



# Characterization of Hydrogen Adsorption by NMR

“DOE Center of Excellence on Carbon-based Hydrogen Storage  
Materials”

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Project ID #  
STP18



# Overview

## Timeline

- Project start date  
2/1/2005
- Project end date  
1/31/2010
- Percent complete  
20%

## Budget

- Total project funding
  - DOE share: \$626,177
  - Contractor share: \$156,542
- Funding received in FY05  
\$65,000
- Funding for FY06  
\$125,000

## Barriers

- Barriers addressed
  - Lack of understanding of hydrogen physisorption and chemisorption
  - Lack of independent evaluation of hydrogen storage capacity

## Partners

NREL (Heben), U. Penn (MacDiarmid), Penn State (Eklund, Chung), ORNL (Geohegan), Caltech (Ahn), LLNL (Baumann, Herberger), Duke (Liu), Rice University (Hauge, Yakobson), Air Products (Pez, Cooper)



# Objectives

## Overall

Using NMR technique to support team members of DOE CbHS CoE in developing reversible carbon-based hydrogen storage materials with 7 wt.% materials-based gravimetric capacity, with potential to meet DOE 2010 system-level targets.

## 2005

- NMR system for quantitative in-situ measurement of H<sub>2</sub> adsorption up to 100 atm  
----Instrument construction and testing
- NMR measurements of H<sub>2</sub> adsorption in doped polyaniline (U Penn: MacDiarmid)  
----Verify the reported value<sup>(1)</sup> of **6 wt%** H<sub>2</sub> storage capacity in doped polyaniline with molecular level information.

## 2006

- NMR measurements of H<sub>2</sub> adsorption in B-doped carbon nanotubes (**NREL: Heben**) and B-doped graphite (**Penn State: Chung**)  
-----Evaluate the potential of boron doping for increasing the adsorption energy above **10 kJ/mol**.
- Investigate if boron atoms are incorporated in the framework of nanotubes and graphite and characterize their local structures by NMR.
- Investigate effects of doping treatment on H<sub>2</sub> adsorption in polyaniline (U Penn: **MacDiarmid**)

(1) S.J. Cho, K.S. Song, J.W. Kim, T.H. Kim, K. Choo, Fuel Chemistry Division, 224th Nat. Meet. Am. Chem. Soc., 47 (2002) 790.



# Approach

## *Why NMR?*

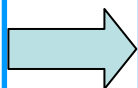
Hydrogen storage materials under current investigation are mostly **heterogeneous**, especially carbon-based materials. The challenges in developing efficient storage materials are:

- Timely recognition and identification of promising **adsorption sites** with suitable **adsorption enthalpy**.
- Optimization of the **number** of such adsorption sites.

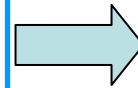
Because of the heterogeneous nature, promising adsorption sites may be present but not abundant in the materials of initial study. Screening materials by simply measuring the total amount of adsorption may overlook systems that are actually promising but not yet optimized in terms of the number of adsorption sites. The importance of NMR relies on its potential capabilities of

- Measure adsorption isotherms separately for each type of adsorption sites making promising adsorption sites more transparent.
- Provide valuable structure information on the nature of such adsorption site as well as the molecular dynamics of adsorbed hydrogen.
- Needs only about **20 mg** of carbon-based materials for isotherm measurement because of the high sensitivity of  $^1\text{H}$  NMR.

**Proton NMR  
spectral  
analysis and site  
identification**



**In-situ NMR  
measurement of  
adsorption isotherms for  
each type of adsorption  
sites up to 100 atm**



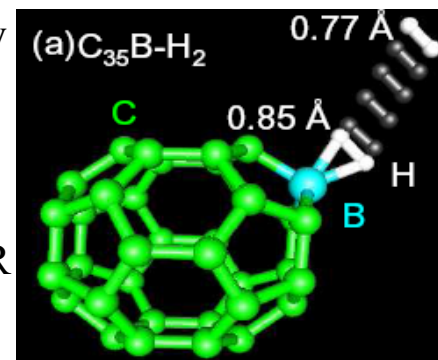
**NMR characterization of the  
nature of promising  
adsorption site and explore  
ways to enhance the number  
of adsorption sites**



# Background

**Issues:** Although carbon is light weight, no interactions with  $H_2$  have been positively identified with adsorption energy in the range of 15-40 kJ/mol, an ideal range of adsorption energy for reversible hydrogen storage at room temperature. Theorists in our team have predicted adsorption by boron doping. Both B-doped single-walled carbon nanotubes (SWNTs) and B-doped graphite are being investigated in our NMR study intending to answer two basic questions:

- (1) **Is the number of incorporated boron substantial in the carbon framework and, if yes, how?**
- (2) **Is boron doping effective in raising the adsorption energy?**



