization of material design based on this site specific knowledge.

Feedback loop for Material Optimization



Synthesis

Vary active sites, interface

Adsorption

- Bulk Isotherms
- Bulk rate of adsorption/desorption
- Correlation of uptake to surface properties

Characterization

High-pressure *in situ* Measurements

- Active Sites
- Hydrogen Location
- Hydrogen Interactions

Knowledge About:

- ***Site Specific*** *Structure Composition (P-C-T) Relationships*
- *Site contributions to adsorption energies and mass transfer rates*

Optimized Storage Material

Standard methods for *in situ* high pressure characterization

Figure 1. Schematic of work plan and feedback loop to optimize materials

On-going Work

	Synthesis	Method Development	Characterization High-P	Hydrogen Adsorption
	New Materials	TDS: Mass Spec		Gravimetric, P < 20 bar
		New Differential Volumetric P→ 100 bar		Quality Contro Standardizatio
			In situ Raman measurements Capillary Heating	
NEW! 	"Standard" Materials		"Standard" Materials	"Standard" Materials

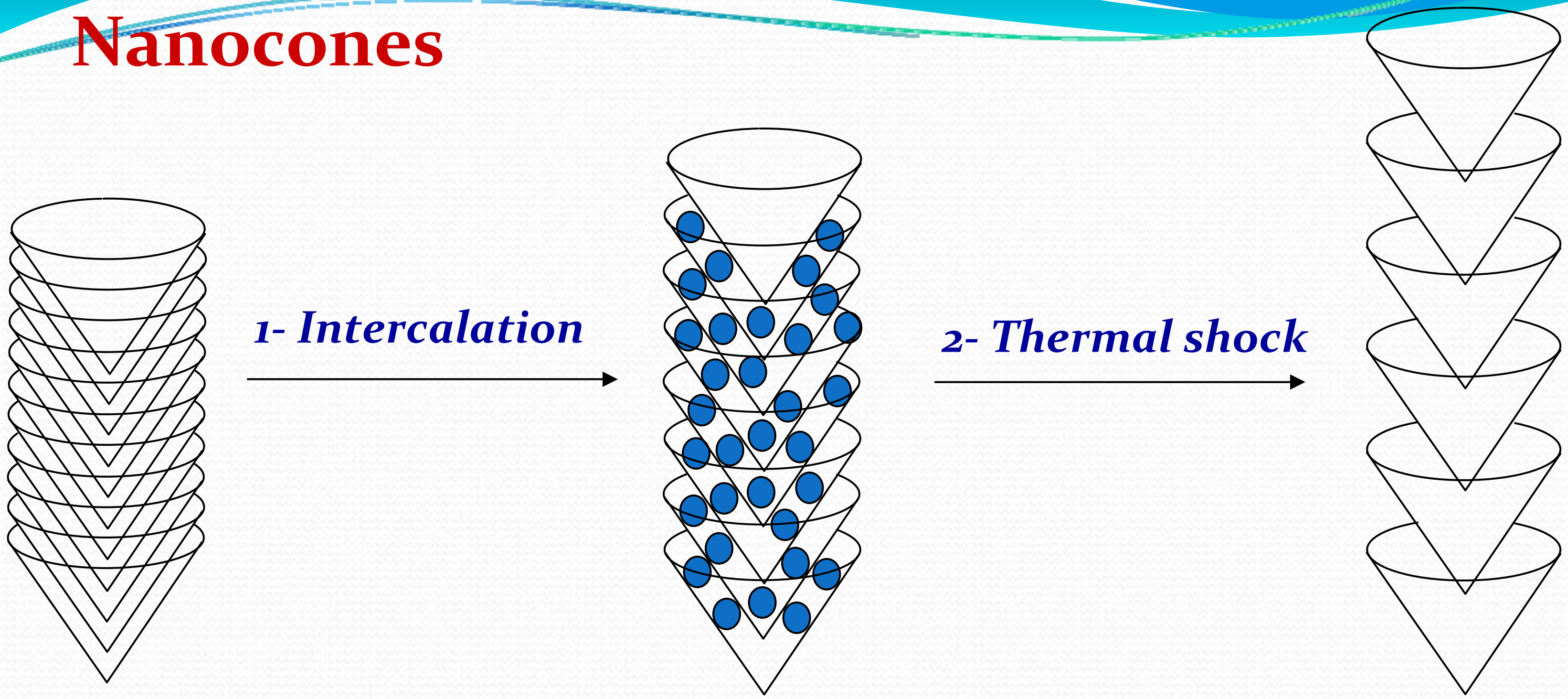
Results and Discussion: Outline

- New Materials
  - Exfoliated graphite nanofibers
  - Metal-intercalated graphite nanofibers

- New Methods
  - New Adsorption equipment
  - High-pressure, in situ Raman (and other)

- "Standard" Materials *Metal-doped Nanocarbons*
  - 1% Pt/GNF
  - 1% Pt/SWNT
  - *Compared to: 5% Pt/Act. Carbon (STREM chemicals)*

Exfoliated Graphite Nanofibers / Nanocones



1- Intercalation

2- Thermal shock

Interlayer (or “inter-cup”)
spacing =3.4 Å

Graphite intercalation
compound

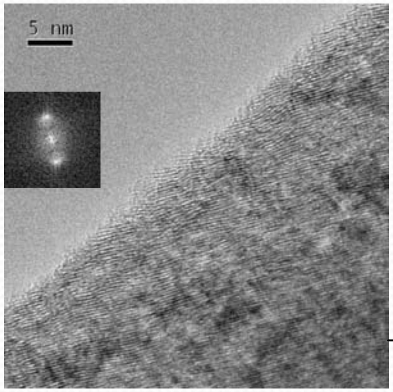
Interlayer spacing >3.4 Å
Defects Facilitate Uptake

Notes:

- For graphite, expansion of over 100x have been reported
- ‘Exfoliation’ also used to describe separation of nanotube bundles
- Exfoliation of carbon fibers and graphite tends to lead to highly irregular structures

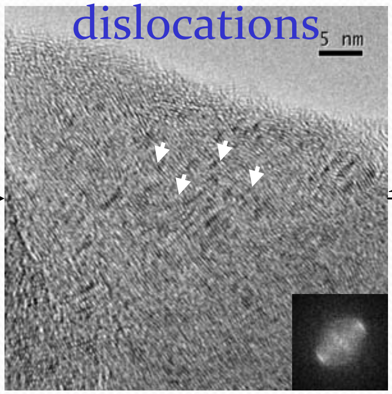
Explore: Synthesis Variations of the EGNF structure

Start: 0.34 nm



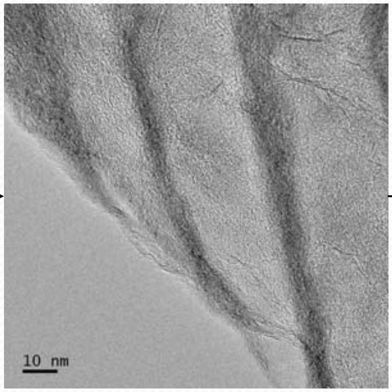
Intercalation
Thermal Shock

0.35 nm;
dislocations



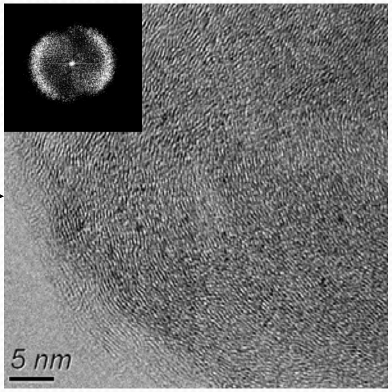
Anneal

5-50 nm

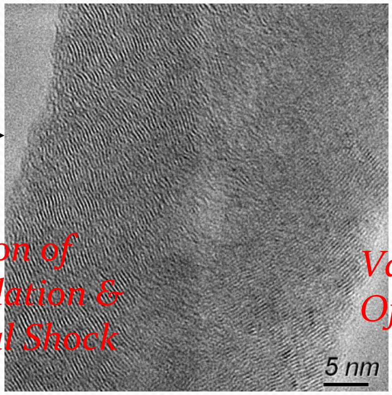


CO2

<0.4 nm

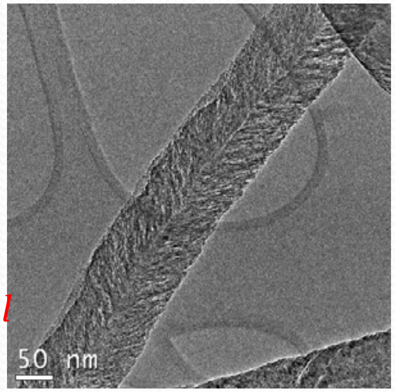


Variation of
Intercalation &
Thermal Shock



~0.4 nm

Variation
Of Anneal

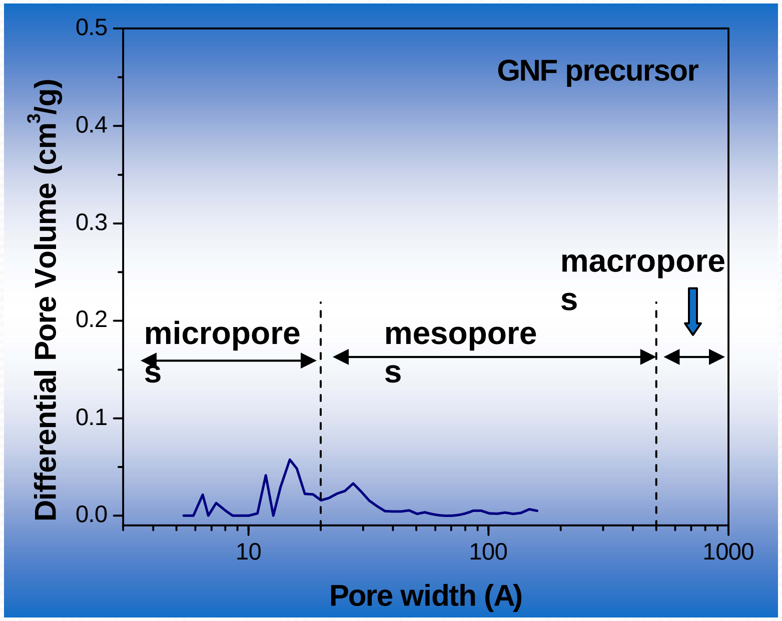


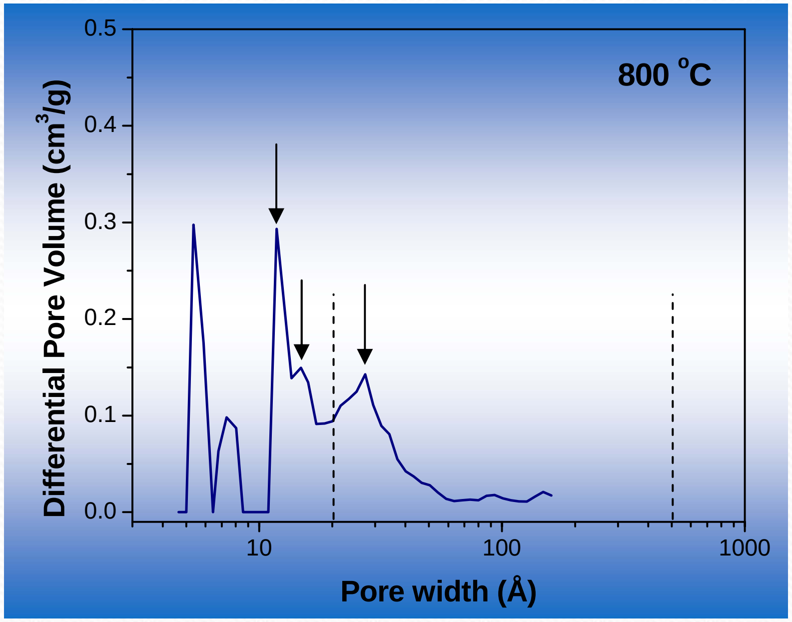
Large pores
start to form

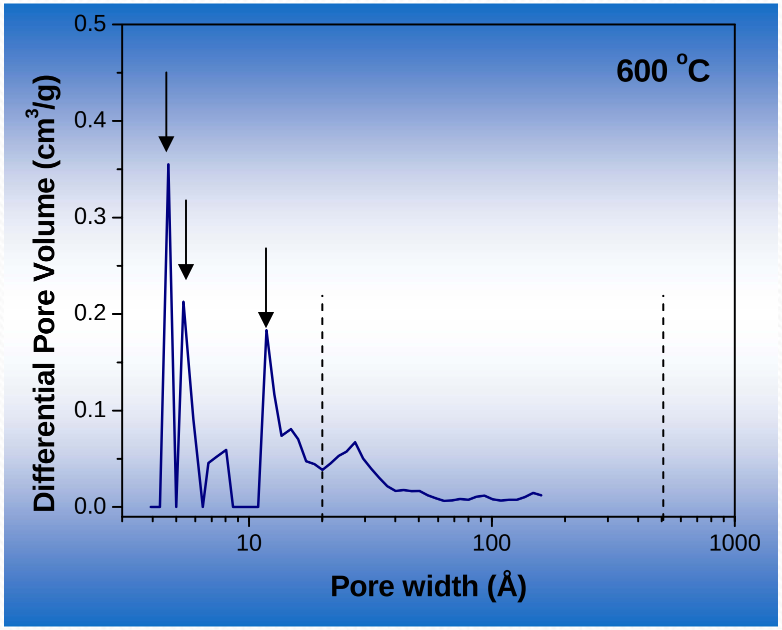
J. Phys. Chem. B,
2005, 109, 12710.

