IV.C.1j Characterization of Hydrogen Adsorption by NMR

Yue Wu (Primary Contact),
Alfred Kleinhammes, B.J. Anderson,
and Qiang Chen
Department of Physics and Astronomy and Curriculum in Applied and Materials Sciences
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599-3255
Phone: (919) 962-0307; Fax: (919) 962-0480
E-mail: yuewu@physics.unc.edu

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

Contract Number: DE-FC36-05GO15081

Project Start Date: February 1, 2005
Project End Date: January 31, 2010

Objectives

- Add low temperature capability (77 K) to *in situ* high pressure (100 atm) nuclear magnetic resonance (NMR) probe.
- Study the effectiveness of boron doping in enhancing the binding energy of hydrogen in graphitic carbon.
- Analyze the structure of boron-doped carbon using NMR.
- Perform adsorption studies of single walled carbon nanohorns.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

(Q) Reproducibility of Performance

Technical Targets

Within the Hydrogen Sorption Center of Excellence (HSCoE), our task is to use NMR to provide microscopic information on hydrogen adsorption in materials synthesized by HSCoE partners. NMR furnishes microscopic and quantitative information on adsorption processes. It also provides information on the structure of adsorption sites. Such information provides feedback to efforts in materials synthesis and theory in designing materials to reach the DOE targets.

Accomplishments

- Built, tested, and used low temperature probe for NMR study down to 77 K.
- Determined binding energy of H_2 to boron-doped graphitic materials to be 11 kJ/mol.
- Established optimal annealing temperature for boron-doped graphitic material to be in the range of 400 to 800°C.
- Determined the amount of incorporated boron in graphitic materials and their local structures.
- Determined binding energy of hydrogen to carbon nanohorns to be 7.1 kJ/mole.

Introduction

Our study aims at providing a quantitative tool for investigating hydrogen adsorption and identifying promising adsorption mechanisms in sorbent materials. We use NMR to characterize local structures of the sorbent materials 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 sites whereas traditional methods measure the total amount of adsorption.

Approach

NMR relies on its high spectral selectivity – H_2 in different environments will contribute to different lines in the spectrum thus permitting clear distinction between gaseous and bound hydrogen. NMR spectra, taken as a function of temperature and H_2 pressure, yield direct information on hydrogen capacity, while isotherms are used to compute binding energies. The molecular dynamics of hydrogen are explored using

relaxation and exchange experiments. In order to simultaneously measure temperature and pressure dependences, a low temperature probe was designed and built, making *in situ* low temperature and high pressure NMR measurements possible.

The improved NMR setup was used to study boron-doped graphitic material (B-G) provided by Mike Chung's group at Penn State and carbon nanohorns made by David Geohegan's group at Oak Ridge National Laboratory.

Results

Boron-Doped Graphitic Material (with Mike Chung, Penn State)

Graphitic clusters with substitutionally doped boron is suggested by theory [1] to provide an efficient adsorption site for H_2, with binding energy enhanced over that found in pure carbon. B-containing polymeric systems carbonized at certain temperature were provided by Dr. Chung and were investigated systematically. The NMR results showed that the binding energy is indeed enhanced in such systems. It was found that the optimal carbonization temperature is around 600°C where the material has not reached the ordered graphitic structure. Figure 1(a) is a typical ^{1}H NMR spectrum where a peak associated with adsorbed H_2 (line 3) is well separated from the gaseous H_2 peaks (lines 1 and 2). We obtain adsorption isotherms by determining the peak intensity versus pressure for each peak. As previously reported, the intensity of line 3 in Figure 1(a) grows nonlinearly with H_2 pressure. The Langmuir fit to the data yields a binding energy of 11 kJ/mol. This is close to the targeted value range of 15 to 20 kJ/mole for binding energies of H_2 in storage materials. We repeated similar measurements on many B-doped samples and this observation is confirmed in those samples as well. Unfortunately, the amount of adsorption with such high binding energy is quite low, a few tenths of one wt%. In the search for the "best" processing methods, Dr. Chung carbonized the B-containing polymerized precursor at temperatures from 400°C to 1,500°C. The sample pyrolized at 1,500°C shows no indication of H_2 adsorption. The optimal carbonization temperature ranges between 400°C to 800°C. A more perfect graphitic structure might not be more favorable for hydrogen adsorption than the more disordered one. This agrees with theory, which shows that confined electrons are more favorable.