Shengbai Zhang, NREL

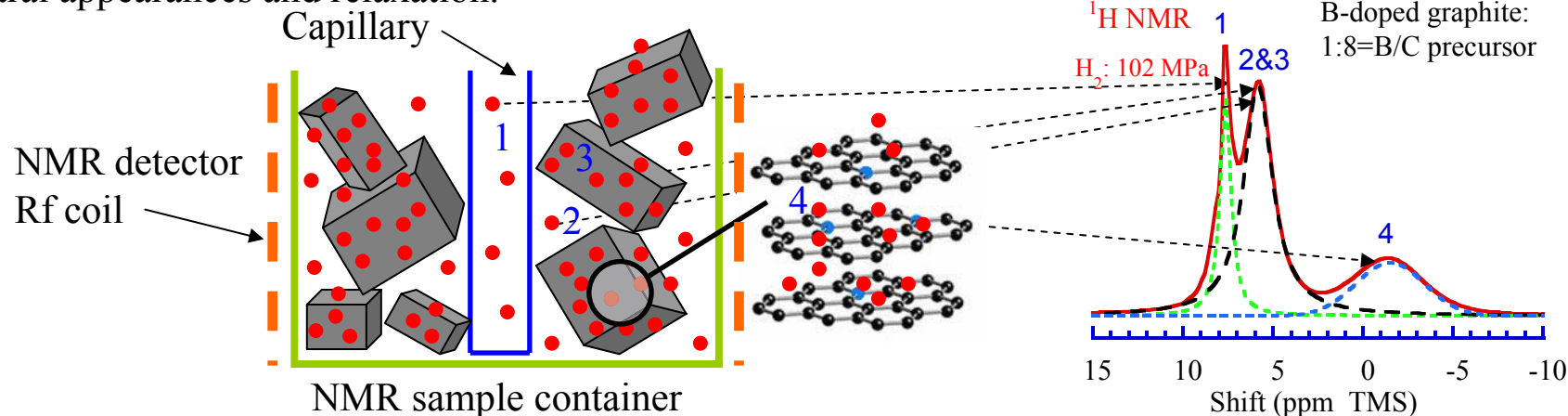
**Peaks NMR detects:** An illustration using B-doped graphite.

**Peak 1:** Free gas in the capillary standard,

**Peak 2&3:** Free gas in the unfilled space of the sample region (2) and adsorbed  $H_2$  on outer surfaces of grains (3).

**Peak 4:** Adsorbed  $H_2$  on surfaces in confined regions such as nano-slit pores and nano-voids.

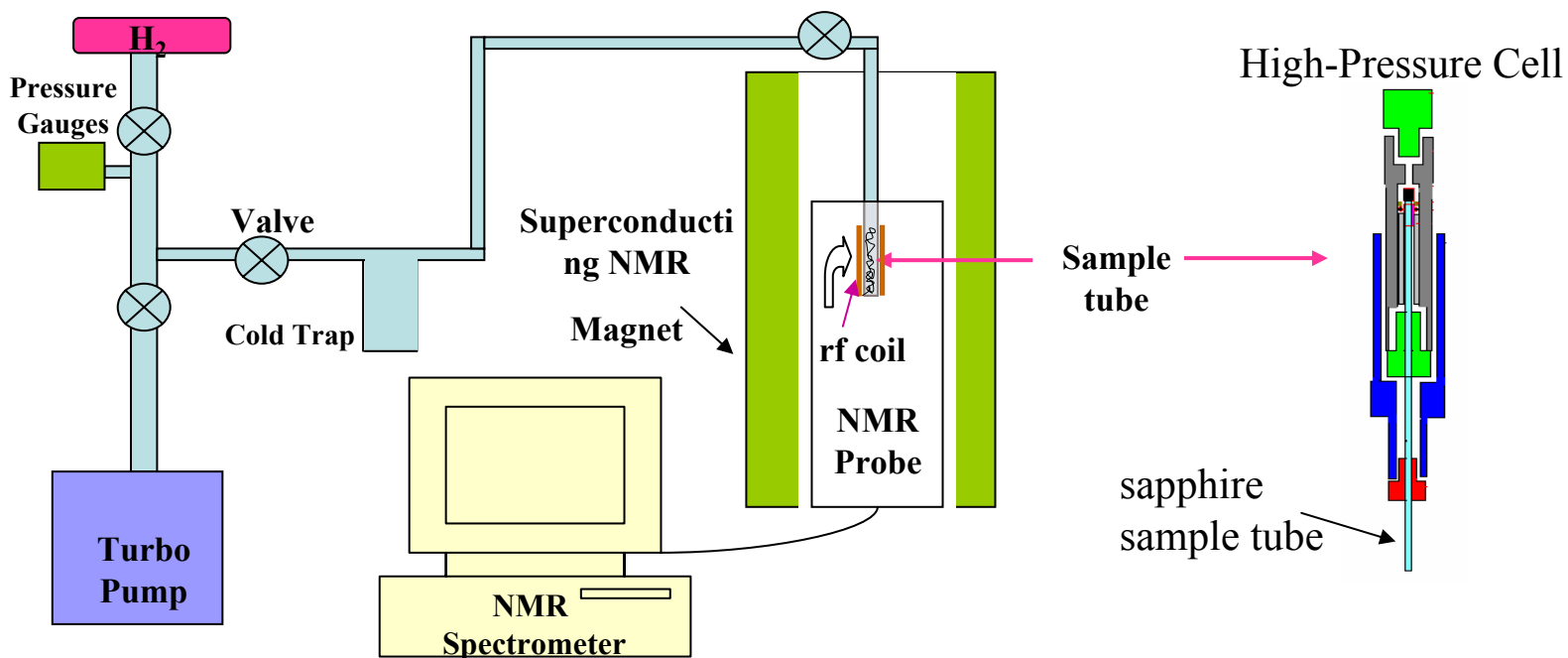
**In addition:** Atomic hydrogen upon dissociation of  $H_2$  can also be observed which have characteristic signatures in spectral appearances and relaxation.