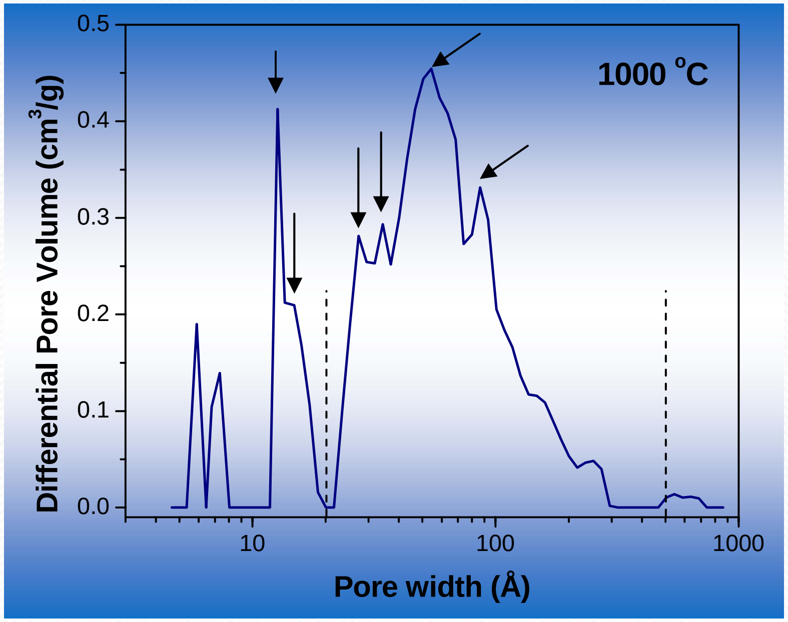
Pore size distribution

Measured by Nitrogen physisorption using DFT









Metal-intercalated Graphite Nanofibers / Nanocones

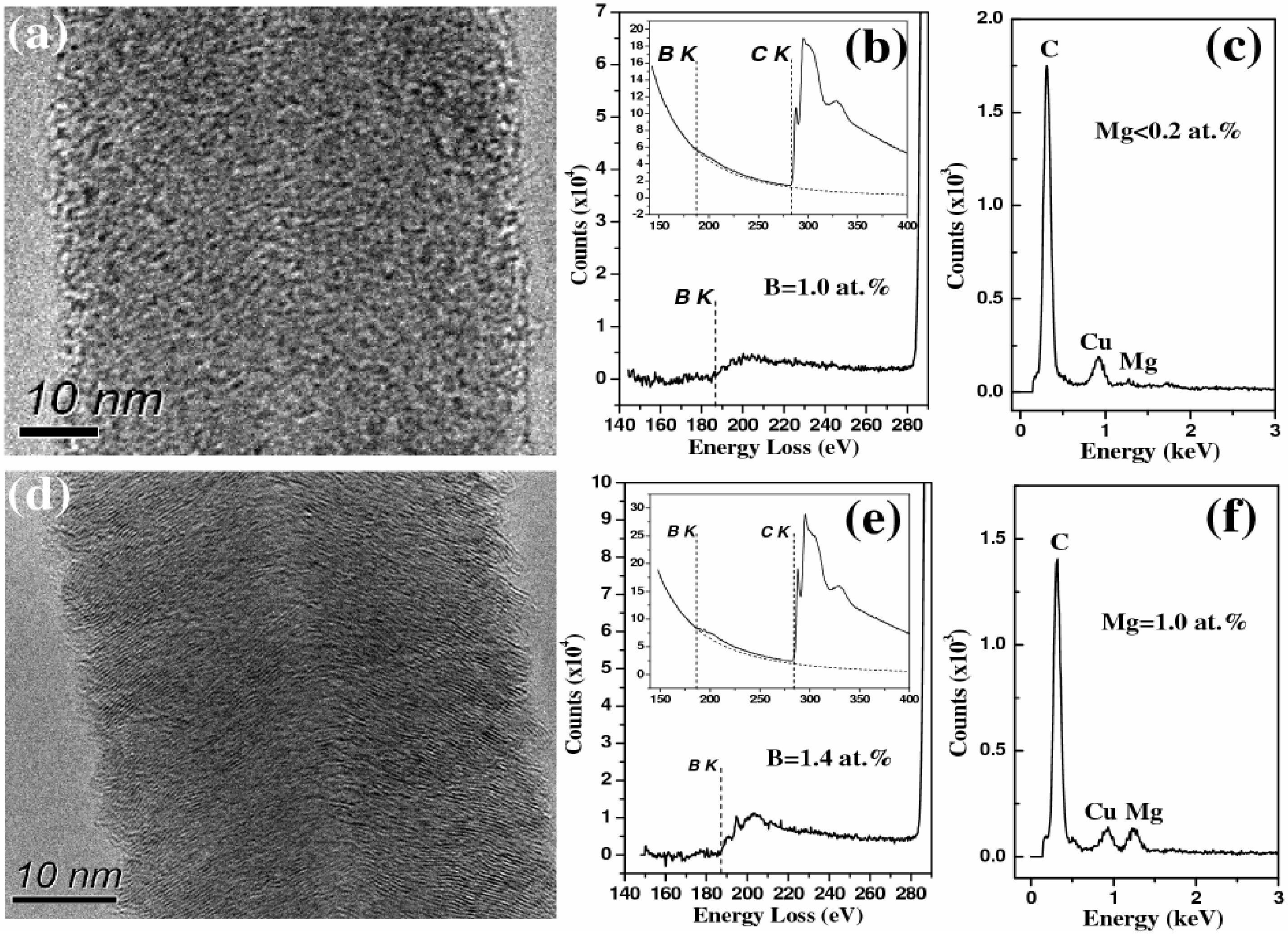
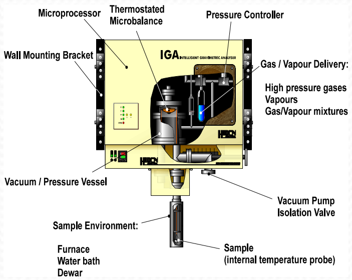


Figure 3: HRTEM (a, d), EELS (b, e) and EDS (c, f) of MgB_2 intercalated GNF. EELS shows a 1 at% of intercalated B while EDS shows a 0.2-1.0 at% intercalated Mg.

Fonseca, Gutierrez, Lueking, In Preparation, 2007.

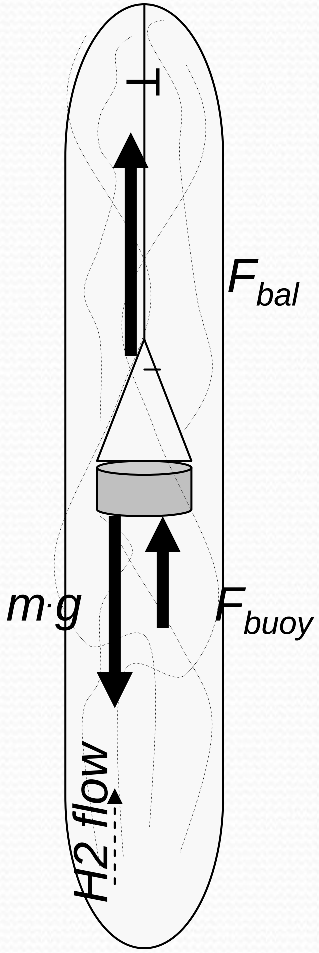
II. H_2 Adsorption Methods

- 1. Gravimetric
  - Hiden Isochema IGA-003
  - Pressures up to 20 bar
  - Temperatures up to 500 C



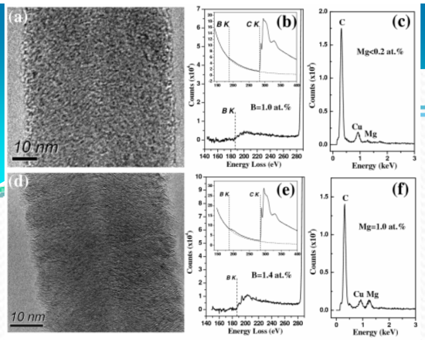
Operating Principle

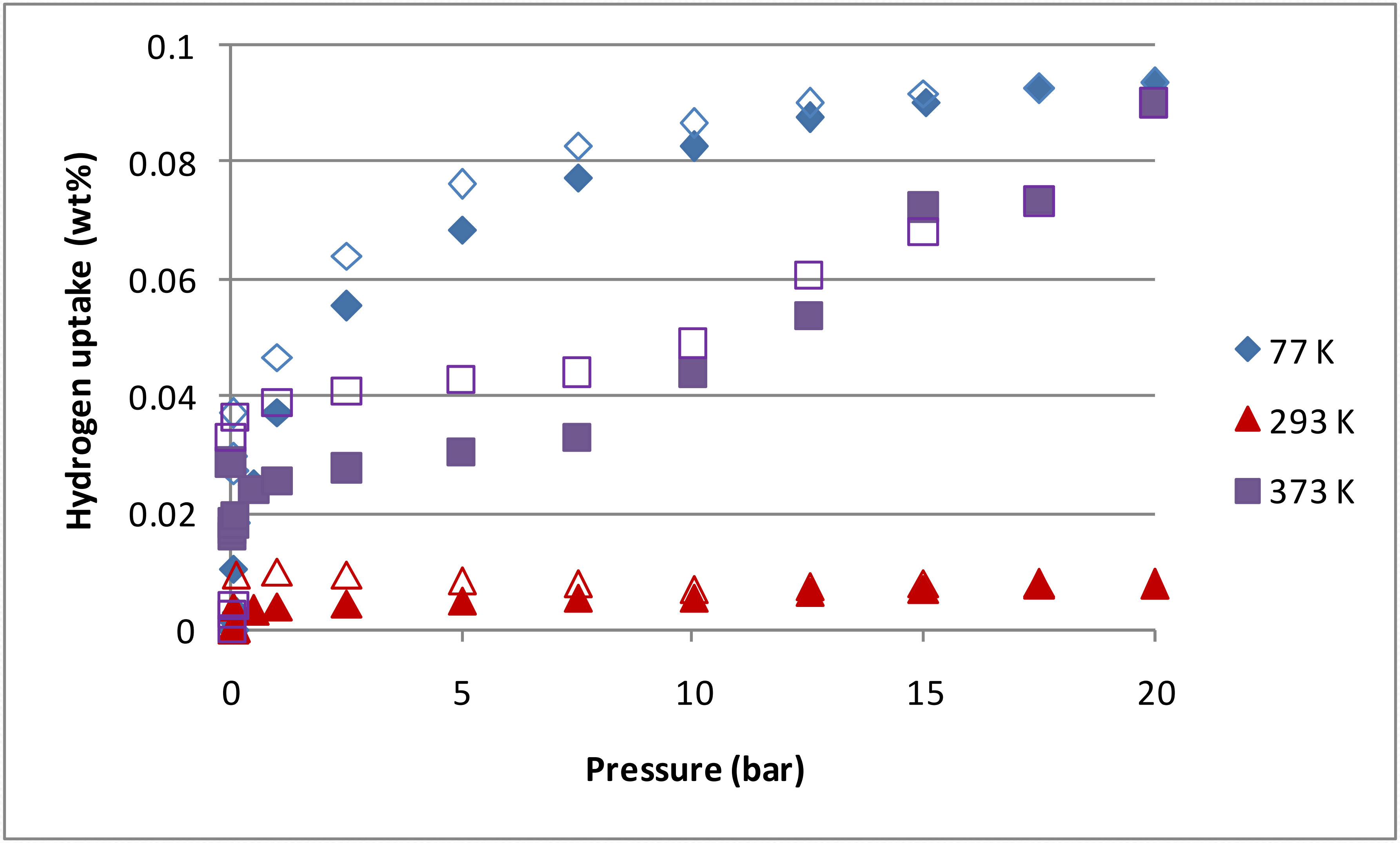
- Direct measurement of sample mass as adsorption gas contacts the sample
- Precise temperature control
- *In situ* treatments

