

## IV.C.11 Characterization of Hydrogen Adsorption in Carbon-Based Materials by NMR

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### Partner Approach

The primary goal of our investigation is to identify potentially promising carbon-based systems for hydrogen storage based on a detailed understanding of adsorption mechanisms and structures. We use nuclear magnetic resonance (NMR) to characterize local structures and employ high-pressure NMR to measure adsorption isotherms and molecular dynamics. A crucial difference between NMR-measured adsorption isotherms and traditional gravimetric and volumetric measurements is that NMR can measure adsorption isotherms separately for each type of adsorption site whereas traditional methods measure the total amount of adsorption. Traditional methods can easily overlook adsorption sites that are promising in adsorption enthalpy but are present in small amount before optimization. This can be a big problem since hydrogen storage materials under current investigation are mostly heterogeneous with many different sites, especially carbon-based materials. The usefulness of NMR is based on its potential capabilities for:

- Measuring adsorption isotherms separately for each type of adsorption sites making promising adsorption sites more transparent.
- Providing valuable structure information on the nature of such adsorption sites as well as the molecular dynamics of adsorbed hydrogen.

- Needing only about 20 mg of carbon-based materials for isotherm measurement because of the high sensitivity of  $^1\text{H}$  NMR.

This unique NMR approach of measuring adsorption isotherms enabled us to demonstrate experimentally for the first time that B-doped carbon-based systems indeed possess adsorption sites with promising adsorption enthalpies of 11 kJ/mol.

### Partner FY 2006 Results

We implemented a unique approach to quantitatively measure the amount of  $\text{H}_2$  adsorption using NMR. Figure 1 is an illustration of our sample arrangement. We placed a capillary inside the NMR sample tube. The  $\text{H}_2$  gas inside the capillary with known volume provides an in situ standard for the number of  $\text{H}_2$ . Using this method we have quantitatively measured adsorption isotherms for a variety of carbon-based materials with the focus on B-doped SWNT samples (from team partner NREL) and B-doped highly disordered graphite samples (from team partner Penn State). Figure 2 shows the  $^1\text{H}$  NMR spectrum of the B-doped graphite sample exposed to 100 atm  $\text{H}_2$ . This spectrum shows, in addition to the expected peaks, a peak (labeled 4) that is associated with adsorbed  $\text{H}_2$  in confined nanopores. This is the first time that such an adsorption peak was observed where the peak is clearly separated from the free  $\text{H}_2$  peak (2&3). This allows us to determine the adsorption isotherm individually associated with each  $\text{H}_2$  peak. Such adsorption isotherms are shown in Figure 3. The isotherms are clearly linear for the capillary  $\text{H}_2$  (1) and free  $\text{H}_2$  (2&3). It is clearly not linear for the adsorbed  $\text{H}_2$ . Using the Langmuir isotherm analysis we obtained an adsorption energy of 9.2 kJ/mol. More detailed analysis shows that the adsorption energy is in fact close to 11 kJ/mol. The amount of adsorption is very small, about 0.2 wt% at 100 atm. However, there is a potential to increase this number significantly. The material is very dense with a very small surface area and the level of B doping is about 1%. Both numbers could be improved significantly in future materials development. Similar results were obtained in B-doped SWNTs with adsorption energy of 11 kJ/mol.

