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

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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: 2 kWh/kg
- Energy density: 1.5 kWh/L

Accomplishments

- Completion and publication of a detailed computational model of the well-established, reversible hydrogen spillover process in Pt/MoO_3.
- A predictive model was developed for H spillover dynamics on carbon materials and the first complete model, including every stage of the H spillover mechanism, was generated.
- Completion of the calculations of H_2 physisorption energies for F^- intercalated graphite.
- A method was developed for the controlled temperature programmed desorption of BF_4^- intercalated graphite to produce samples of F^-/BF_4^- intercalated graphite.
- Measurement of hydrogen isotherms (excess capacity) of mixed F^-/BF_4^- intercalated graphite showing a high adsorption enthalpy of ca. 12 kJ/mol H_2.

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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 Hydrogen Sorption Center of Excellence (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 porous graphite intercalation complexes. Obtaining the materials for adsorption testing will require exploratory materials syntheses and may require entirely new synthetic strategies. 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. When needed, advanced techniques such as correction for helium adsorption effects on H_2 isotherms may be employed.

Results

Computational Modeling of Hydrogen Spillover Mechanisms for Hydrogen Storage. Within the HSCoE, hydrogen spillover in lightweight materials has emerged as an important technique for storing hydrogen at near-ambient temperatures. Understanding the underlying spillover mechanisms is essential for the design and development of novel hydrogen storage materials that will assist in meeting the DOE hydrogen storage system targets. The hydrogen spillover process includes three consecutive steps. In the first step, H_2 molecules undergo dissociative chemisorption with metal catalysts. Subsequently, H atoms on the catalyst surfaces migrate to the substrate in the vicinity of the catalyst particles. Finally, H atoms near the catalysts diffuse to the surface or bulk sites away from where the catalyst particles reside. We have previously reported our detailed studies of the first steps of dissociative chemisorption and migration to a metal oxide substrate. We now report the continuation of this computational modeling study including a mechanism for hydrogen migration on carbon material surfaces and the detailed energetics of C-H bond formation in a number of spillover substrates under investigation in the HSCoE.

A key question regarding hydrogen migration is whether H atoms, after C-H bond formation, are able to diffuse to other sites of the graphene sheet by a mechanism that involves breaking the C-H bonds. Our calculations yield a high activation energy of 0.78 eV for diffusion of hydrogen from one carbon atom to an adjacent carbon atom. This energy is close to the

C-H bond formation energy and only slightly lower than the activation energy required to desorb a H atom from the carbon surface. Therefore, we explored another possibility for diffusion via physisorption of H atoms. Density functional theory calculations suggest that there is an energy barrier to forming a C-H bond of approximately 0.2 eV when a H atom approaches a graphite surface. The barrier arises from the structural changes induced by pulling the C atom out of the graphene plane. If the H atom remains "hot" (ie. has enough kinetic energy) after dissociation, transfer from the catalyst, and diffusion across the surfaces of the support and bridges, this activation barrier can be readily overcome and a C-H bond would then be formed. However, if the atom becomes kinetically "cold", it will be blocked by the activation barrier, located approximately 2.5 Å above the graphene plane, and the H atom can only be physisorbed. Our calculated physisorption energies for H atoms on a graphene sheet and selected SWNTs are less than 0.1 eV. The potential energy surface is flat, indicating a site-independent behavior. If the H atom is physisorbed on graphene, it can move across the plane with minimal energy changes.

In our studies of the energetics of C-H bond formation, we performed a molecular dynamics (MD) simulation of H atoms on a single graphene sheet. Our results indicate that H atoms located <2.5 Å from the substrate react with the graphene immediately and most of the H atoms are chemisorbed within 0.25 ps. The substrate structure undergoes substantial relaxation and the interacting C atoms pucker out of the plane to form C-H bonds with a bond length of *ca*. 1.15 Å. In parallel, most of the H atoms in layers >2.5 Å from the graphene rapidly form H_2 molecules, which subsequently become weakly physisorbed on the graphene sheet. No diffusion of chemisorbed H atoms to other chemisorption sites was observed during the 4 ps simulation time. However, Eley-Rideal recombination, in which a gas-phase H atom rects with a C-H bond to form an H_2 molecule, was observed, suggesting that the surface C-H bonds are rather weak compared with the C-H bonds in organic molecules. We found that Eley-Rideal recombination on the graphene sheet is a significant process that results in depletion of the chemisorbed H atoms from the substrate. The C-H bonds are not well ordered with respect to each other on the graphene sheet, despite the fact that the structural configuration with alternative C-H bonds on graphene, i.e. one C-H bond above the plane adjacent to another C-H bond below the plane, is thermodynamically more favorable than the structure with randomly distributed isolated C-H bonds. This suggests that the chemisorption process is kinetically controlled.