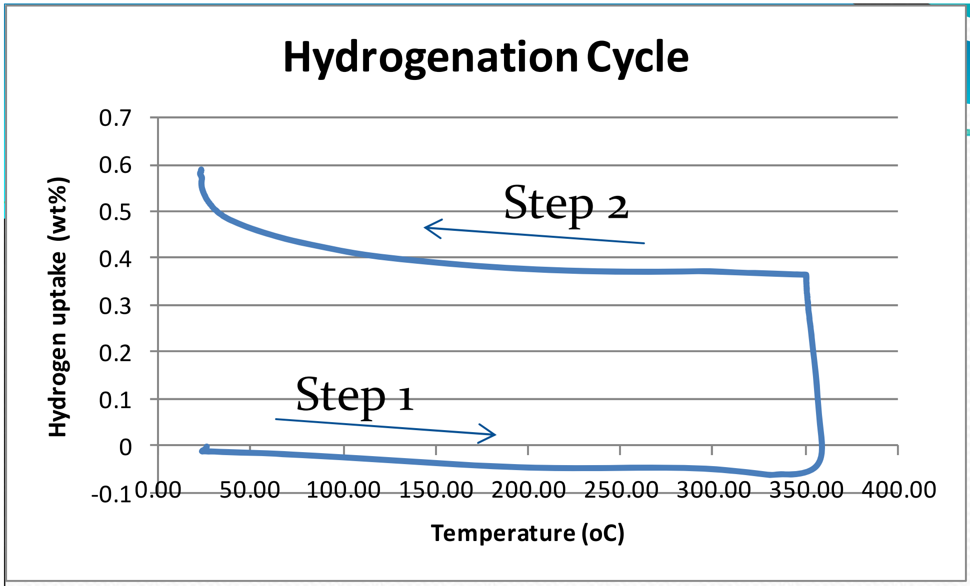


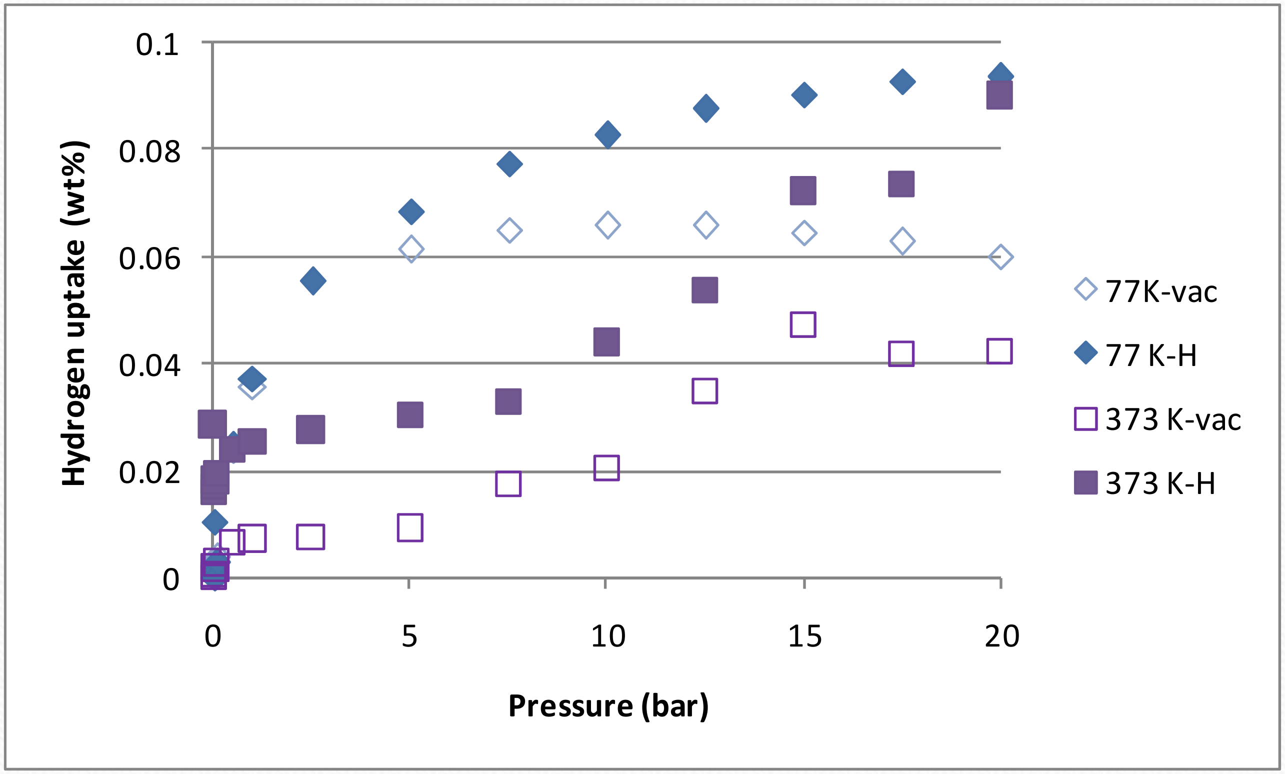
Potential artifacts

- Buoyancy
- Water contamination
- Contamination of sample


(a)
10 nm
(b)
B K
C K
B=1.0 at.%
Counts (x10⁴)
Energy Loss (eV)
(c)
C
Mg<0.2 at.%
Cu
Mg
Counts (x10³)
Energy (keV)
(d)
10 nm
(e)
B K
C K
B=1.4 at.%
Counts (x10⁴)
Energy Loss (eV)
(f)
C
Mg=1.0 at.%
Cu Mg
Counts (x10³)
Energy (keV)


Hydrogen uptake (wt%)
0.1
0.08
0.06
0.04
0.02
0
0
5
10
15
20
Pressure (bar)
77 K
293 K
373 K


Hydrogenation Cycle
Hydrogen uptake (wt%)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
Temperature (oC)
Step 2
Step 1


Hydrogen uptake (wt%)
0.1
0.08
0.06
0.04
0.02
0
0
5
10
15
20
Pressure (bar)
◇ 77K-vac
◆ 77 K-H
☐ 373 K-vac
■ 373 K-H

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  - Metal-intercalated graphite

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  - *Compared to: 5% Pt/Act. Carbon (STREM chemicals)*

H_2 Adsorption Methods

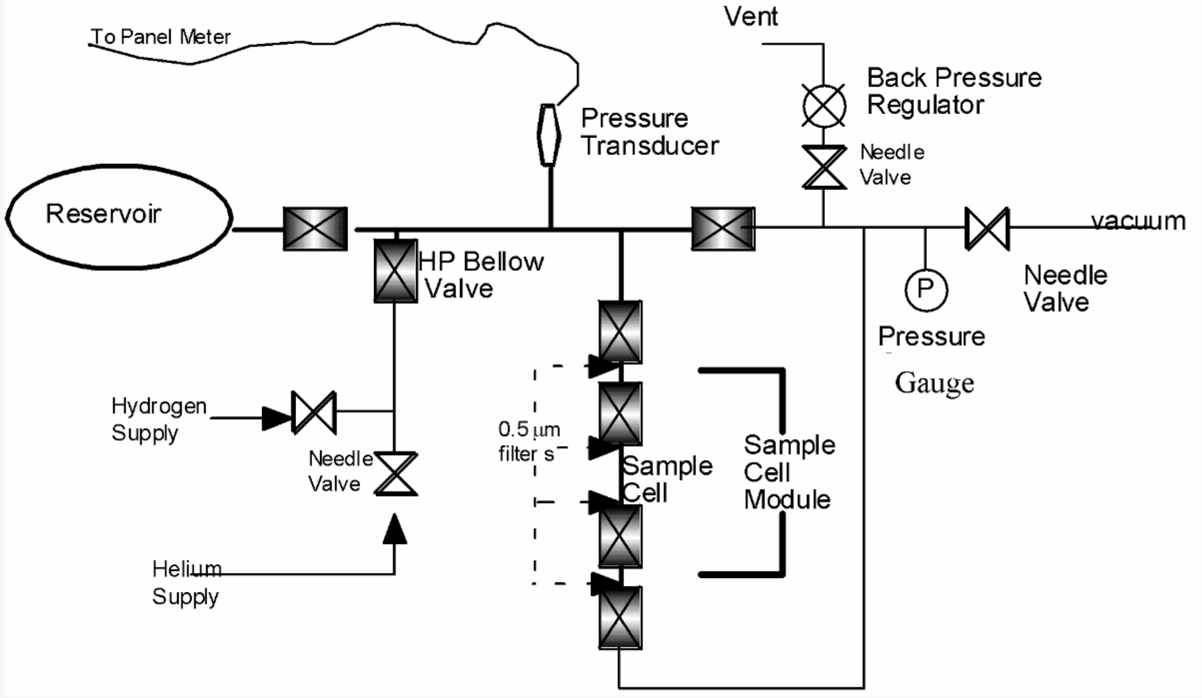
2. Volumetric

Collaboration with K. Adu

Assumptions:

No leaks

Pressure in sample cell is zero at time 0

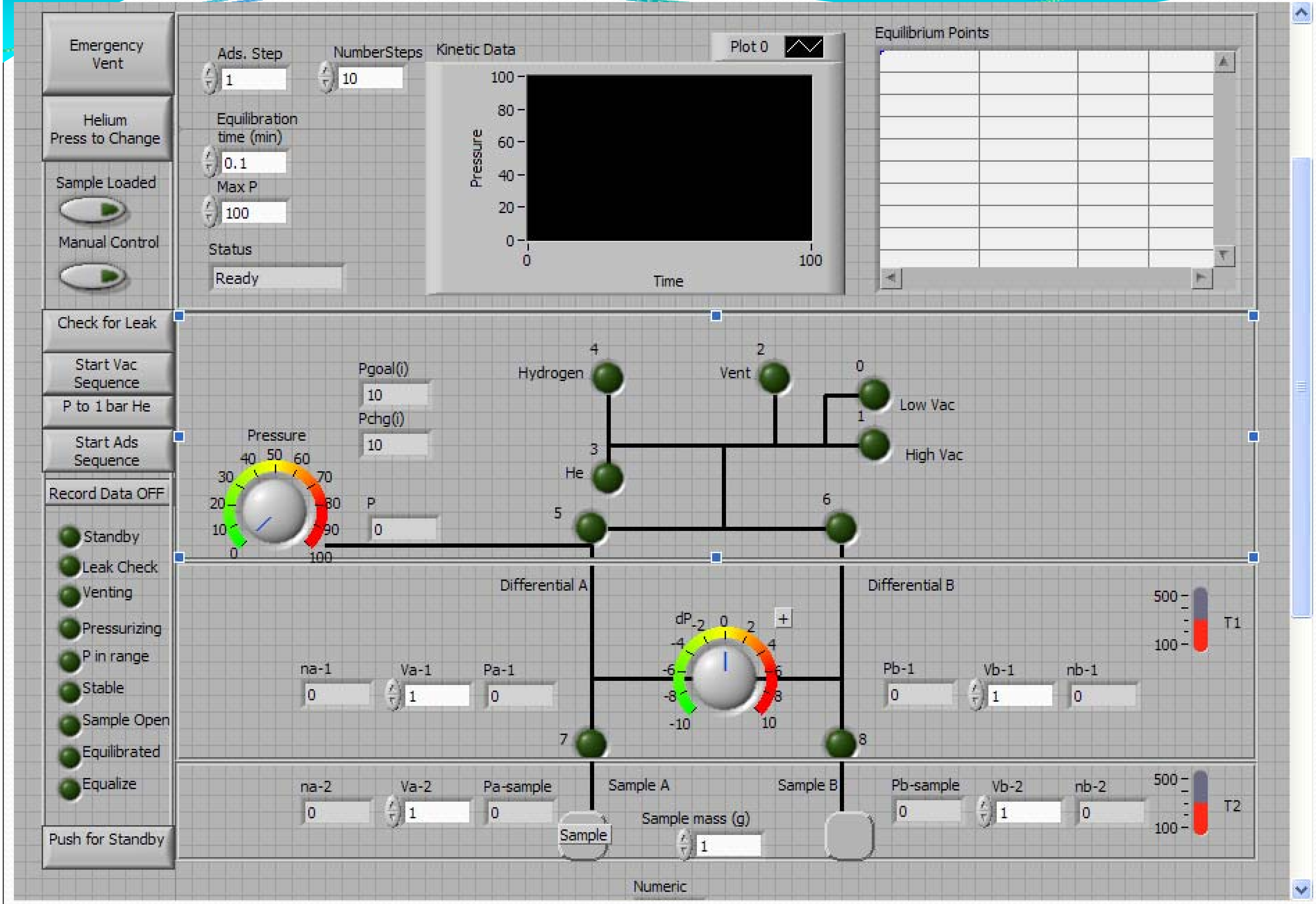


To get final amount adsorbed:

Need accurate sample mass

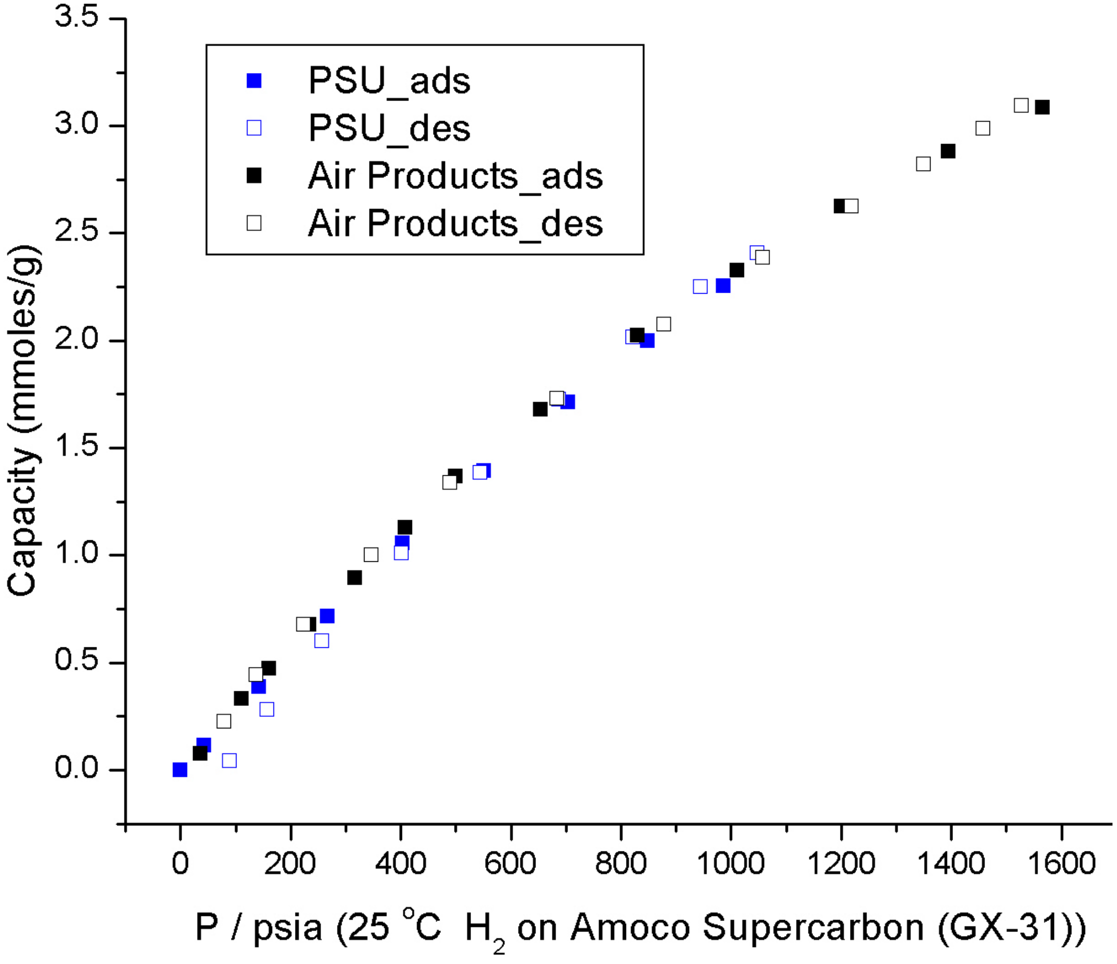
(Is it the same as what you put in?)

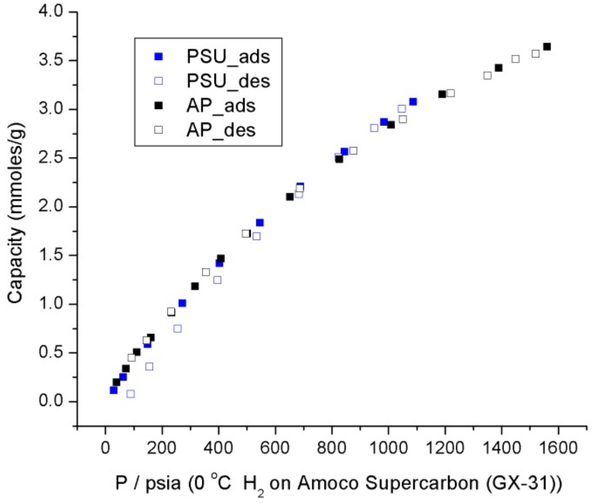
$$n_{ads} = \frac{P_1 V_1}{z_1(P,T)RT_1} - \frac{P_F V_F}{z_F(P,T)RT_F}$$

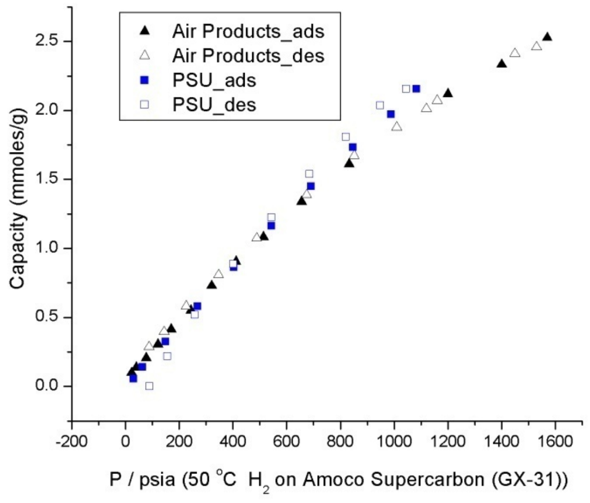


Ads. Step: 1
NumberSteps: 10
Equilibration time (min): 0.1
Max P: 100
Status: Ready
Pgoal(i): 10
Pchg(i): 10
P: 0
na-1: 0
Va-1: 1
Pa-1: 0
Pb-1: 0
Vb-1: 1
nb-1: 0
na-2: 0
Va-2: 1
Pa-sample: 0
Sample mass (g): 1
Pb-sample: 0
Vb-2: 1
nb-2: 0

Quality Check







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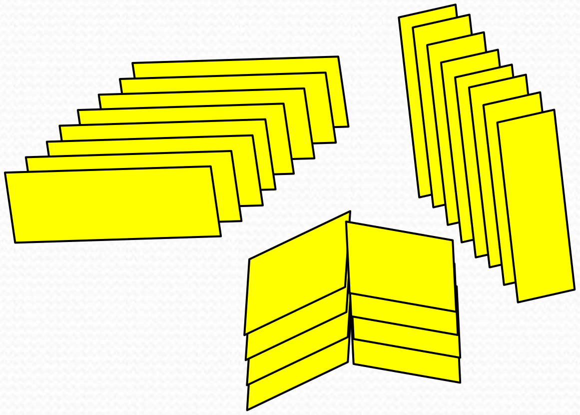
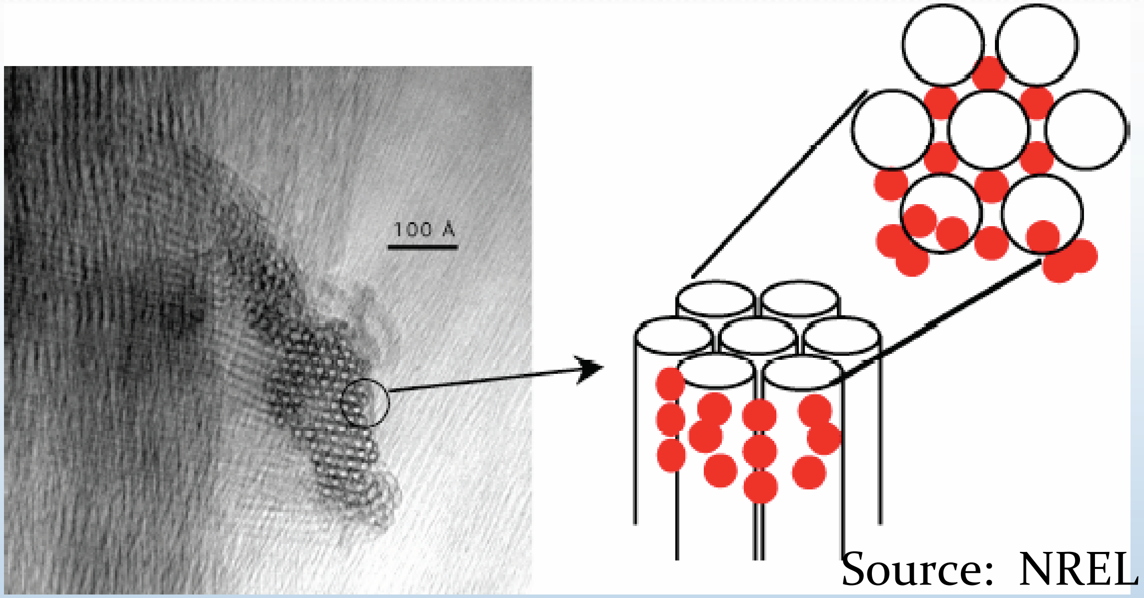
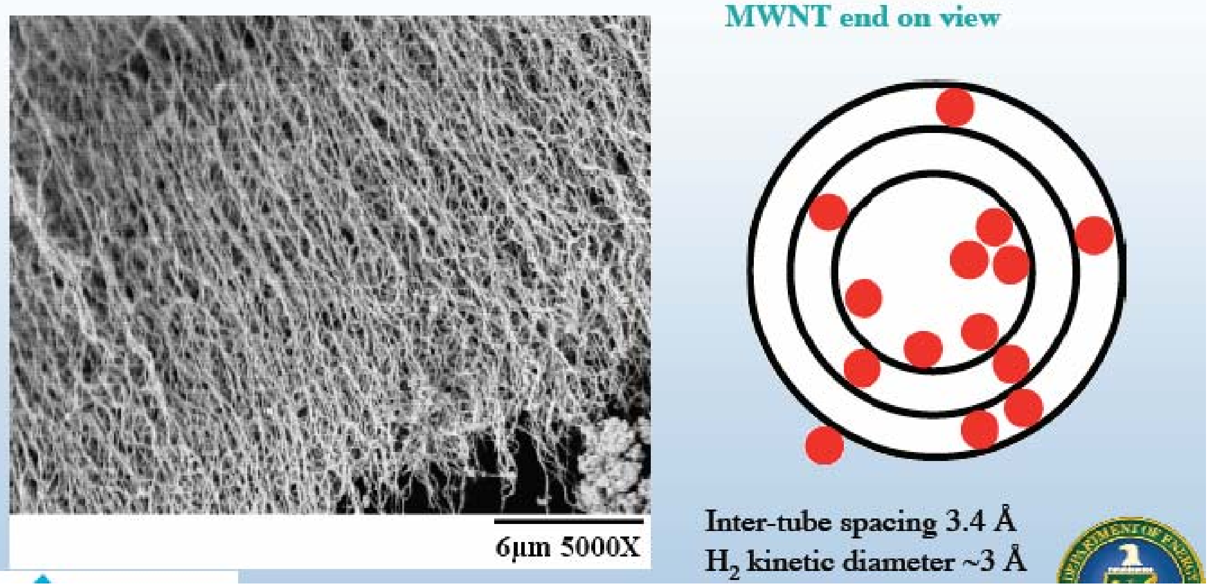
Nanocarbons