# Technical Accomplishments

- Advanced NMR instrument by constructing an NMR system for in-situ  $H_2$  adsorption measurements to high pressure ( $>100$  atm)

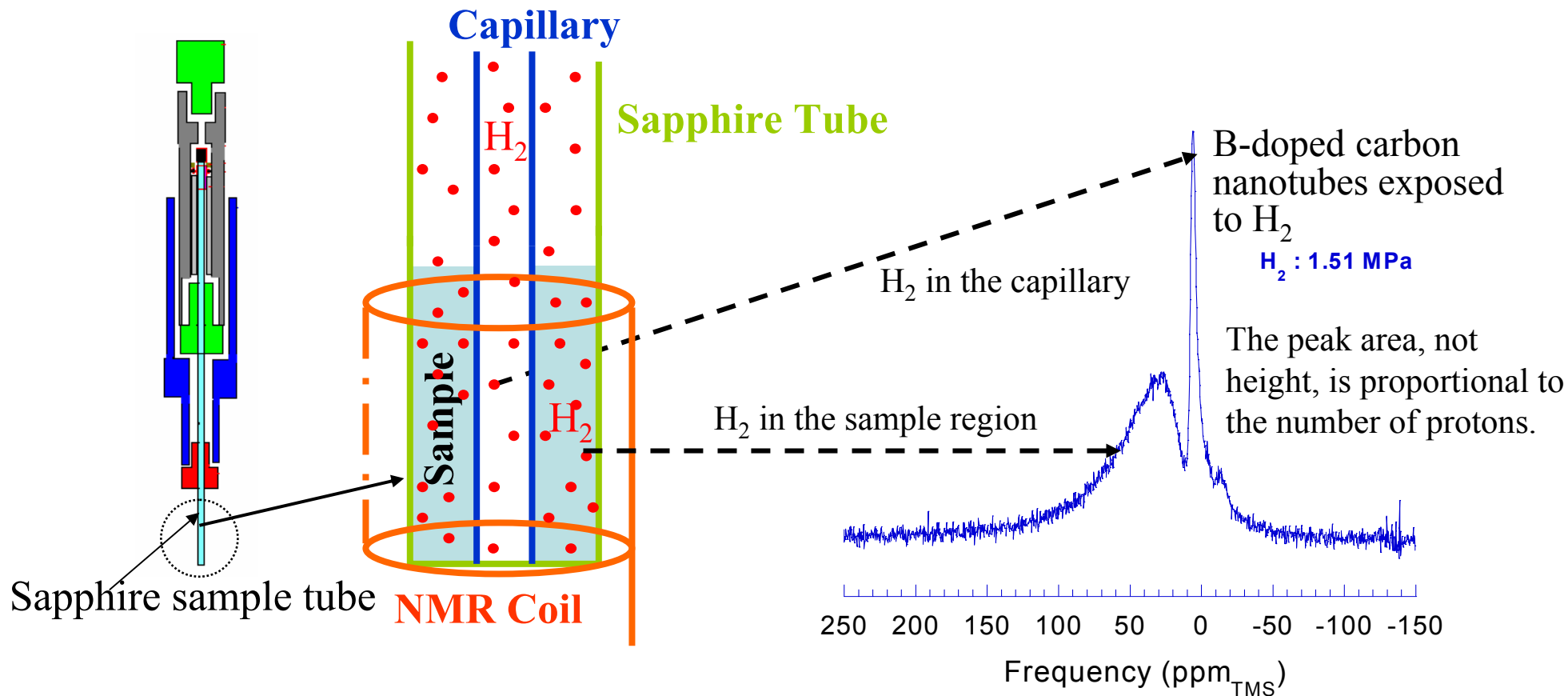


This new 200 MHz NMR system is **available to partners** to provide detailed hydrogen adsorption capacity and site specific binding energies for advanced nanostructured materials over a wide pressure (vacuum to  $>100$  atm). Recently, measurement capabilities to  $\sim 80$  K has been designed and is being implemented on this NMR system. This will give us additional capabilities with wide temperature range (80 to 300 K).



# Technical Accomplishments

- Developed a method with internal standard for quantitative NMR detection of  $H_2$

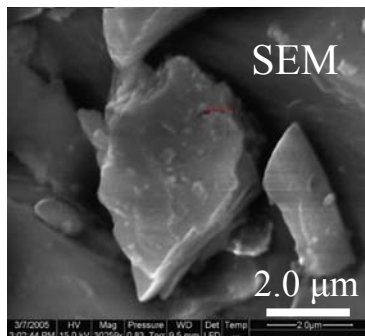


Since we know the volume of the capillary and the volume of the sample region, the ratio of the broad versus narrow peak intensities leads directly to the volumetric density under the sample packing condition. Since the weight of the sample is known, gravimetric density can also be calculated. In case the adsorbed peak is resolved, direct measure of Gibbs adsorption can be obtained.