Additional MD simulations indicate that the efficiency of hydrogenation of graphitic materials could be enhanced by using carbon materials with curved surfaces (e.g. fullerenes, Figure 1). To gain an

understanding of this 'curvature effect' we examined the hydrogenation energies of various fullerenes and calculated the average C-H bond energies at several levels of hydrogenation (Figure 2). When forming only one C-H bond per fullerene, the C-H bond energy generally decreases with fullerene size, reflecting the strong influence of carbon material curvature on the C-H bond strength. For higher percentages of hydrogenation, the calculated C-H bond energies decrease monotonically with the fullerene size. For larger fullerenes, the average C-H bond energy varies in a relatively small range, within ~0.4 eV, with respect to hydrogenation percentage; a larger variation of C-H bond energies vs. hydrogenation percentage for smaller fullerenes, particularly C_{20}, was found since these fullerenes exhibit higher reactivity. Compared
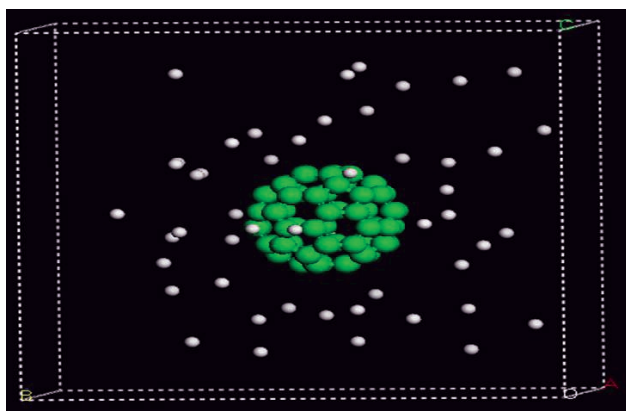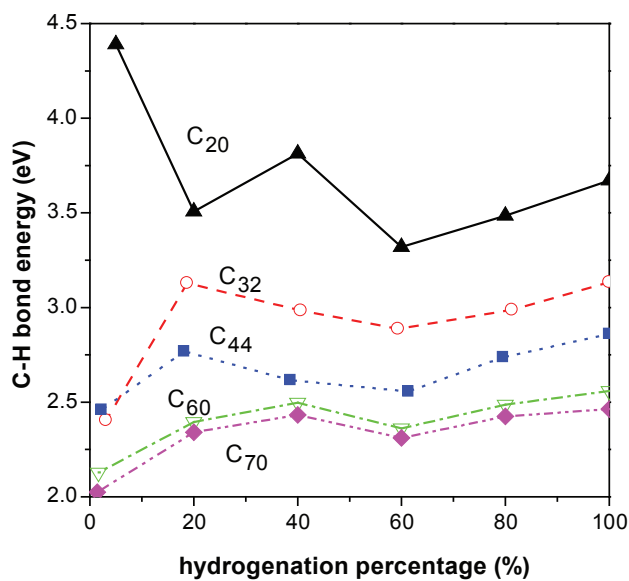
with the typical C-H bond energy in organic molecules (~4.3 eV), the average C-H bond energies in fullerenes, except C_{20}, are much smaller. The key challenge to make these materials useful for hydrogen storage will be to find a catalytic process that allows the C-H bonds to be broken.

Synthesis and Hydrogen Adsorption Testing of Anion-Intercalated Graphitic Carbon Materials. The goal of this task is to synthesize porous anion-intercalated graphitic carbon materials (e.g. graphite fluoride materials containing "semi-ionic" C-F bonds) and evaluate these materials for hydrogen storage at near-ambient temperatures. As reported previously, intercalated fluoride anions are predicted to significantly increase the heat of adsorption for hydrogen in carbon-based materials which will increase the effective hydrogen storage capacity at practical operating temperatures in a hydrogen storage system.