- Single-wall nanotubes
- Multi-wall nanotubes
- Graphite Nanofibers





Source: NREL

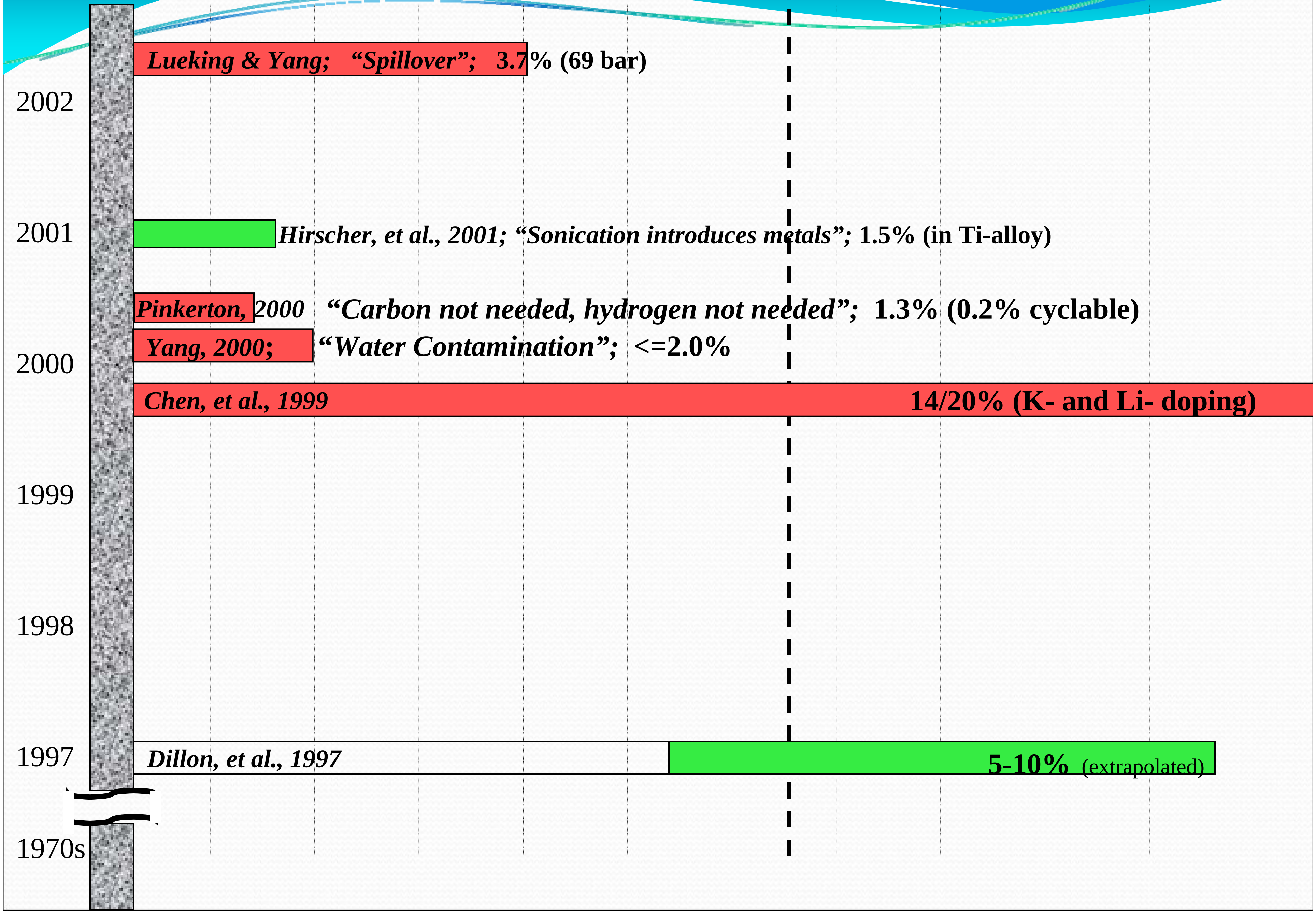


MWNT end on view

Inter-tube spacing 3.4 Å

H_2 kinetic diameter ~3 Å

Evolution of hydrogen storage reports…Carbon nanotubes



Lueking & Yang; "Spillover"; 3.7**% (69 bar)**

Hirscher, et al., 2001; "Sonication introduces metals"; **1.5% (in Ti-alloy)**

Pinkerton, *2000* ***"Carbon not needed, hydrogen not needed";*** **1.3% (0.2% cyclable)**

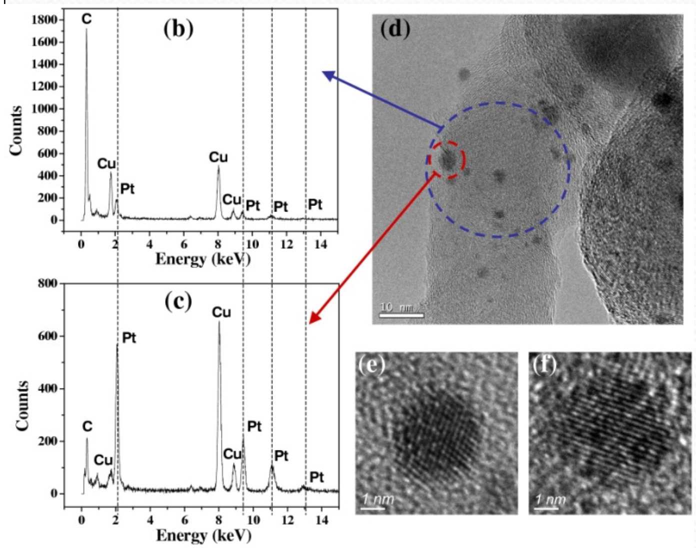
Yang, 2000; "Water Contamination"; **<=2.0%**

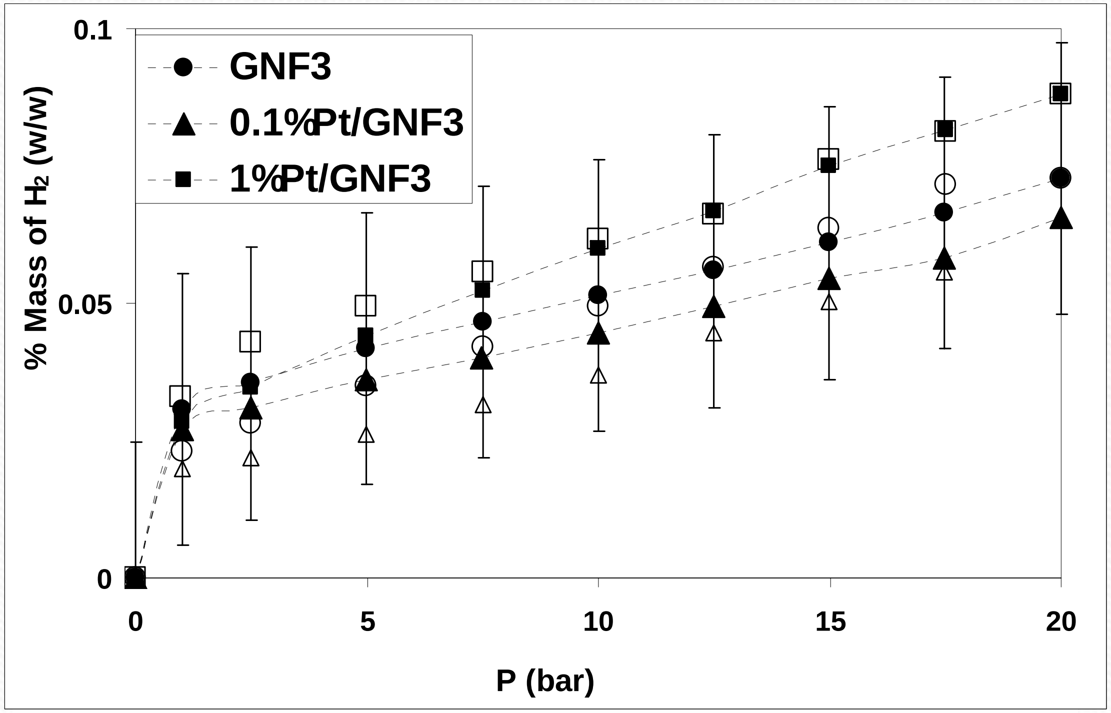
Chen, et al., 1999 **14/20% (K- and Li- doping)**

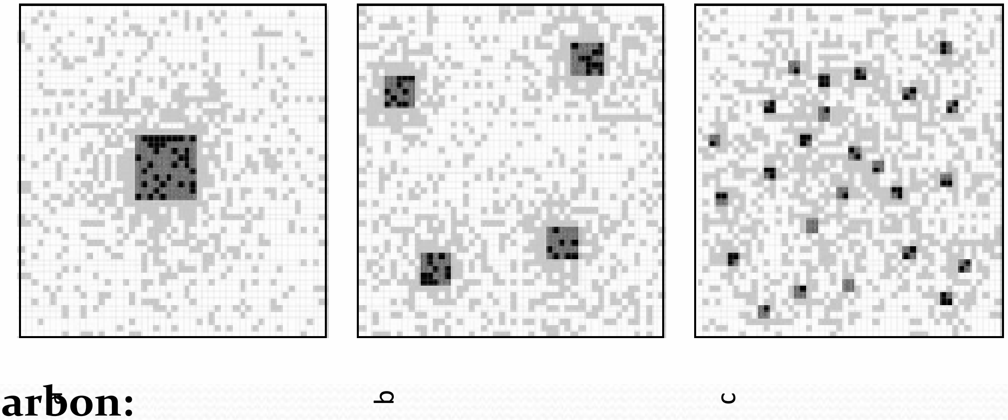
Dillon, et al., 1997 **5-10%** (extrapolated)

Justification

1. Previous work in our laboratory ➔ A few Unanswered Questions about active sites







Hydrogen Storage in Metal-assisted Carbon:
Jain … Lueking, J. Phys. Chem. C. 111, 1788, 2007.

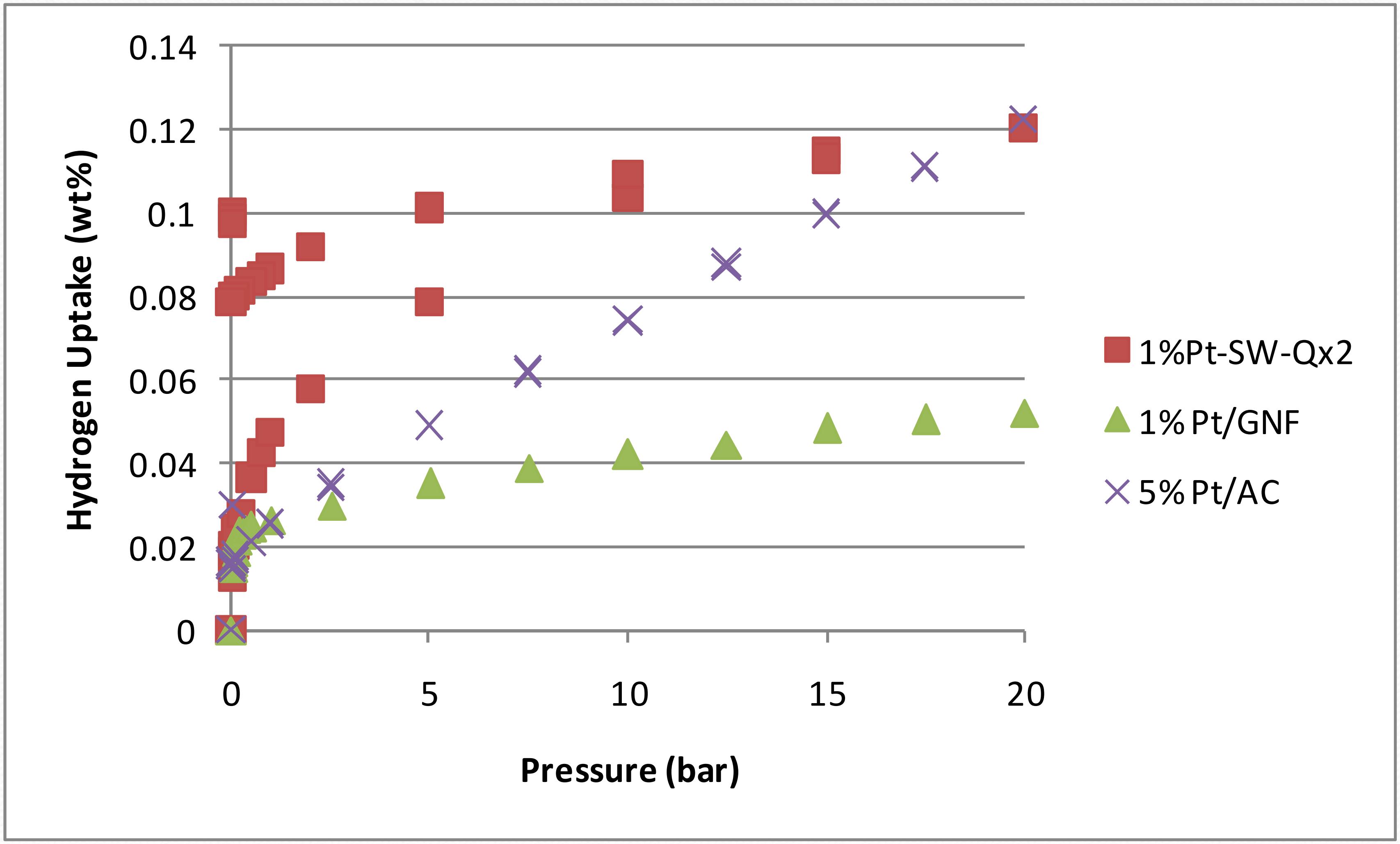

Hydrogen Uptake (wt%)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
5
10
15
20
Pressure (bar)
1%Pt-SW-Qx2
1% Pt/GNF
5% Pt/AC