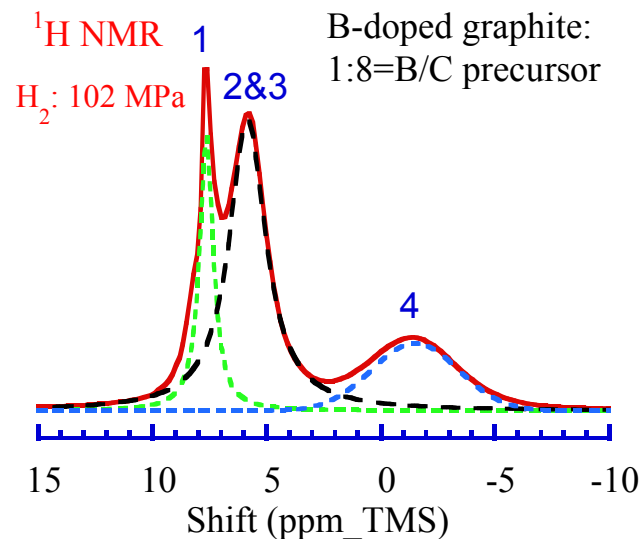


# Technical Accomplishments

- Achieved spectrum-resolved observation of adsorbed  $\text{H}_2$  in B-doped graphite



**B-doped graphite:** Chung, Penn State, CbHS CoE partner. The material is synthesized using B-containing organic precursors, low-temperature polymerization, and carbonization upon 800°C annealing. SEM and BET studies show very small surface area in the as-synthesized materials.



**$^1\text{H}$  NMR spectrum** resolves adsorbed  $\text{H}_2$ , peak (4) at -1.5 ppm, from free  $\text{H}_2$ . The substantial up-field shift (free  $\text{H}_2$  gas at 6.9 ppm) is consistent with adsorption on graphene layers with large diamagnetic susceptibility.

As proven in our earlier publication on gas adsorption in SWNTs<sup>1</sup>, this demonstrates that NMR is also able to recognize  $\text{H}_2$  adsorption environments in B-doped carbon materials, an important type of materials investigated by the CbHS CoE. This gives more detailed information for identifying promising adsorption site.

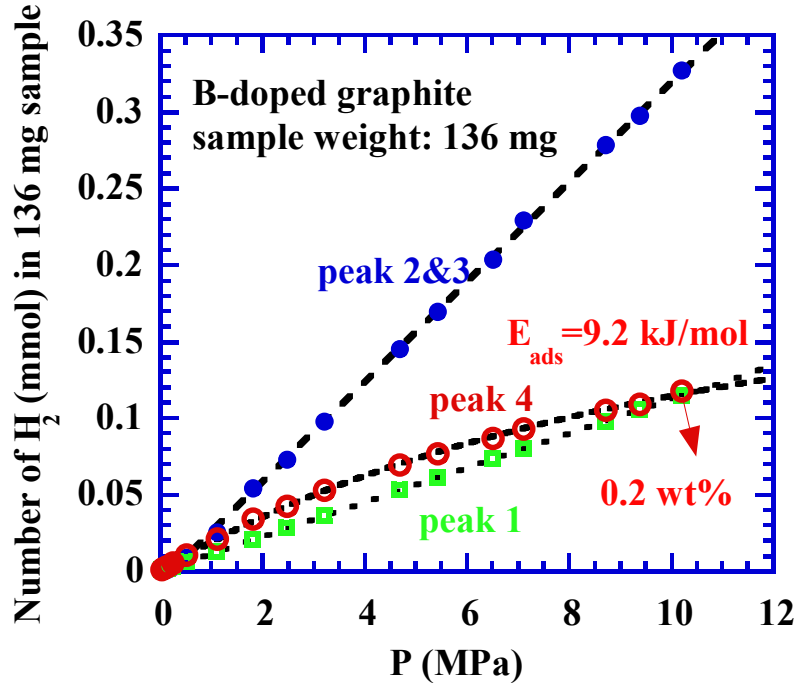
<sup>1</sup>A. Kleinhammes, S.-H. Mao, X.-J. Yang, X.-P. Tang, H. Shimoda, J. P. Lu, O. Zhou, and Y. Wu, *Phys. Rev. B.* **68**, 075418 (2003).





# Technical Accomplishments

- Measured, for the first time, site-specific H<sub>2</sub> adsorption isotherms of B-doped graphite



**Adsorption Isotherms:** Peak intensities of the <sup>1</sup>H NMR spectrum are shown as functions of pressure. Dashed lines are fits with the Langmuir equation.