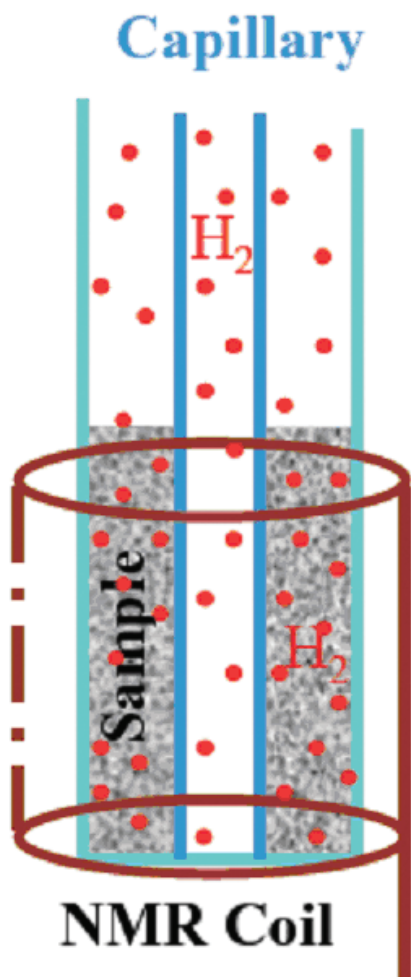


FIGURE 1. Illustration of Specialized NMR Sample Cell used at UNC

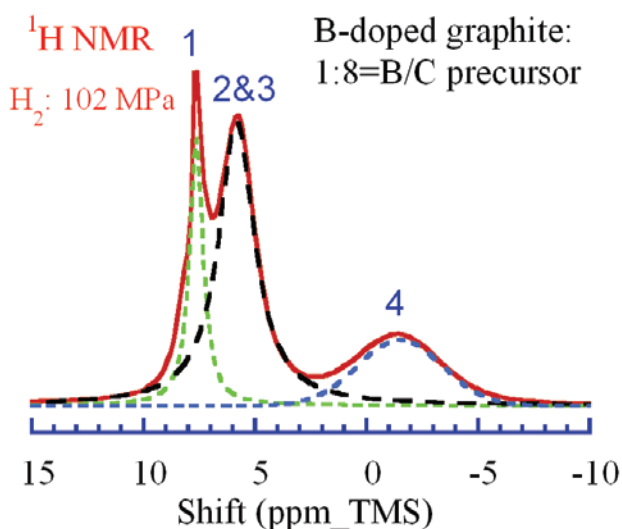


FIGURE 2. NMR Spectra of B-Graphite

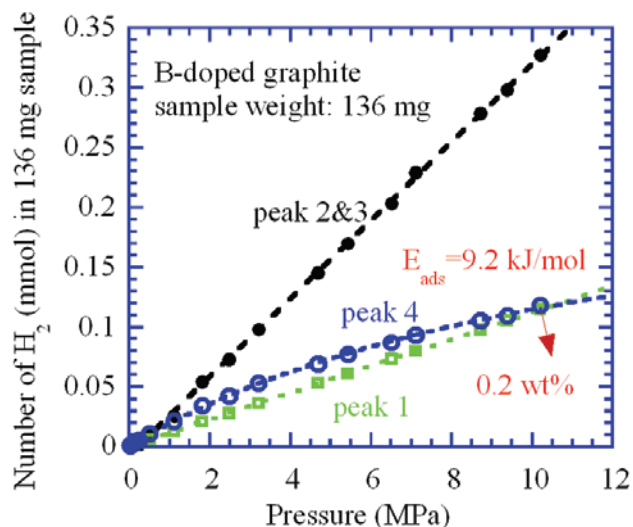


FIGURE 3. Isotherms of B-Graphite Measured Using the NMR Spectra

We also analyzed the structure of boron sites in B-doped SWNTs and graphite and found that the B atoms reside in puckered planes rather than flat graphene surfaces.

#### Partner FY 2007 Plans

- Determine the origin of the enhanced adsorption energy in B-doped graphite and SWNTs and evaluate the potential of the corresponding adsorption sites for achieving 7 wt% storage.
- Implement adsorption measurement capabilities at 80 K for evaluating adsorption capacities and investigating adsorption mechanisms.
- Quantitatively measure adsorption isotherms of other carbon-based systems including doped polyaniline and Pt-decorated nanohorns.

#### FY 2006 Publications/Presentations

1. "Nuclear Magnetic Resonance Studies of Hydrogen Adsorbed on Carbon based Materials," Presentation at 2005 MRS Fall Meeting, Boston, November 27, 2005.
2. "Adsorption study of Hydrogen in Carbon based Materials as Measured by Nuclear Magnetic Resonance," Presentation at 2006 APS March Meeting, Baltimore, March 13, 2006.
3. "Hydrogen Adsorption in Carbon based Materials - a Quantitative Study using Nuclear Magnetic Resonances," presentation at 2006 MRS Spring Meeting, San Francisco, April 17-21, 2006.
4. "Hydrogen Adsorption in Carbon-Based Materials Studied by NMR," presentation at 209<sup>th</sup> ECS Meeting, Denver, CO, May 7-12, 2006.