We have found that tetrafluoroborate intercalation complexes of graphite (C_xBF_4) provide a route towards fluorinated graphite based on literature reporting that the thermolysis of a graphite fluoroborate releases BF_3 at 148-200°C, resulting in C_xF. While the synthesis of C_xBF_4 has been published by several groups, the characterization of the thermal decomposition remains poorly understood. Graphite fluoroborates were synthesized by exposing graphitic carbons to a mixture of F_2 and BF_3 (1:2 molar ratio). These materials were characterized using a variety of spectroscopic techniques, including X-ray diffraction and solid-state nuclear magnetic resonance (NMR), which can be used to verify the intercalation of graphite and provide data on the degree of intercalation. ^{19}F and ^{11}B NMR data were also used to provide data on the both the composition of the intercalated species and the ionic/semi-ionic/covalent nature of the C-F. The thermolysis of a graphite fluoroborate was studied by temperature programmed desorption (TPD) which was used to determine the decomposition temperature for the desired BF_4^-/F^- ratio in the hydrogen adsorption samples (Figure 3).

Hydrogen capacity measurements on thermally treated $C_{20}BF_4$ showed ~0.2 wt% uptake at 298 K and 100 bar, with a heat of hydrogen adsorption of ~12 kJ/mol. While the storage capacity is very low, this heat of adsorption is approximately two times higher than those measured for materials such as activated carbon. The small observed capacity may be attributed to a lack of surface area (75 m²/g from N_2 sorption data). NMR studies revealed low levels of C-F or F[-] species in the C_xBF_4 samples, both as-prepared and thermally treated. The lack of substantial amounts of semi-ionic or ionic F may also contribute to the low H_2 capacity measurement (Figure 4). The potential exists to increase the isosteric heat and capacity if a sample with more F[-] species can be synthesized. To improve H_2 adsorption, we are focusing on three strategies: 1) intercalation

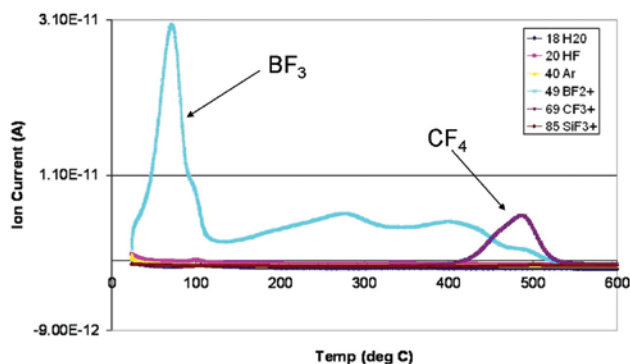**FIGURE 1.** Snapshot of MD Simulation of Atomic Hydrogen Interactions with C_{60}

FIGURE 2. Plot of C-H Bond Energy (eV) vs. the Extent of Hydrogenation for Known Fullerenes (C_{20}-C_{70})

FIGURE 3. TPD Spectrum for C_xBF_4 Sample

FIGURE 4. Hydrogen Isotherms on a Thermally Treated C_xBF_4 Sample – The inset is a plot of the calculated isosteric heat of adsorption vs. coverage from the isotherm data.

of higher surface area graphitic materials with F_2 and BF_3; 2) increase intercalation to a first stage material to maximize fluoride concentration; 3) intercalation of hexafluorophosphate (PF_6^-) to increase graphene layer spacing to provide better H_2 access and possibly more facile decomposition and loss of PF_5 to give F^-.

Our previous reports have suggested that the heat of adsorption for H_2 in the graphite fluoride materials will be higher for N-doped carbons. Efforts continue towards generating nitrogen-doped graphite by chemical vapor deposition (CVD) using acetonitrile vapor. CVD-grown $C_{19}N$ can be purified of Ni catalyst through stirring/sonication of graphite fibers in hydrochloric acid. However, scaling up the synthesis of the CVD-grown $C_{19}N$ has proved to be challenging. Increasing the amount of Ni catalyst decreased yields and nitrogen incorporation. Dispersing the Ni catalyst across larger surface areas in the CVD reactor, together with an increased vapor concentration of acetonitrile improved yields, but resulted in N doping levels of only $C_{70}N$ to $C_{80}N$. By keeping all other conditions the same as that used to make $C_{19}N$ fibers, and simply doubling the flow rate of argon feed gas through the acetonitrile-filled sparger, we observed a 6-fold increase in yield, while incorporating enough nitrogen to yield a material with the formula $C_{26}N$.