$$n(P, T) = n_{\infty} \frac{bP}{1 + bP}$$

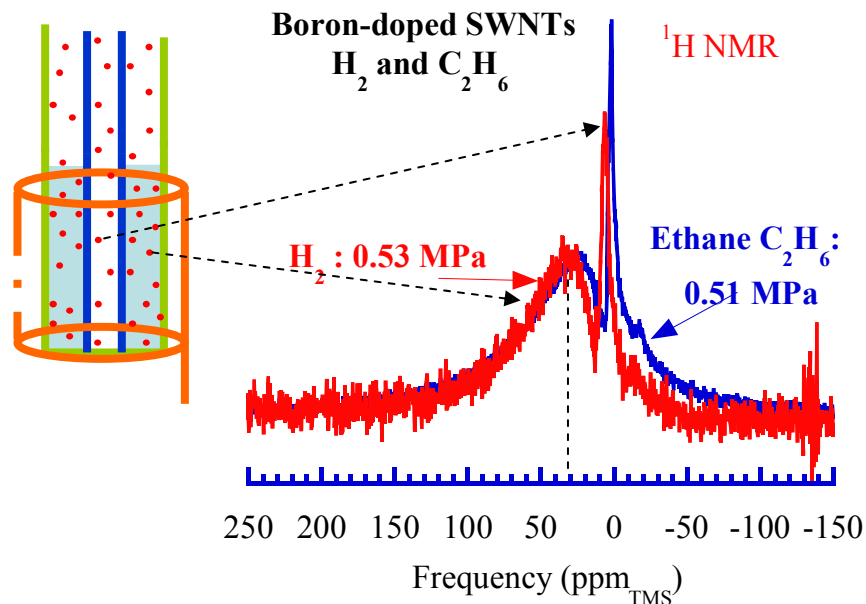
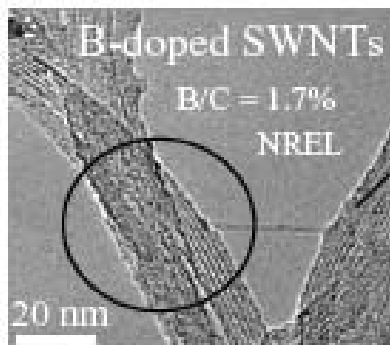
$$b = \frac{\sigma}{\nu_0 \sqrt{2\pi m k_B T}} \exp(E_{\text{ads}} / k_B T)$$

Error bars are of the size of symbols.

Peak 1 and peak 2&3 depend linearly on pressure even up to 10 MPa as expected for free H<sub>2</sub> gas and adsorption with adsorption energy  $E_{\text{ads}}$  comparable to  $kT$ . Peak 4 shows nonlinear pressure dependence. Using the Langmuir equation, an estimate of  $E_{\text{ads}} = 9 \pm 1 \text{ kJ/mol}$  is obtained. However, the intensity of this peak is rather weak, **0.2 wt%** at 100 atm. corresponding to #H<sub>2</sub>:#B~1:1. This result shows that B-doping could improve the adsorption energy substantially but the number of adsorption sites in the current material is too small. There is a need to increase the surface area or the disorder of B-doped graphite.



# Technical Accomplishments



**B-doped SWNTs:** Heben, NREL, CbHS CoE partner. The B-doped SWNTs was produced at NREL using laser ablation and was purified.

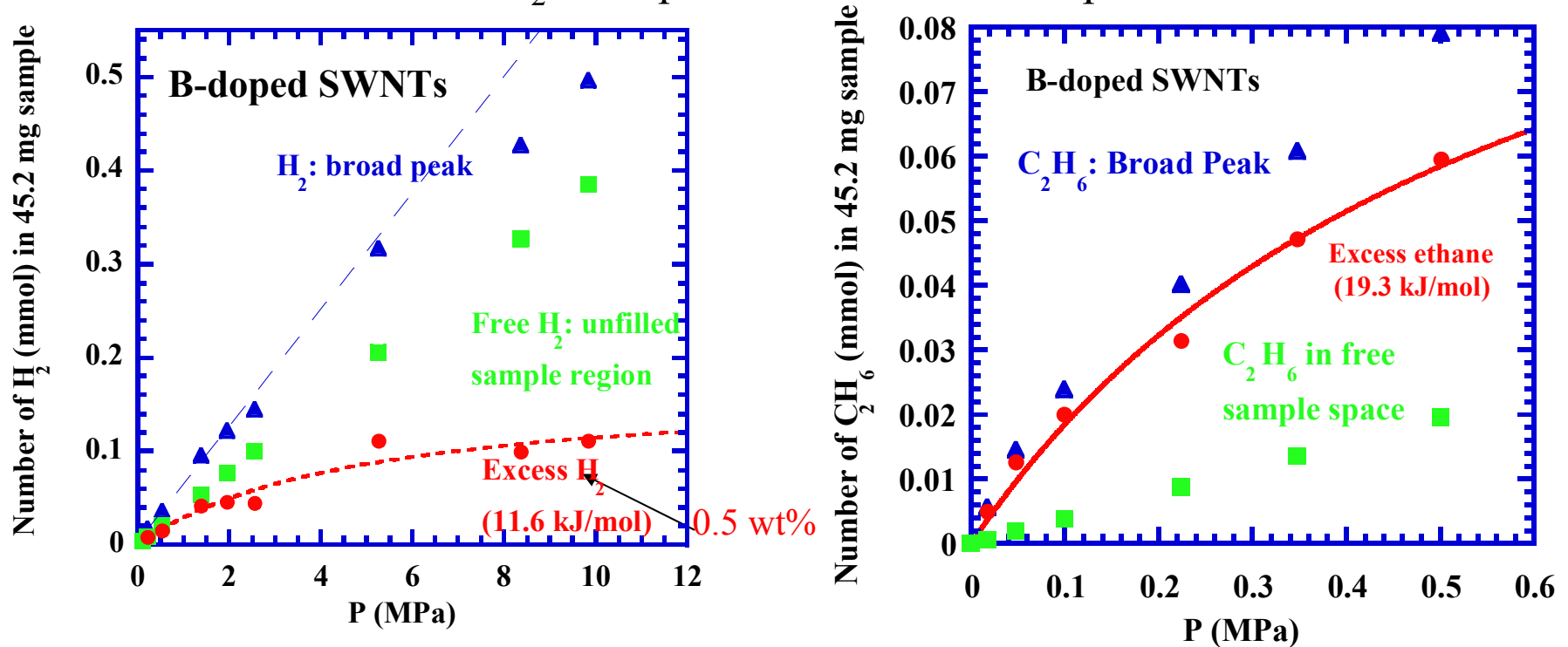
Here, free  $H_2$  in the unfilled space of the sample region (2) and adsorbed  $H_2$  (3, 4) all contribute to a single broad peak. Unlike in B-doped graphite, the residual magnetic catalytic particles cause significant line broadening and give rise to the large 30 ppm shift. Effects of magnetic particles are further evaluated by comparing with  $^1H$  NMR of ethane with known adsorption properties in SWNTs such as adsorption energy.