Low temperature measurements add further proof that line 3 indeed is associated with adsorption. Figure 1(b) shows a comparison of low temperature spectra taken at 115 K and pressures of 2 MPa and 9 10^{-5} MPa (0.7 Torr), respectively. Although the H_2 pressure varies by orders of magnitude between the two measurements, the adsorption peak is nearly as

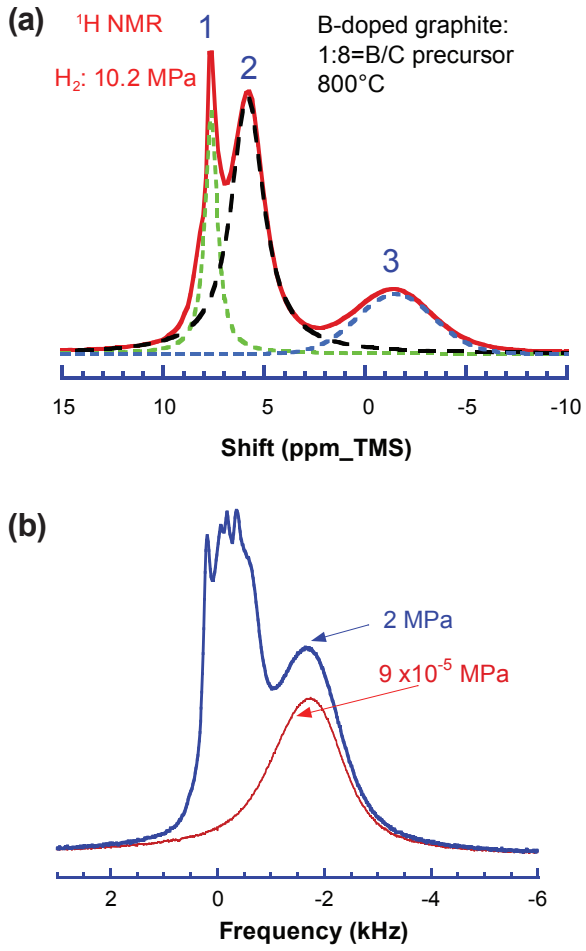

FIGURE 1. (a) Room temperature ^{1}H spectrum of H_2 at 102 atm in B-doped graphite carbonized at 800°C. (Lines 1 and 2 correspond to H_2 gas in capillary [gauge standard], and free space within sample, line 3 represents H_2 in confined nanopores.) (b) ^{1}H spectra of H_2 at given pressure (indicated in the figure) and 115 K.

prominent at 0.7 Torr as at high pressure, proving unambiguously that hydrogen is bound to the substrate at 115 K.

Since the samples carbonized at various temperatures showed different adsorption characteristics, learning more about the local structure around the boron site appeared necessary. As shown in Figure 2(a), we conducted ^{11}B measurements to determine the boron content as well as to acquire some knowledge about the site symmetry around the boron inserted into the carbon matrix. With increasing carbonization temperature, the boron content decreases, as shown in Figure 2(b). In addition, the center of gravity of the spectra shifts upfield (to the right in the figure). The tendency of the shift is expected for conversion from the precursor (measured with a chemical shift of +68 ppm) to graphite-doped with a minute amount of boron and indicates that the material pyrolized at 1,500°C is similar to graphite. Materials with intermediate annealing temperatures in