Table 1: Characterization of the samples used in the study

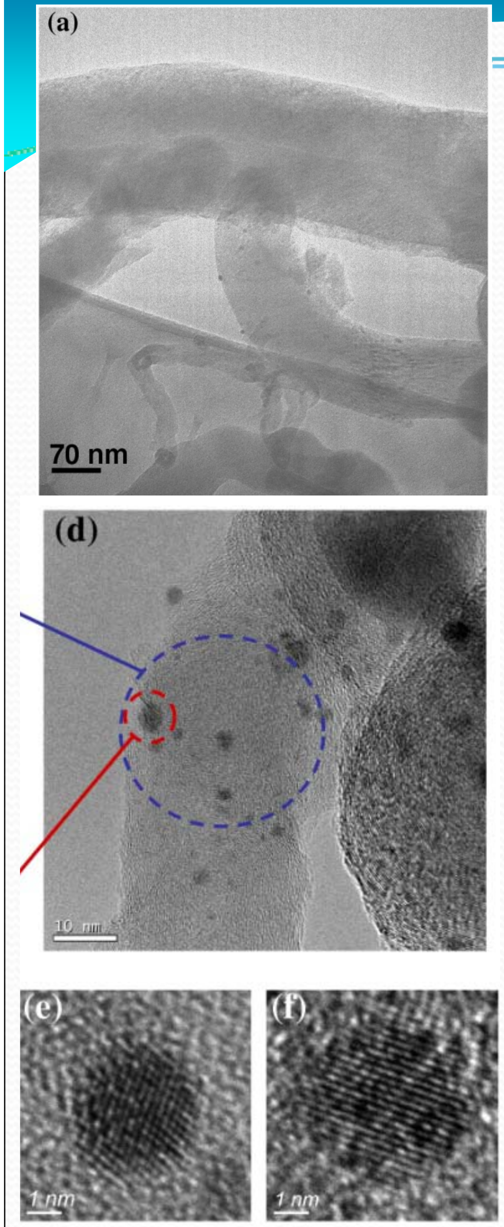
	GNF		SWNT		AC
	Undoped	1% Pt	Undoped	1% Pt	5% Pt
Surface Area (m^2/g)	100.9 ± 5[b] 115 (#11)	94.3	642.5	542.2	822.2
Pore Volume (cm^3/g)	0.147 ± 0.01[b]	0.17	0.54	0.49	0.64
Micropore Volume[c] (cm^3/g)	0.028	0.0139	0.245	0.121	0.33

[a] Not determined due to low sample quantity

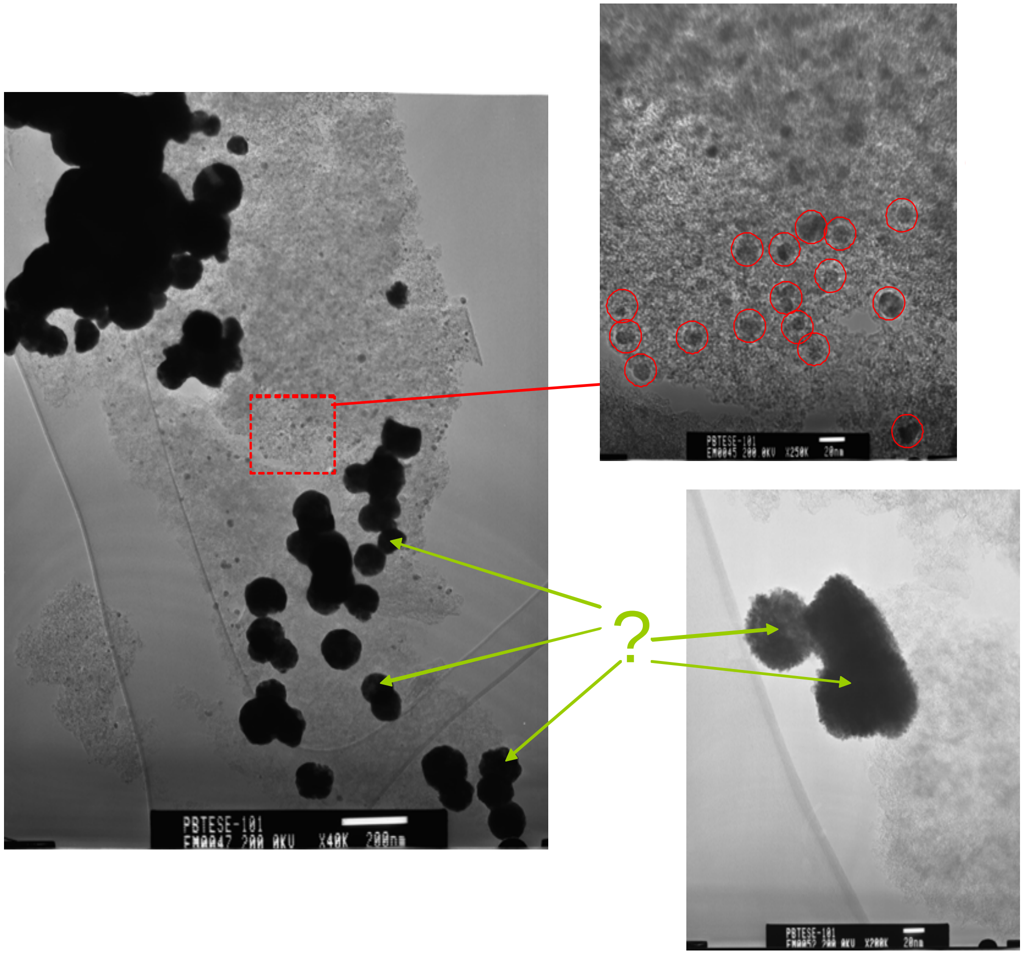
[b] Undoped GNF was run three times; average is reported together with standard deviation

[c] Calculated by Non-local Density Functional Theory

[d] Error in He density is measurement is ±0.1g/cm^3

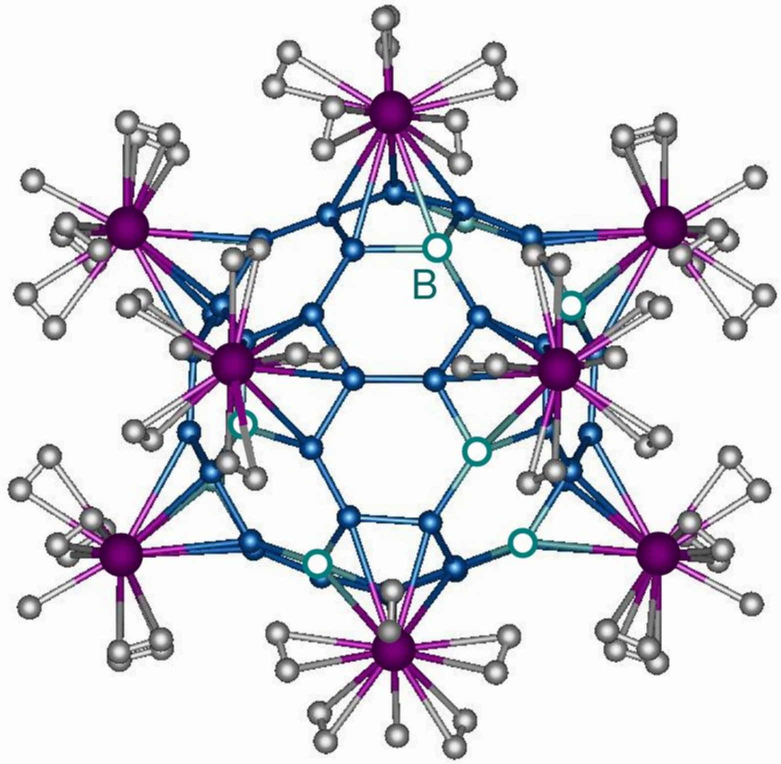


vs



Pt/GNF

Pt/Act.Carbon



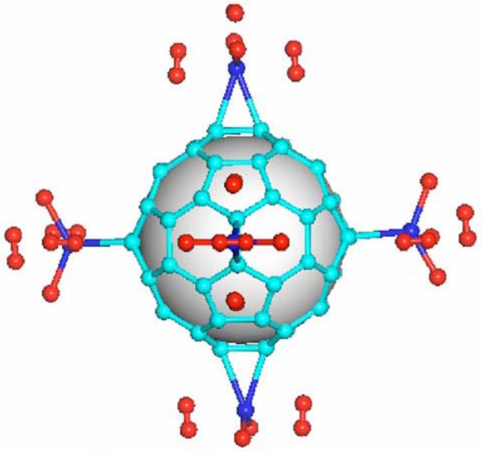
7.7 wt% for $Ti_{14}C_{13}$
0.17-0.89 eV/H_2

9wt% for $C_{48}B_{12}[ScH(H_2)_5]_{12}$
0.3 eV/H_2

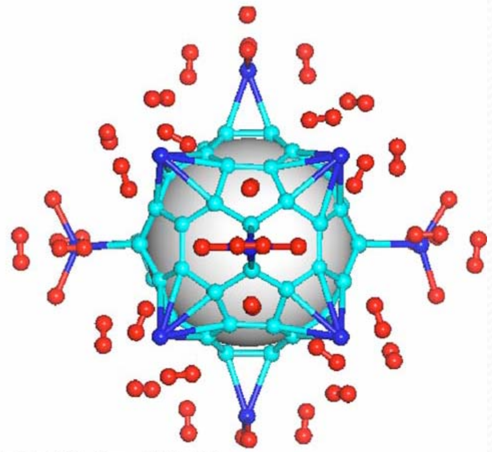
Y. F. Zhao, et al., Phys Rev Lett 94, 155504 (2005)
Dillon, et al., Mater. Res. Soc. Symp. Proc. 167 (200
Zhao, et al., Chem Phys Lett 425, 273-277 (2006).

7.5 wt% for Ti – C_{60}

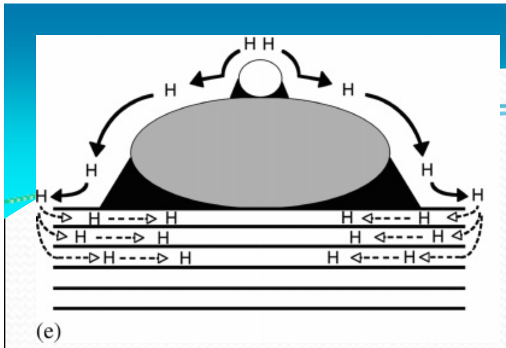
Yildrim et al., PRB 2005
Dag et al., PRB 2005 (Pt + SWNT)