Quantitative analysis shows that NMR detection of  $H_2$  works in B-doped SWNTs although the resolution is reduced compared to B-doped graphite by the presence of magnetic particles. As a result, a skeletal volume of the material needs to be estimated to calculate the wt% of adsorption.



# Technical Accomplishments

- Measured  $\text{H}_2$  adsorption isotherm of B-doped SWNTs

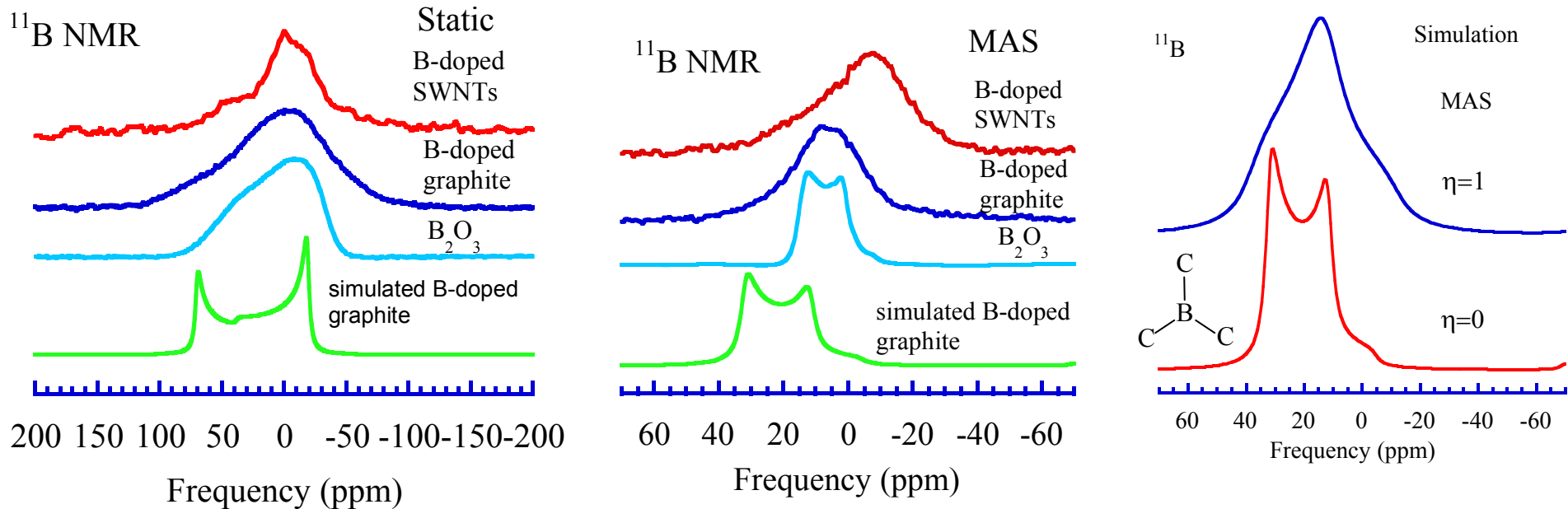


**Adsorption Isotherms** of  $\text{H}_2$  and ethane in a 45.2 mg B-doped SWNTs sample. Based on an estimate of skeletal density for SWNTs,  $1.3 \text{ g/cm}^3$ , and the peak intensity of  $\text{H}_2$  gas in the capillary, we can estimate the contribution to the broad line from free  $\text{H}_2$  in the unfilled space of the sample region. This led to the estimation of excess  $\text{H}_2$  shown above. Using the Langmuir equation, an adsorption energy of  **$12 \pm 2 \text{ kJ/mol}$**  is obtained for  $\text{H}_2$ . Again, the amount is quite small, 0.5 wt%. The measurement error is somewhat larger than in B-doped graphite due to the broader linewidth, the largest uncertainty in determining wt% and adsorption energy comes from the need of evaluating the skeletal density.



# Technical Progresses

- Carried out  $^{11}\text{B}$  solid-state NMR study of boron coordination in B-doped graphite and B-doped SWNTs



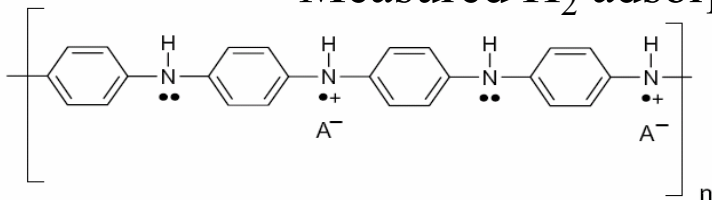
Static and magic-angle-spinning  $^{11}\text{B}$  NMR spectra at 9.4 Tesla of B-doped graphite and B-doped SWNTs.