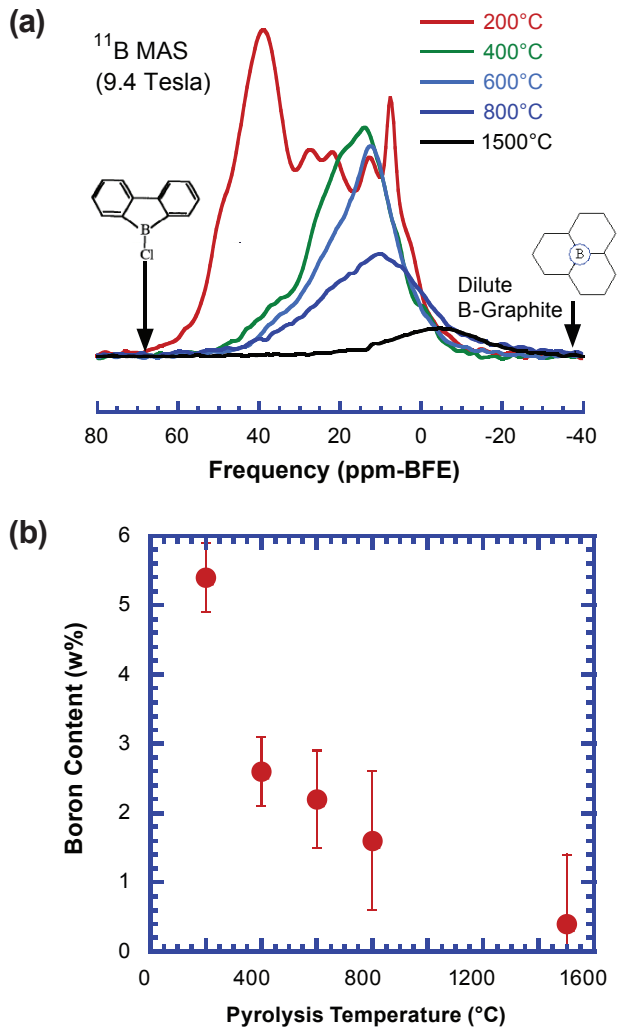

FIGURE 2. (a) ^{11}B NMR spectra of B-doped carbon samples prepared at various pyrolyzing temperatures. (b) Boron content determined by ^{11}B NMR.

the range of 400 to 800°C appear to be disordered on the graphitic scale, thus, providing the right structure for H_2 adsorption if the boron content could be raised.

In summary, the high binding energy for H_2 to boron-doped graphitic material shows the material's promise as a hydrogen storage medium. However, the porosity and boron content need to be increased. Dr. Chung has provided us with new samples based on a different precursor which is intended to increase both the porosity and the boron content.

Pt Decorated Carbon Nanohorns (with David Geohegan and Hui Hui, Oak Ridge National Laboratory)

NMR measurements on Pt-decorated cut carbon nanohorns show a lower binding energy (7.1 kJ/mol) but a higher porosity than found in B-doped graphitic

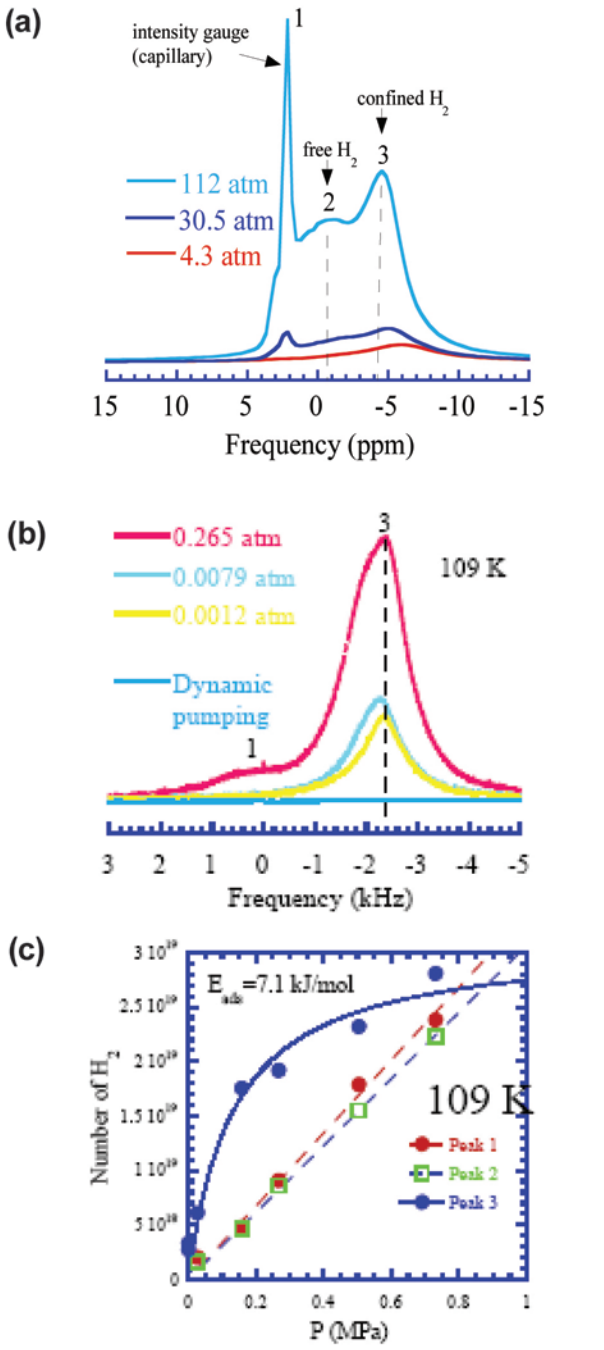

FIGURE 3. (a) Room temperature ^{1}H spectra of H_2 in Pt-decorated carbon nanohorns at various pressures. (b) ^{1}H spectra at 109 K as a function of H_2 pressure in Pt-decorated carbon nanohorns. (c) The isotherms corresponding to peaks in (b).