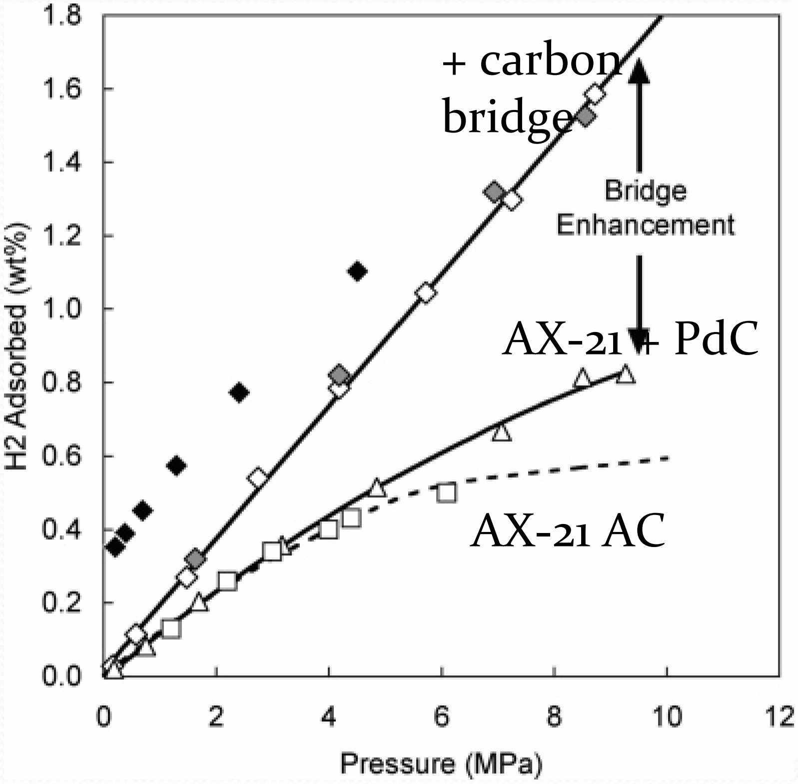


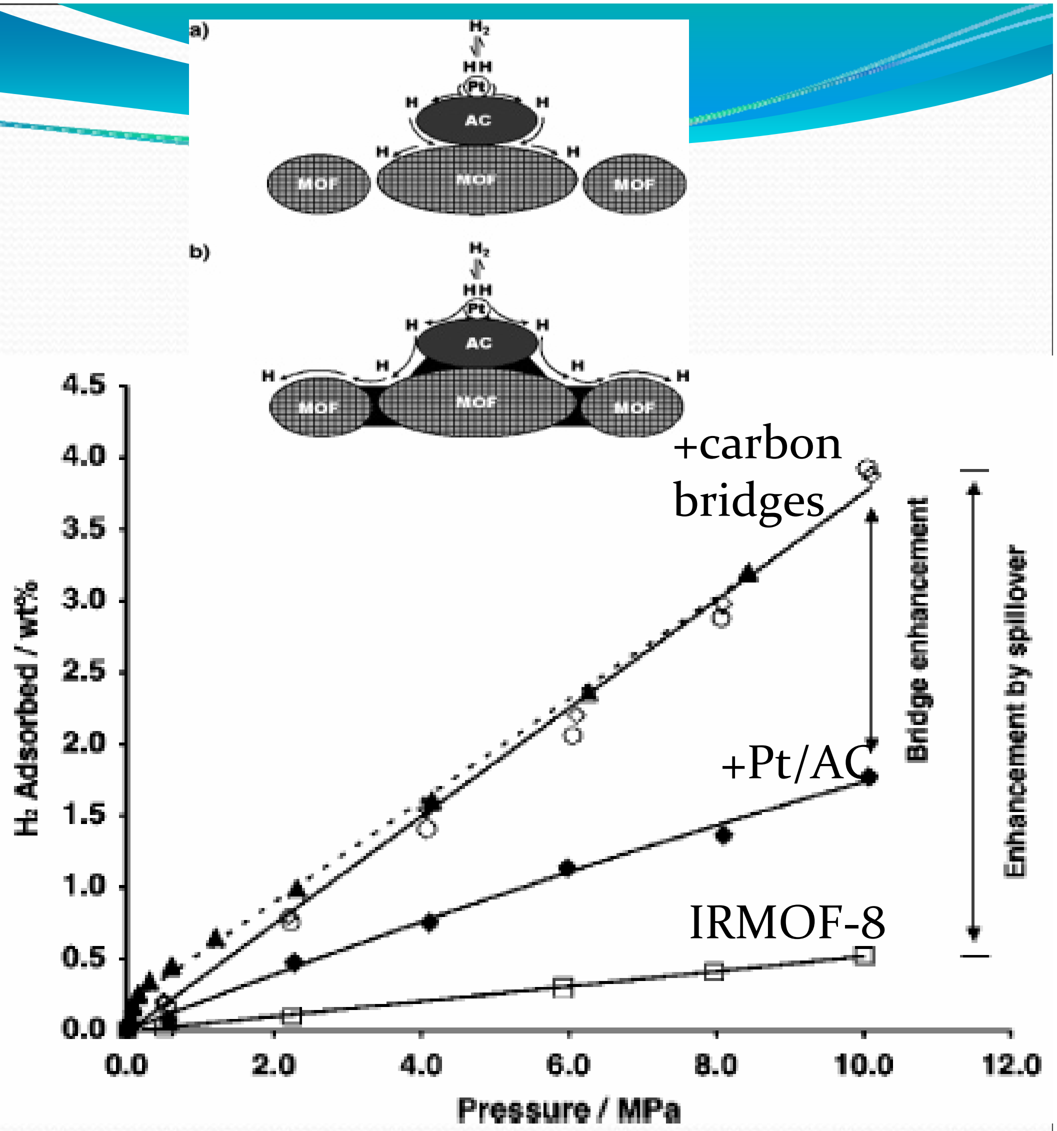
4.6 (3.4) wt% H_2 ●
E_B= 2.368 eV/H_2-3H_2 (2.235 eV)



7.5 (6.7) wt% H_2 ●
E_B= 2.089 eV/4H_2 (2.021 eV)







Lachawiec et al., Langmuir, 2005
Li & Yang, JACS, 2006
Yang et al., J. Phys. Chem. B, 2006

Justification:

2. Evidence in literature for effect after high-pressure H2 exposure

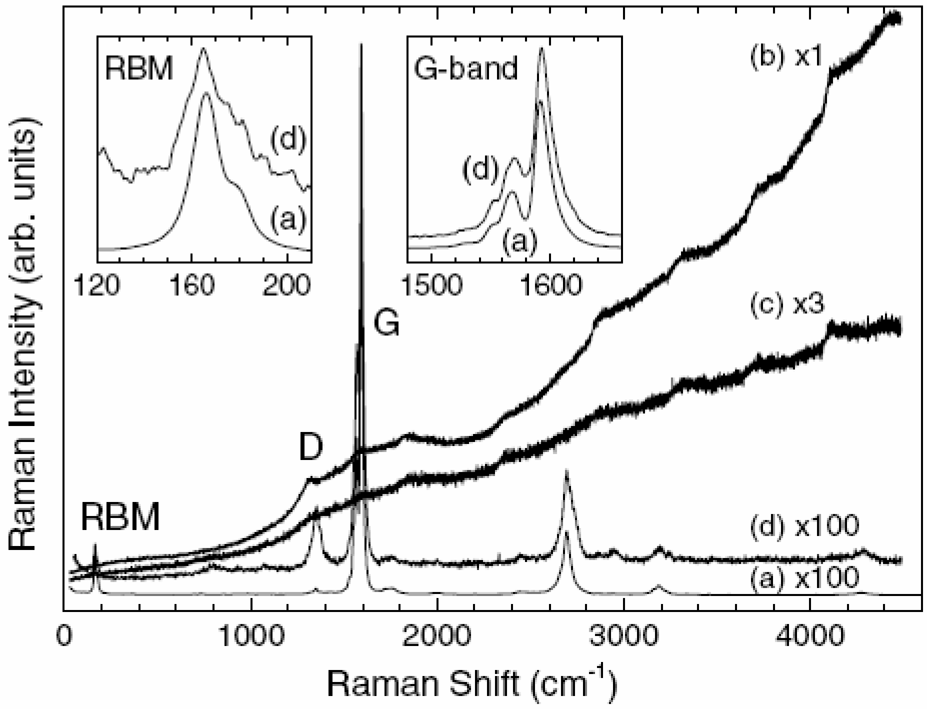


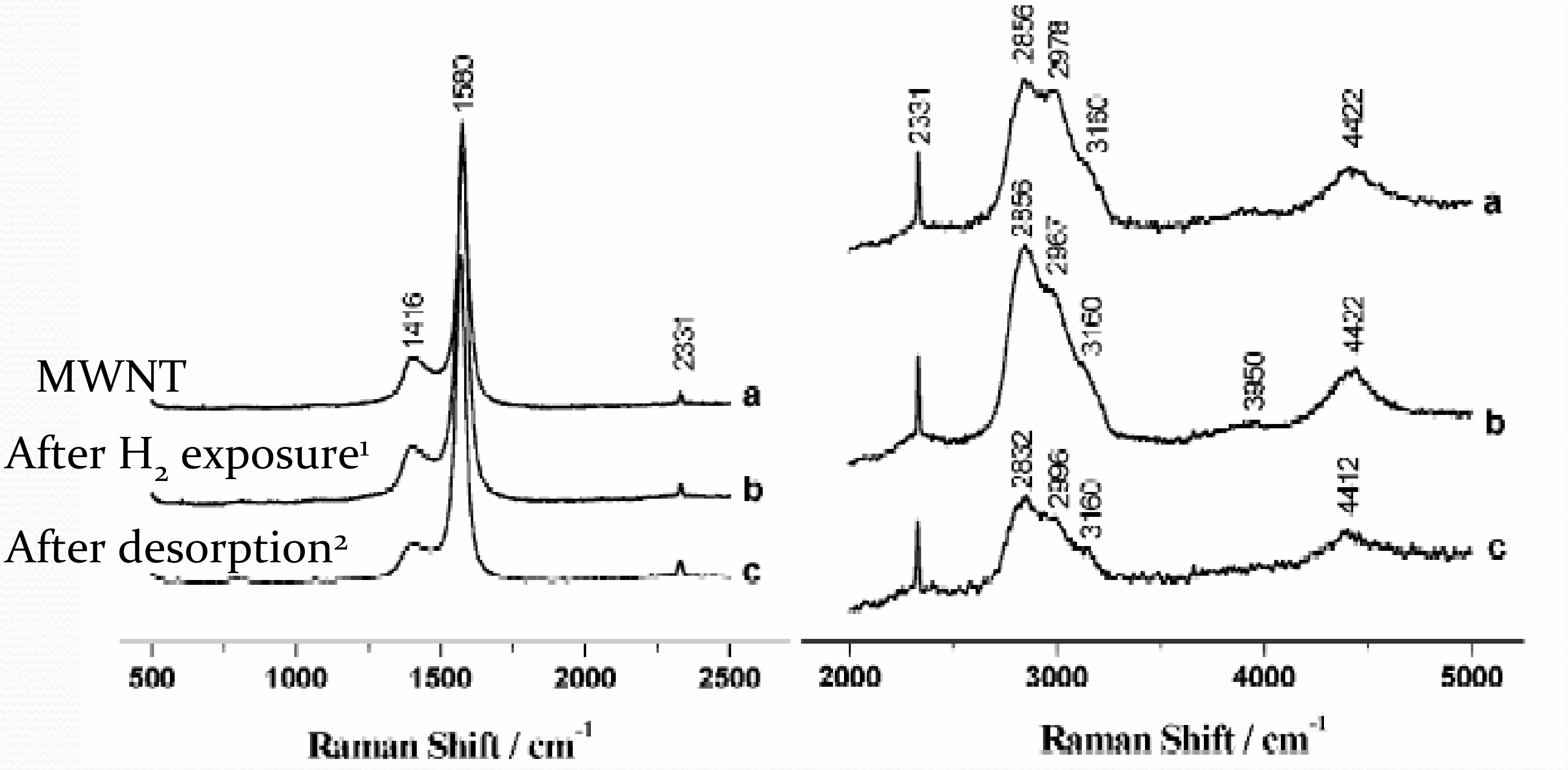
Fig. 1. Raman spectra of (a) pristine SWNT, (b) SWNT-H after annealing in vacuum at ~200 °C for 3 h, (c) at ~350 °C for 3 and (d) at ~550 °C for 1 h. Insets: Raman spectra (a) and (d) in the RBM and the G-band frequency regions.

SWNTs hydrogenated at 5.0 Gpa and 500 C

Meletov et al. Chem. Phys. Lett. (2006), doi:10.1016

Justification:

2. Evidence in literature for effect after high-pressure H2 exposure


MWNT

After H_2 exposure[1]

After desorption[2]

MWNT made with CH_4 or CO, NiMgO catalyst

Zhang et al., Carbon 40 (2002) 2429–2436

[1] vacuum treatment 873 K, 2 hours
H2: 2 Mpa H2, 300 K, 2 hours

[2] Heating to 973 K then cooling

Justification:

2. Evidence in literature for effect after high-pressure H2 exposure

High-pressure capillary employed

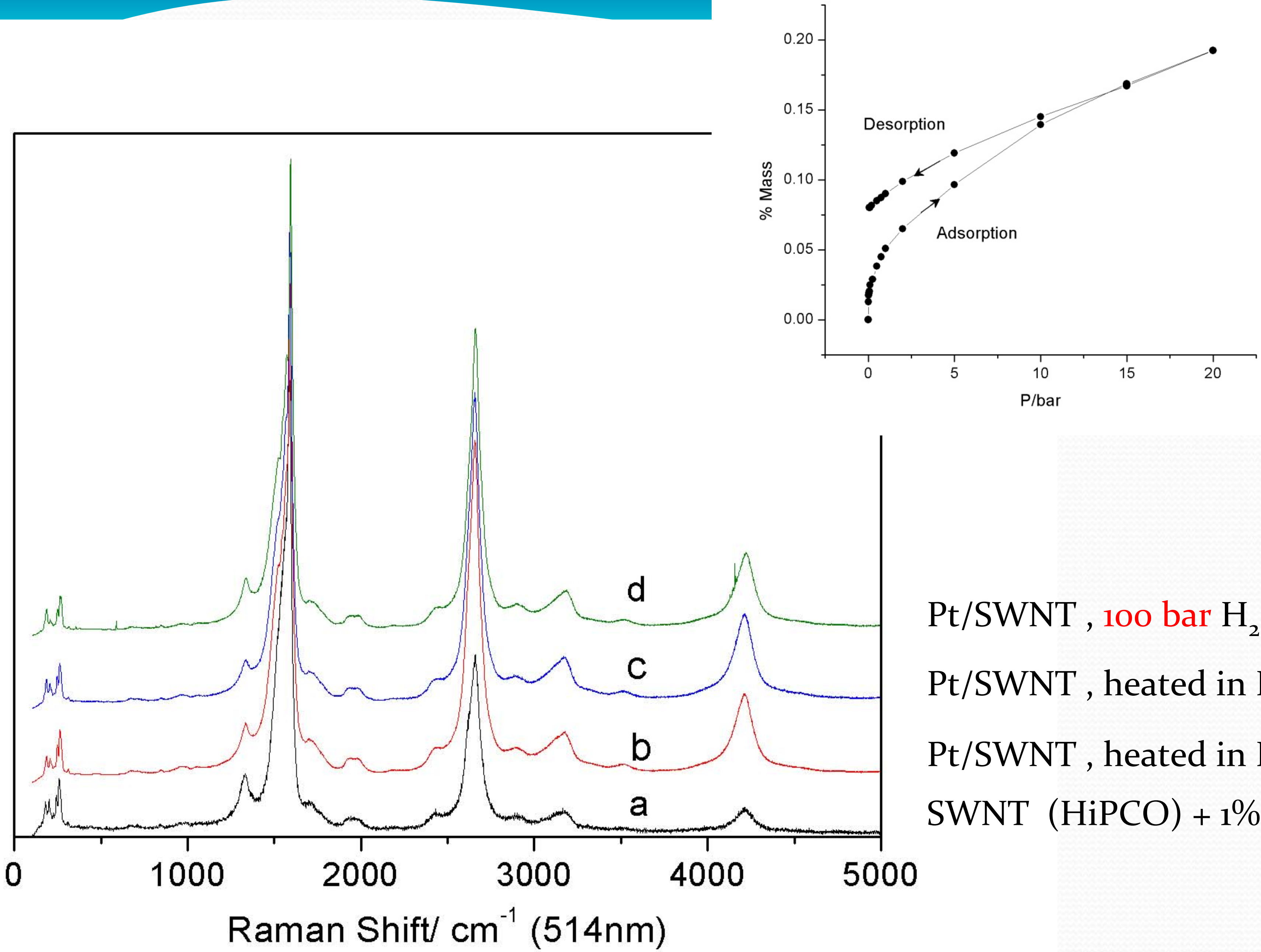
Need for transfer in an inert environment

Current focus: Multi-wavelength Raman

Samples studied to date:

- 1% Pt/SWNT
- MWNT (CH_4 w/ NiMgO)

NEW!