Symmetric quadrupole tensors with  $\eta=0$ , which give rise to the double-horn spectral feature, are expected for substitutionally doped B sites. The spectra of B-doped graphite and B-doped SWNTs agree more with  $\eta=1$  indicating **significant distortion of the equilateral triangle**. The measured large quadrupole interactions **do agree with threefold-coordinated boron sites**. The shift of B-doped SWNTs and B-doped graphite are noticeably smaller than expected from substitutionally doped boron in graphite (or nitride). Further NMR studies, both experimentally and theoretically, are needed to completely understand the nature of B-doping. The value of **B/C is ~1.5%** in B-doped graphite as determined by NMR.

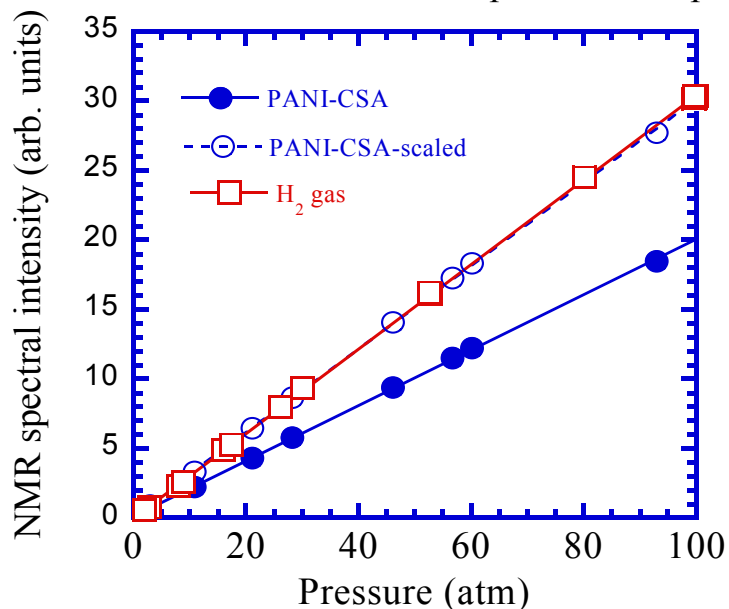


# Technical Progresses

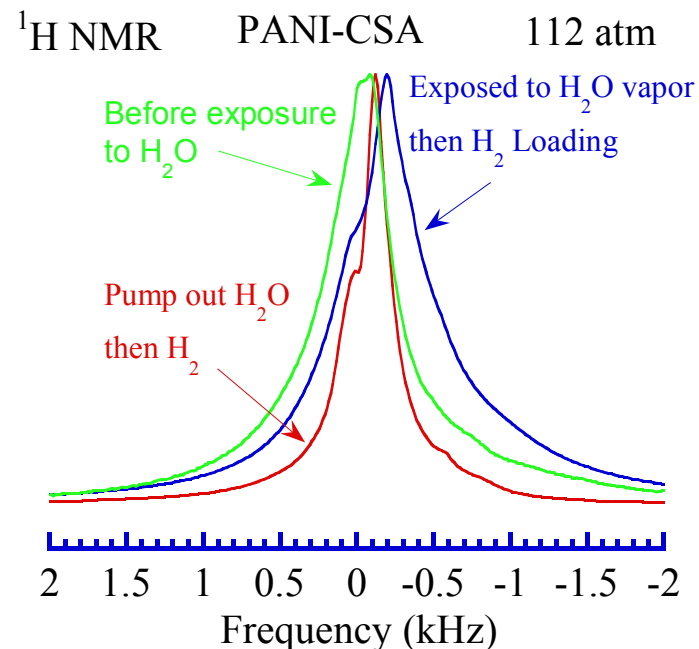
## • Measured $H_2$ adsorption isotherm of doped polyaniline



**Doped polyaniline:** MacDiarmid, U Penn, CbHS CoE partner. Polyaniline (PANI) in emeraldine oxidation state doped with camphorsulfonic acid (CSA)



Since the  $^1H$  spectrum intensity divided by the estimated empty volume in the sample region is exactly the same as that of empty sample tube filled with  $H_2$ , the amount of adsorbed  $H_2$  is negligible.



**Effect of Exposure to Water Vapor :** We observed a change of  $H_2$  adsorption behavior when the PANI-CSA was exposed in-situ to water vapor. Clearly, more understanding of doping (water is known to have that effect for PANI) is needed to evaluate adsorption in doped polyaniline.

The 6 wt% storage capacity reported earlier by Cho is not confirmed in our samples. More work is needed to characterize the sample morphology and the details of doping. Such differences could have some effects on hydrogen storage capacity.



# Technical Accomplishments

We have reached all of our milestones at the current stage of the project.

## Milestones

- Test high-pressure (100 atm) NMR probe and demonstrate accurate H<sub>2</sub> measurement (within 10%) with standard samples (3Q Year 1) **Implemented**
- Obtain adsorption isotherms by NMR for 2 different types of CbHS samples and compare results with TPD, gravimetric, and volumetric measurements (4Q Year 1) **Implemented**
- Provide detailed characterizations of the molecular structures of adsorbents showing promising adsorption properties and demonstrate importance of NMR technique to the mission of the Center (Go/No Go: 3Q Year 2) **Implemented**



# Future Work

- Implement adsorption measurement capabilities at 80 K for evaluating adsorption capacities of carbon-based materials such as B-doped graphite and doped polymers.