Conclusions

Computational Study of Hydrogen Spillover Mechanisms. New understanding of several key steps in the spillover mechanism has been realized:

- Transfer of hydrogen from H-saturated catalyst particle to material.
- Migration of hydrogen atoms on graphene.
- Three publications in print, one submitted for publication.

Experimental and Computational Investigation of Anion-Intercalated Graphite and Nitrogen-Doped Graphite as Hydrogen Storage Materials. Additional simulations of hydrogen adsorption in graphite fluoride; first samples generated for hydrogen adsorption testing.
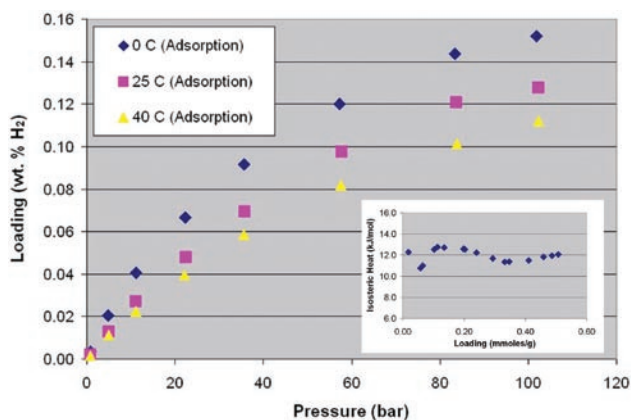
- Computational proof of higher adsorption enthalpy for graphite intercalation complexes vs. activated carbon.
- Synthetic procedure developed to synthesize mixed BF_4^-/F^- intercalation complexes.
- Hydrogen adsorption testing reveals high adsorption enthalpy (~12 kJ/mol) but overall low hydrogen capacity for initial samples with only 75 m^2/g surface area.

Future Directions and Milestones

- Fiscal Year 2008: Find optimal BF_4^-/F^- ratio for maximum H_2 uptake and/or heat of adsorption in intercalated graphite.
- FY 2008: Study BF_4^-/F^- intercalation of N-doped carbon with high N levels (nominal C_5N composition); obtain hydrogen isotherm data on these materials.
- FY 2008: Perform ab initio MD simulations and minimum energy path calculations on BC_3-intercalated compounds.
- FY 2009: Introduce intercalating species, such as F^- and K^+, into BC_3 to:
  – Induce both physisorption and chemisorption
  – Enhance H_2 adsorption kinetics
- FY 2009: Explore the optimal concentration of intercalating species in both BC_3 and N-doped F^- intercalated graphite.

Special Recognitions & Awards/Patents Issued

1. "Hydrogen Storage with Graphite Anion Intercalation Compounds", U.S. patent application (pending).

FY 2008 Publications/Presentations

1. "Mechanistic Study on Hydrogen Spillover onto Graphitic Carbon Materials," Chen, L.; Cooper, A.C.; Pez, G.P.; Cheng, H. *J. Phys. Chem. C.* **111**, 18995 (2007).

2. "On the Mechanisms of Hydrogen Spillover in MoO_3", Chen, L.; Cooper, A. C.; Pez, G. P.; Cheng, H. *J. Phys. Chem. C.* **112**, 1755 (2008).

3. "A Mechanistic Study of Hydrogen Spillover in MoO_3 and Carbon-based Graphitic Materials", Chen, L.; Pez, G.P.; Cooper, A.C.; Cheng, H. *J. Phys.: Condens. Matter* **20**, 064223 (2008).

4. "Hydrogen Spillover in the Context of Hydrogen Storage Using Solid-state Materials", Cheng, H.; Cooper, A.C.; Sha, X.; Chen, L.; Pez, G.P. (*Energy Environ. Sci.*, accepted for publication).

5. "Hydrogen Spillover Dynamics on Carbon Based Materials", Sha, X.; Knippenberg, M.T.; Cooper, A.C.; Pez, G.P.; Cheng, H. (*J. Phys. Chem. C.,* accepted for publication).