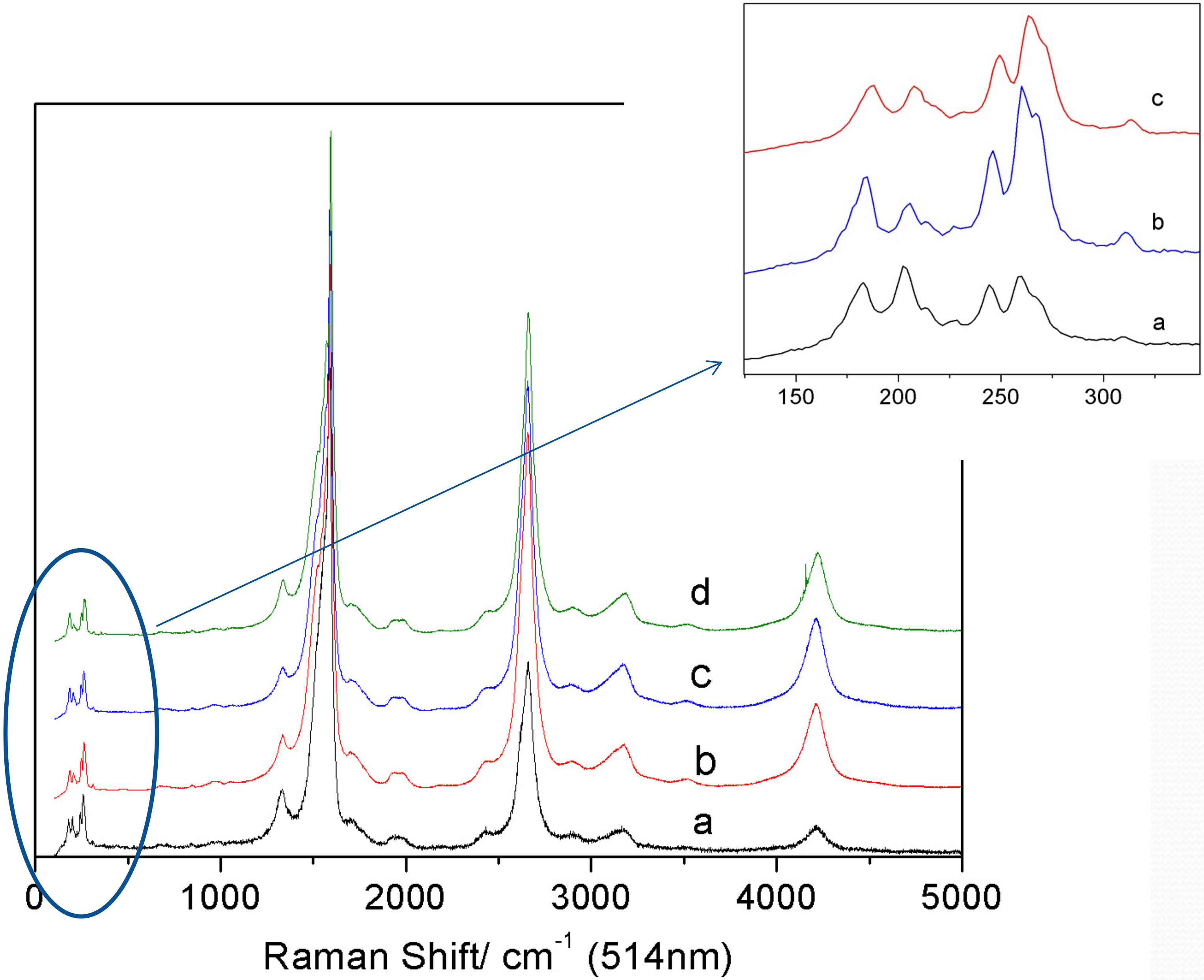


Pt/SWNT , 100 bar H_2

Pt/SWNT , heated in H_2

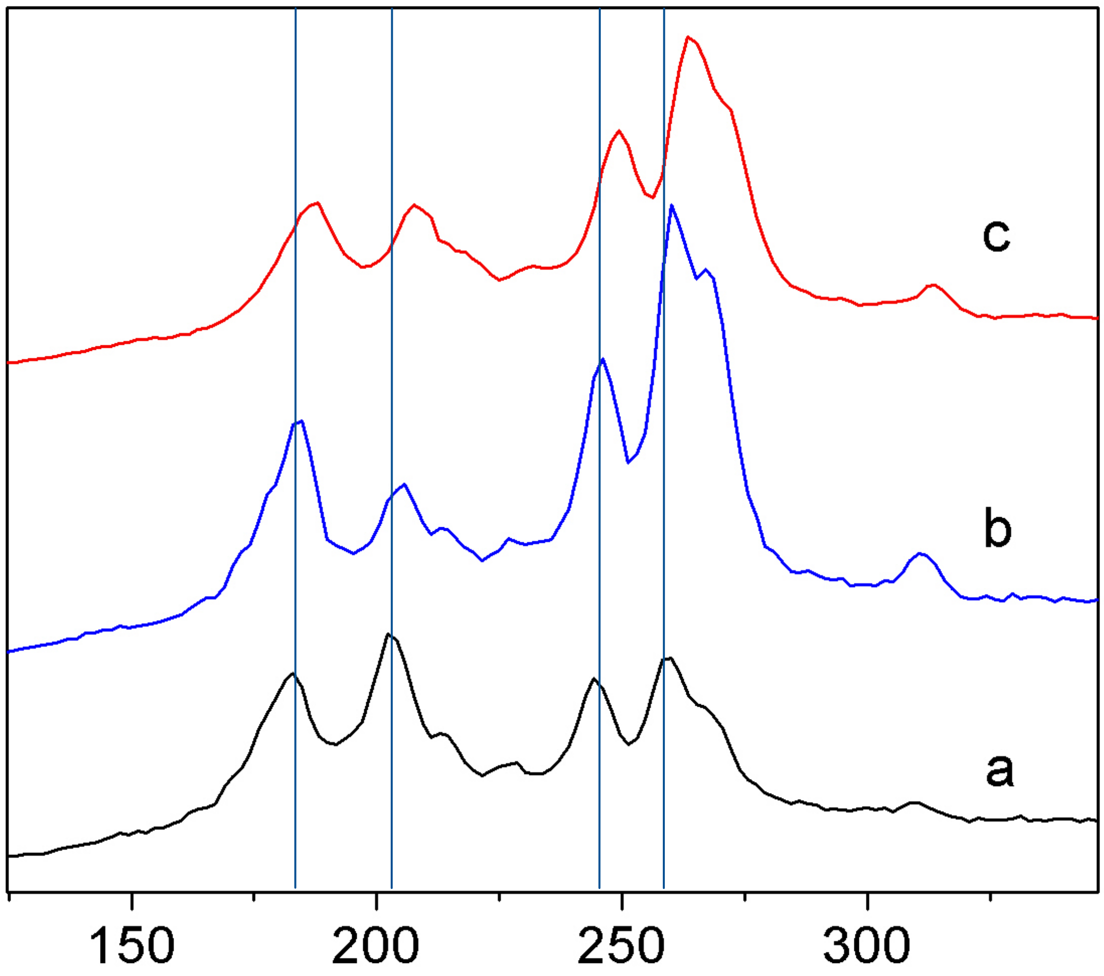
Pt/SWNT , heated in He

SWNT (HiPCO) + 1%Pt



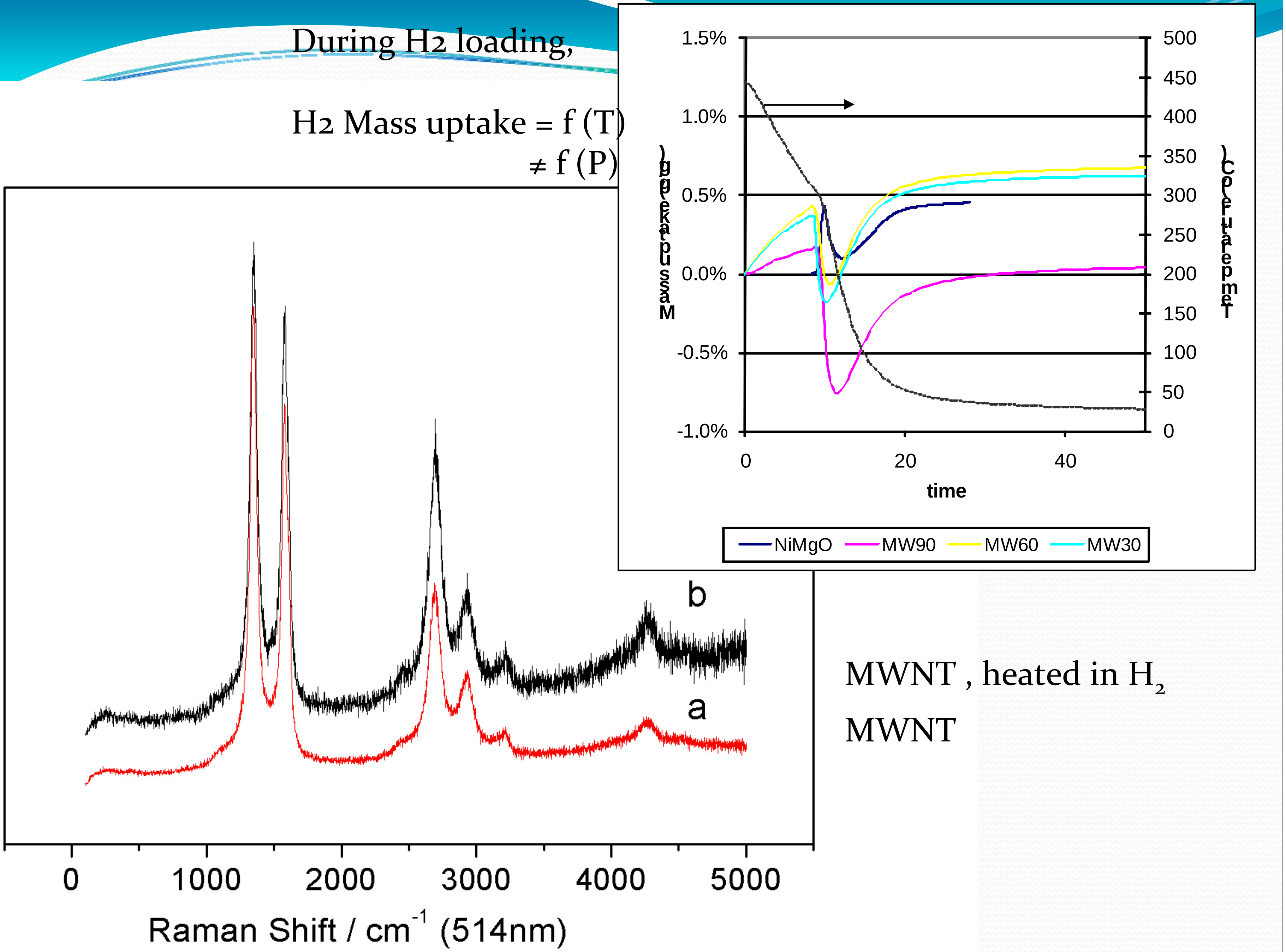
c
b
a
150
200
250
300
d
c
b
a
0
1000
2000
3000
4000
5000
Raman Shift/ cm^{-1} (514nm)

$$\omega_{\mathrm{RBM}} = \frac{A}{d} + B$$



During H2 loading,

H2 Mass uptake = f (T)
≠ f (P)



MWNT , heated in H_2

MWNT

Summary and Conclusions

- Method Development
  - High-pressure, automated differential Sievert's developed, calibrated, and tested at various pressures
  - High-pressure *in situ* Multi-Wavelength Capabilities
- Synthesis
  - "Standard" Materials (starting point for new methods)
  - "New" Materials Synthesized—characterization underway
- Combined Characterization and Uptake
  - Beginning to see an affect of hydrogenation in Raman
  - Hydrogen Uptake appears to be more temperature--rather than pressure--dependent

  * May be a function of carbon precursor or "active" adsorption sites

THANK YOU!

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Li


Fonseca


Badding

TEM


Gutierrez

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