IV.C.1g Enabling Discovery of Materials With a Practical Heat of Hydrogen Adsorption

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Contract Number: DE-FC36-05GO15074

Project Start Date: March 1, 2005
Project End Date: February 28, 2010

Objectives

- Development and testing of new materials with high H_2 storage density and appropriate enthalpy of hydrogen adsorption.
- Development of enabling technologies for H_2 storage materials development.
  - Accurate, predictive computational methodologies for new materials discovery and mechanistic understanding.
  - Characterization tools for accurate H_2 storage measurements.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(C) Efficiency
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The project team is conducting fundamental computational and experimental studies of hydrogen storage in carbon-based materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: $4/kWh net
- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L

Accomplishments

- Predictive computational modeling has revealed that crystalline BC_3 is an attractive target material for hydrogen storage. Unlike graphite, chemisorption of hydrogen in BC_3 provides a chemical driving force for H_2 penetration into the lattice.
- The energies of hydrogen diffusion of chemisorbed hydrogen in BC_3 were calculated, showing that hydrogen diffusion on the surface is unlikely at moderate temperatures.
- While the bond dissociation energies of chemisorbed hydrogen in BC_3 suggest that hydrogen binding may be irreversible at high levels of hydrogenation, our computational modeling suggests a path forward by incorporating substitutional nitrogen atoms in the lattice. The average absorption energies for materials that incorporate nitrogen are significantly lower.
- Our experimental capabilities were enhanced to allow the use of pure fluorine for the synthesis of graphite intercalation complexes (GIC). 1st stage GIC, containing fluoride anions, were prepared using pure F_2 and characterized for hydrogen storage capacity and heat of adsorption.
- New synthetic strategies for the preparation of high-surface-area templated boron-doped carbon have been developed.

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Introduction

An efficient, cost-effective hydrogen storage system may well be an enabling technology for the widespread introduction of hydrogen fuel cells to the domestic marketplace. We are collaborating with partners in the HSCoE to identify, synthesize, and test novel materials that exhibit heats of adsorption of hydrogen superior to known materials. This involves predictive computational modeling, materials synthesis, and advanced methods of hydrogen adsorption characterization.

Approach

The project approach is designed to enable and execute discovery of materials with "practical heats" of hydrogen adsorption. These practical heats are hydrogen adsorption enthalpy ranges which allow for the charging and discharging of hydrogen storage materials at near-ambient temperatures and reasonable hydrogen pressures (i.e. 3-100 bar). Our approach utilizes the development of general quantitative computational models for new materials discovery. The accuracy of these methods is very important in order to realize a more practical overlap between computational and experimental work (e.g. modeling the mechanism of hydrogen spillover). Ultimately, the goal is to translate our predictive computational modeling to development and testing of new H_2 storage materials. Our current, novel hydrogen storage materials development is based upon theoretical predictions of high H_2 storage density and enthalpy for boron-doped carbon materials. Once well-characterized samples of the potential hydrogen storage materials have been synthesized, accurate measurement techniques are employed to obtain hydrogen isotherms and heats of adsorption. Advanced techniques such as correction for helium adsorption effects on H_2 isotherms may be employed as necessary.

Results

Computational Modeling of Hydrogen Storage Materials

Recent results by Zhang and Alavi suggest that if H_2 molecules are placed inside the lattice of BC_3, they will undergo nearly spontaneous dissociative chemisorption with formation of C-H bonds at the carbon atoms adjacent to boron [1].

There are literature reports that BC_3 has been synthesized experimentally by reacting BCl_3 with benzene at 800°C via chemical vapor deposition [2]. The balanced reaction scheme is as follows:

$$2\ BCl_3 + C_6H_6 \rightarrow 2\ BC_3 + 6\ HCl$$

Our calculated lattice spacing of BC_3 is in good agreement with the experimental value (calculated 6.79 Å vs. experimental 6.84 Å). AB stacking of the BC_3 layers appears to be the most stable structure, but this has not been resolved experimentally. Our molecular orbital analysis indicates that the empty p_z orbital of B, which is perpendicular to the BC_3 plane, overlaps with the σ-orbital of H_2, the highest occupied molecular orbital, leading to electron transfer from H_2 to BC_3 and H_2 bond dissociation.

A key question is whether H_2 molecules can penetrate the narrow interlayer spaces of crystalline BC_3. Our minimum energy path calculations indicate an interlayer space opening (Figure 1) upon reaction with hydrogen, which substantially reduces the activation energy. Thus, in confirmation of Zhang & Alavi's findings, H_2 should undergo an almost spontaneous dissociation in BC_3 without the need of a catalyst. The estimated barrier for recombination of the chemisorbed H atoms to form gas-phase H_2 is approximately 0.5 eV.