carbon. Typical room temperature ^{1}H NMR spectra are shown in Figure 3(a). Here, peak 3 is associated with H_2 confined inside nanohorns. While the intensity of all observed NMR lines increase linearly with pressure at room temperature, that is not the case at low temperature. At low temperature, the adsorption at low pressure is dominated by peak 3, as shown in

Figure 3(b), indicating that hydrogen is predominantly bound. Accordingly, the isotherm for peak 3 is nonlinear as shown in Figure 3(c). A Langmuir fit yields a binding energy of 7.1 kJ/mol. That value agrees with H_2 adsorption energies measured on curved graphene surfaces.

In summary, carbon nanohorns, even when decorated with Pt, show predominantly adsorption energies of graphene-based structures. At low temperatures, hydrogen within the nanohorns adsorbs on to the graphene surface. It remains to be seen if Pt-decoration could lead to spillover effect in nanohorns.

Conclusions and Future Directions

- Boron-doped graphitic material is a promising material with H_2 binding energy of 11 kJ/mol and will be further explored. Dr. Chung provided us with a series of samples annealed at various temperatures based on a novel precursor and processing method, that are expected to provide higher boron content and porosity.
- Carbon nanohorn samples have a large natural porosity. Pt-decorated nanohorns could exhibit spillover effect and will be investigated by NMR.
- We received aerogel samples from Ted Baumann via Channing Ahn. Dr. Ahn already measured the hydrogen capacity using his Sievert apparatus. The measurements are part of an ongoing effort to establish that NMR produces quantitative results in agreement with conventional methods on identical samples.
- Dr. Baumann is preparing boron-doped aerogels that are also activated. We intend to do NMR measurement on those samples and compare the results with those obtained on Dr. Chung's samples. ^{11}B and ^{13}C measurement are also planned to elucidate the local structure.
- Hank Foley has provided nanoporous carbonaceous samples with and without boron doping, thus, providing an immediate check on the effectiveness of boron doping on otherwise identically prepared samples. Those samples will also be investigates using ^{11}B and ^{13}C NMR to obtain information on the local structure within the samples.

FY 2007 Publications/Presentations

1. Shenghua Mao, Alfred Kleinhammes, Qiang Chen, Yue Wu, Michael Chung, Jeff Blackburn, and Michael J. Heben, "Hydrogen Adsorption in Boron Doped Graphite and Single Walled Carbon Nanotubes Probed by 1H Nuclear Magnetic Resonance Measurements," 2006 MRS Fall Meeting, Boston, Nov. 2006. Abstract No. Z6.7.

2. Alfred Kleinhammes, Shenghua Mao, Qiang Chen, Yue Wu, Michael Chung, Jeff Blackburn, and Michael J. Heben, "NMR-a Sensitive Tool for Probing Minority Adsorption Sites in Carbon Based Hydrogen Storage Materials," 2006 MRS Fall Meeting, Boston, Nov. 2006. Abstract No. MM1.3.

3. Yue Wu, "Hydrogen Adsorption in Carbon-Based Materials Studied by NMR," APS SESAPS Meeting, Nov. 2006. Abstract No. BA00002.

4. Yue Wu, Alfred Kleinhammes, Robert Anderson, and Shenghua Mao, "Hydrogen Adsorption in Carbon-Based Materials Studied by NMR," 2007 APS March Meeting, Denver, March 5–9, 2007. Abstract No. J39.00010.

5. Alfred Kleinhammes, Youmi Jeong, Mike Chung, and Yue Wu, "NMR Evidence of Binding Energy Enhancement for Dhydrogen in B-Doped Graphitic Carbon," 2007, submitted.

6. Youmi Jeong, T. C. Mike Chung, Alfred Kleinhammes, and Yue Wu, "Synthesis of Boron-Substituted Carbon (B/C) Materials Using Polymeric Precursors and Evaluation for Hydrogen Physisorption," 2007, submitted.

References

1. Y-H. Kim, Y. Zhao, A. Williamson, M.J. Heben, and S. B. Zhang, *Phys. Rev. Lett. 96*, 016102 (2006).