*----Present- June 30, 2006*

- Determine the origin of the enhanced adsorption energy in B-doped graphite and SWNTs and to evaluate the potential of the corresponding adsorption sites for achieving 7 wt% storage

*----Present-December 31, 2006*

If the result of this investigation is positive, continue the research in 2007

*----September 30, 2007*

- Quantitative measurement of adsorption isotherms of doped polyaniline with variable doping treatments

*----October 1-September 30, 2007*

- Quantitative measurement of adsorption isotherms of nanohorns and other carbon-based materials identified by the DOE CbHS CoE.

*----January 1-September 30, 2007*



# Project Summary

**Relevance:** Provided a unique method for quantitative determination of H<sub>2</sub> adsorption along with information on microscopic structures and dynamics.

**Approach:** In-situ NMR measurement up to 100 atm with internal intensity calibration.

## **Technical Accomplishments and progress:**

- Obtained the first spectrum-resolved measurement of adsorbed H<sub>2</sub> and the corresponding adsorption isotherm (Gibbs adsorption) in B-doped graphite. However, this capability is hindered in B-doped SWNTs due to the presence of residual magnetic particles which could lead to error in wt% determination. An error of 20% in wt% determination is possible depending on the amount of magnetic particles present.
- Demonstrated experimentally the potential of boron doping for enhancing adsorption energy above **10 kJ/mol** in carbon-based materials.
- Determined that all three types of samples investigated, including B-doped SWNTs, B-doped graphite, and doped polyaniline, possess storage capacity less than 1 wt% at RT and 100 atm. Increasing surface areas, such as in B-doped graphite, might enhance significantly their storage capacity.
- Provided unique and detailed information on the structure of boron sites in doped materials.

## **Future Research:**

- Complete the studies of materials under current investigation, expand the studies down to 80 K, and start investigation of other promising materials from CbHS CoE.





# Summary Table

## Materials Investigated by NMR

<b>Materials</b>	<b>Adsorption Isotherms</b>	<b>Wt % (RT, 100 atm))</b>	<b>Adsorption Energy</b>	<b>Structure Analysis</b>
Doped polyaniline (samples: MacDiarmid, U Penn)	X	<0.5%	<4 kJ/mol	
Boron-doped single-walled carbon nanotubes (samples: Heben, NREL)	X	~0.5%	12 kJ/mol	X
Boron-doped graphite (samples: Chung, Penn State)*	X	<0.5%	9 kJ/mol	X



# Publications and Presentations

1. Characterization of Hydrogen Adsorption in Carbon-Based Materials by NMR  
Talk at DOE Carbon-based Hydrogen Storage Center of Excellence Kick-off Meeting, Washington, DC, January 13, 2005.
2. Characterization of Hydrogen Adsorption in Carbon-Based Materials by NMR  
Poster at 2005 DOE Hydrogen Program Annual Merit Review  
Crystal City, VA, May 23-26, 2005.
3. Gas Adsorption in Carbon-Based Materials Studied by NMR  
Poster at IPHE International Hydrogen Storage Conference, Lucca, Italy, June 22-24, 2005.
4. Nuclear Magnetic Resonance Studies of Hydrogen Adsorbed on Carbon based Materials  
Talk at 2005 MRS Fall Meeting, Boston, November 27 - December 2, 2005.
5. Adsorption study of Hydrogen in Carbon based Materials as measured by Nuclear Magnetic Resonance  
Talk at 2006 APS March Meeting, Baltimore, March 13–17, 2006.
6. Hydrogen Adsorption in Carbon based Materials - a Quantitative Study using Nuclear Magnetic Resonances  
Talk at 2006 MRS Spring Meeting, San Francisco, April 17-21, 2006.
7. Hydrogen Adsorption in Carbon-Based Materials Studied by NMR  
Talk at 209<sup>th</sup> ECS Meeting, Denver, CO, May 7-12, 2006.



# Critical Assumptions and Issues

- *Problem* Residual magnetic particles of catalysts used for single-walled carbon nanotube production could cause significant  $^1\text{H}$  NMR line broadening. This could wipe out some of the signals and lead to underestimation of the storage capacity by NMR.  
*Solutions* (1) Estimate the degree of magnetic broadening by comparing with  $^1\text{H}$  NMR spectrum of adsorbed ethane, which is more sensitive to magnetic broadening. (2) Compare NMR measurements with gravimetric and volumetric measurements. (3) Improve sample purification.
- *Problem* Although we did obtain  $^{13}\text{C}$  NMR spectra of carbon-based materials for structure analysis, the experiment is very time consuming which prevents detailed studies using a variety of powerful NMR techniques.  
*Solutions* (1) Explore ways with partners to synthesize  $^{13}\text{C}$  enriched materials, especially for promising systems. (2) Implement high-field NMR studies at the National High Magnetic Field Lab with better sensitivity and better resolution.
- *Problem* This is currently beyond the scope of our project but it would be very informative to carry out double-resonance NMR measurements in-situ under high-pressure  $\text{H}_2$  and down to 80 K or below. This could provide direct information on where adsorption occurs.  
*Solutions* (1) Over short term, complementary information can be obtained by neutron scattering in collaboration with our partner at NIST. (2) Over long term, such system could be constructed with support if certain systems emerge with great storage potential and warrant detailed studies of structures and adsorption mechanisms.