We next studied the energy barriers to migration of chemisorbed hydrogen in BC_3 by first placing C-H bonds in selected positions on a sheet of BC_3. The barriers were then estimated by calculating the energies of moving a hydrogen atom from one carbon atom to another carbon atom in the plane. Several site migrations were evaluated: 1 to 2 (movement to adjacent carbon), 1 to 3 (movement to a site two carbon atoms away in the same ring), and 1 to 4 (movement across the ring). The results indicate that the lowest barrier (0.5 eV) is observed for a 1 to 2 migration. The barriers for the 1 to 3 and 1 to 4 migrations were calculated to be 1.3 and 0.8 eV, respectively.

The absorption of hydrogen in BC_3 leads to a range of energies, depending on the concentration of hydrogen in the hydrogenated material. We find that higher hydrogen concentrations lead to higher the average absorption energies (Figure 2). This suggests that at high hydrogen concentrations, the hydrogen binding may be irreversible. Fortunately, an avenue for moderating the

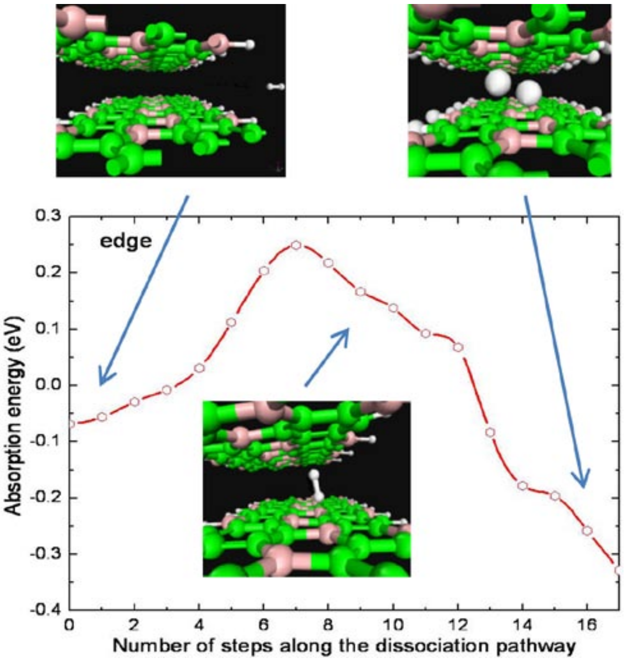

FIGURE 1. Illustration of individual points and energy changes during the minimum energy path for hydrogen entry into the BC_3 interlayer space and subsequent dissociative chemisorption.

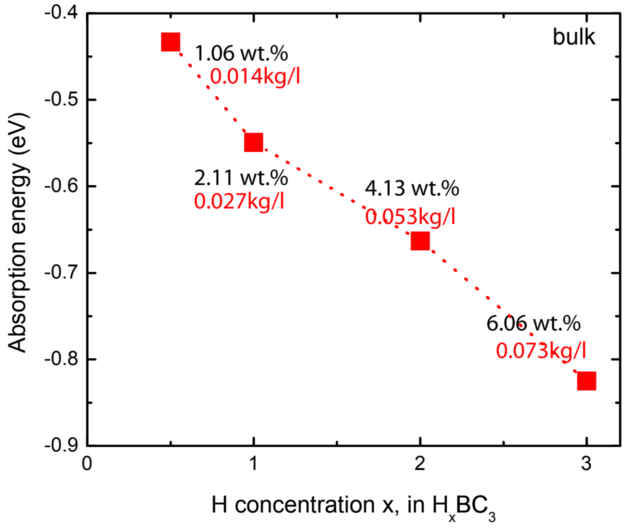

FIGURE 2. Calculated values for the average absorption energy of hydrogen in BC_3 as a function of the hydrogen concentration.

absorption energies may be possible by incorporating other atoms in the material. The addition of nitrogen to the layered BC_3, illustrated in Table 1, results in a decrease in the hydrogen absorption energies. While the average absorption energy of hydrogen in H_3BC_3 is -0.83 eV/H_2, the average absorption energies for materials that incorporate nitrogen are significantly lower.

TABLE 1. Calculated average absorption energy of hydrogen in BC_3 and nitrogen-incorporated BC_3.

Formula	Average Absorption Energy
H_3BC_3	-0.83 eV/H_2
$H_3B_{0.75}C_3N_{0.25}$	-0.60 eV/H_2
$H_3B_{0.5}C_3N_{0.5}$	-0.37 eV/H_2

Synthesis and Hydrogen Storage Testing of Graphite Intercalation Complexes

We have been engaged in a study of the adsorption of hydrogen by fluoride-containing GICs. This was motivated by previously reported computational modeling that suggested a substantial interaction of molecular hydrogen with fluoride ions. Unfortunately, our experimental results have indicated that despite the observation of high hydrogen adsorption enthalpies, the as-produced GIC did not lead to substantial hydrogen storage densities due to the low surface area and low pore volume of the GIC. Therefore, we brought the investigation of GIC for hydrogen storage to a close in the second quarter of Fiscal Year 2009.

Results reported in the past year demonstrated that 2nd stage graphite fluoride compounds demonstrated high heats of adsorption, but also had low surface areas and hydrogen capacity. Therefore, in FY 2009 we expanded our experimental capabilities to include the use of 100% fluorine in the preparation of GIC. We demonstrated that 1st stage graphite intercalates of fluoroanions could be obtained by employing pure rather than diluted F_2 in the co-intercalation chemistry with BF_3 into graphite. While our prior synthesis of 2nd stage GIC resulted in a large increase in the surface area of graphite from 15 m^2/g to 70-120 m^2/g, additional surface area expected for the 1st stage GIC did not result from our new materials (Figure 3). The low surface area contributes to very low hydrogen adsorption at near-ambient temperatures, despite a heat of adsorption as high as 14 kJ/mol at low coverage (Figure 4).

In an attempt to increase the surface area of the GIC, we employed graphitic host materials with higher native surface area. The repetition of the 1st stage C_xBF_4 GIC synthesis and activation was carried out with higher surface area graphite fibers. The resulting material provided H_2 adsorption performance comparable to

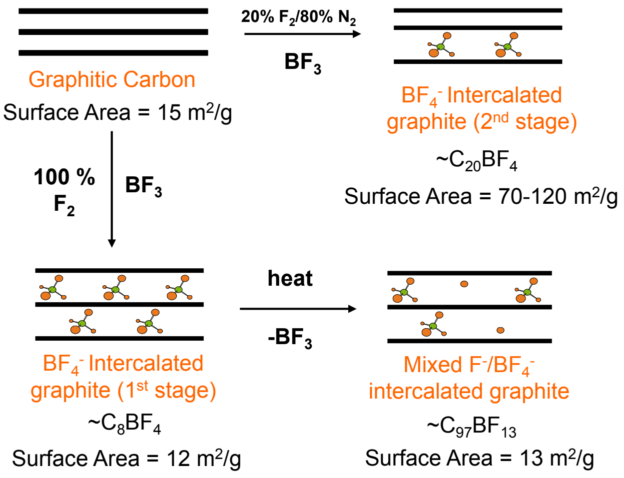

FIGURE 3. Elemental analysis and surface areas of 1st and 2nd stage GIC.

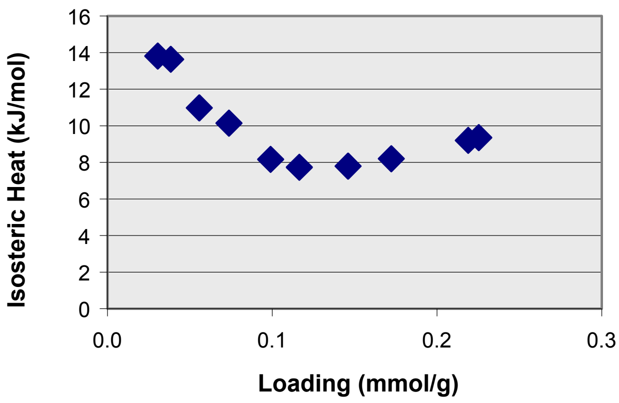

FIGURE 4. Isosteric heat of adsorption for hydrogen on 1st stage GIC.

the carefully activated graphite C_xBF_4 and 2nd stage analogs. Following the analysis, it became apparent that the graphite fiber precursors were not 100% graphitic, thus detracting from their overall potential capacity; additionally it is possible that a portion of the graphitic plates are capped, precluding their proper intercalation.

Because accessibility of H_2 to the opened galleries is believed to be the primary challenge in relation to the current materials, it was suggested that single-wall nanotube (SWNT) carbon be employed as a material that inherently possesses exceptional accessibility of gases to the annular zones between packed nanotube bundles. Knowledge exists around the fluorination of nanotubes and even suggests that some fluorinated sites possess a relatively high ionic character; [3] however, there do not appear to be any reports of utilizing this apparent ionic character to complex Lewis acids. Thus, we repeated the BF_4^- intercalation using a SWNT carbon as the host material. The GIC synthesis was conducted using 20% fluorine because of concerns regarding the high surface area and reported reactivity of the SWNT substrate towards oxidizers. The intercalation of the SWNT was verified by tensimetric uptake of reactant gas, as well as direct observation of shifts in the radial breathing modes in the Raman spectrum.

The oxidizing content of the material obtained by iodometric titration was very close to the stoichiometry of $C_{10}BF_4$ obtained from elemental analysis. The material activated at 50°C gave a H_2 uptake of 0.24 wt% H_2 @ 100 atm. and 25°C (with a low isosteric heat of <8 kJ/mol H_2). Activation at 100°C did not change the oxidizing capacity of the material, but dramatically improved the isosteric heat of adsorption (0.24 wt% H_2 @ 100 atm and 25°C; isosteric heat ~11-12 kJ/mol H_2). However, this enhancement does not exceed the performance of the precursor, except with a slight advantage in isosteric heat performance, which is further evidence that the fluoride ion is beneficial to the adsorption of H_2.

Synthesis and Hydrogen Storage Testing of Boron-Doped Carbon Materials

Starting in the second quarter of FY 2009, we have begun investigation of novel forms of high-surface-area, boron-substituted carbon materials for hydrogen storage. This work is being performed in collaboration with Penn State University. However, there are unique aspects of materials preparation that will be pursued independently in our project.

As part of our collaboration with the group of Prof. Chung at Penn State, we have spent considerable time and effort to measure hydrogen isotherms at a variety of temperatures on several samples of boron-substituted carbon. A BC_x substrate (designated HPA18-500; surface area ~700 m^2/g), reported to contain 7 atomic % boron, was analyzed by hydrogen isotherms at multiple temperatures to obtain more accurate isosteric heat values. The new data clearly shows a fairly uniform heat of about 10-11 kJ/mol-H_2.

Based upon the H_2 adsorption results from the BC_x material obtained from Penn State, it is apparent that producing a material with significantly higher surface area is required in order to make a valid comparison with model materials (i.e., activated carbons) and maximize the hydrogen adsorption capacity. Our initial concept for generating materials with higher surface area and microporosity is to employ a templating process as described in the literature [4]. We have begun this study by using a liquid precursor for the carbonization (boron phenylacetylide) developed by the Penn State group [5].

Conclusions and Future Directions

In summary, our studies suggest that the fluoride ion is positively affecting the energy of interaction of hydrogen with GIC. Unfortunately, the hydrogen adsorption capacities are limited. Although difficult to prove absolutely, the following are possible causes for the lack of hydrogen storage performance. These ultimately lead to the conclusion that there is reduced accessibility of H_2 to the intercalated fluoride ions and low effective surface area:

- 1st stage GIC are more likely to form considerably less ionic, more covalent C-F bonds upon activation, which will affect overall hydrogen storage performance and planarity of the graphene sheets.
- The ions employed as the pillaring agents (i.e., BF_4^-) are mobile and may form the least energetic domains by clustering, thus reducing the desired porosity. It is noteworthy that the synthetic design of the pillared intercalates relies upon the ability to eject the Lewis acid (i.e., BF_3) at a relatively low temperature in order to minimize covalent C-F formation; this effect inherently enhances the mobility of the ions, allowing them to easily aggregate into isolated domains.
- Because of the use of F_2 in the preparation of materials, it is possible that the edges of the graphite sheets can be heavily fluorinated, reducing their accessibility.
- The insertion of the relatively heavy BF_4^- pillaring group provides gravimetric dilution of the hydrogen storage capacity, in addition to physically crowding the galleries (especially for 1st stage materials); when some of the best H_2 adsorption data is normalized to the absolute carbon content, it actually performs quite favorably in comparison to model adsorbents.
- The application of proper activation (selective and uniform removal of evenly spaced Lewis acid groups) of materials is also an area that requires considerable attention, as it potentially may impact each of the above effects.

Future Directions

- Complete synthesis of boron-doped carbon precursor materials and study decomposition pathways.
- Selection of optimal templates for maximizing surface area and micropore volume of template carbons.
- Detailed parametric study of the carbonization reactions of boron-containing precursors in suitable templates, focusing on maximizing surface area, microporosity, and boron atom retention.
- Hydrogen adsorption testing of high-surface-area templated boron-doped carbons.

FY 2009 Publications/Presentations

1. Dynamics of Hydrogen Spillover on Carbon-Based Materials. Xianwei Sha, M. Todd Knippenberg, Alan C. Cooper, Guido P. Pez and Hansong Cheng; *J. Phys. Chem. C*, **2008**, *112* (44), 17465–17470.

2. Hydrogen Absorption and Diffusion in Bulk α-MoO_3. Xianwei Sha, Liang Chen, Alan C. Cooper, Guido P. Pez and Hansong Cheng; *J. Phys. Chem. C*, **2009**, *113* (26), 11399–11407.

3. "Enabling Discovery of Materials With a Practical Heat of Hydrogen Adsorption", presented at the DOE HFCIT Annual Merit Review, May 2009.

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4. H. Nishihara, *et al.*, *J. Phys. Chem. C* **2009**, 113, 3189.

5. T. Chung, *et al.*, *J. Am. Chem. Soc.* **2008**, 130, 6668.