IV.C.1a Designing Microporous Carbons for Hydrogen Storage Systems

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Partner Approach

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. Air Products, an industry leader in hydrogen energy products and systems, has recognized this need, and has strategically focused on developing new hydrogen storage technology using novel, reversible H_2-sorbent materials that will be held in suitable robust, light-weight, low-cost containers. We are collaborating with partners in the Carbon-Based Hydrogen Storage Center of Excellence (CbHS CoE) 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.

Partner FY 2006 Results

"Capsule" Method and H_2 Adsorption Data

We have continued to develop and refine a novel method to characterize hydrogen storage in solid materials. The capsule method is a low-cost and potentially high-throughput method for hydrogen storage measurements at near-ambient temperatures (Figure 1). When an adsorbent in the capsule is exposed to hydrogen and the system has come to equilibrium,

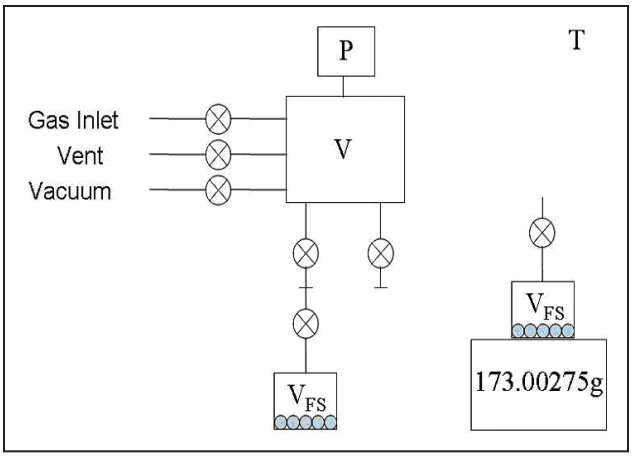

FIGURE 1. Illustration of Apparatus Used for Capsule Method Hydrogen Storage Measurements

the capsule can be sealed with a valve and weighed on a standard 5-place laboratory balance. The total amount of hydrogen in the capsule (excess hydrogen + gaseous hydrogen) is measured by this technique.

One can establish the "free space" within the capsule by expansion of non-adsorbing gas (e.g., helium) from a known volume. It is then possible to measure excess hydrogen uptake by using the free space to calculate the partitioning of total hydrogen weight into gaseous hydrogen (by an equation of state) and excess hydrogen. If equilibrium is achieved at a number of pressures at a constant temperature, an isotherm can be measured using the capsule method. We have benchmarked the performance of the capsule by performing isotherm measurements on GX-31 activated carbon and comparing the results to adsorption isotherms using our differential pressure adsorption unit (DPAU) and a Rubotherm microbalance (Figure 2).

Modifications were made to our DPAU to enable better sample handling and temperature control, so that temperature is now controlled in a previously unregulated regime of the DPAU. Other improvements have made attachment of the sample cells to the DPAU easier, and they allow us to transfer activated samples directly to the DPAU without having to first transfer them to an argon glove box. Removal of this intermediate step is a major time-saving. In addition, the new couplings are easier to manipulate and are less prone to gas leaks during experimentation than were the previous sealing mechanisms. Last, quartz inserts were acquired that render sample addition to and removal from the DPAU test cell much easier and mitigate contamination of the cell. Hydrogen adsorption isotherms were measured on a number of samples from

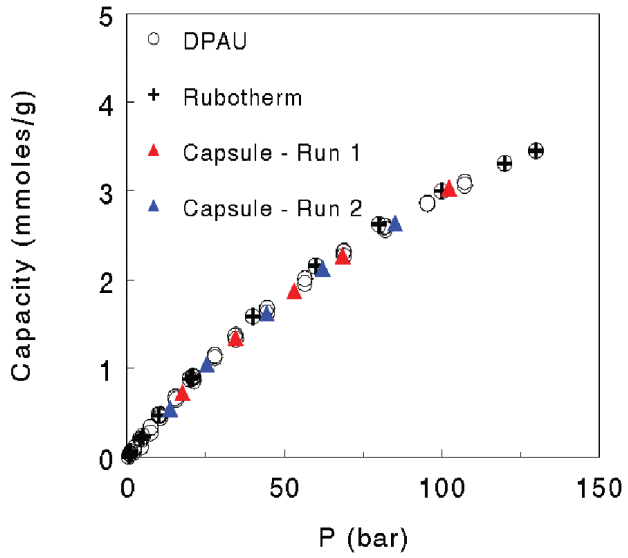

FIGURE 2. Overlay of hydrogen isotherms at 25°C for GX-31 activated carbon, comparing the results of the capsule method to our DPAU and a Rubotherm microbalance.

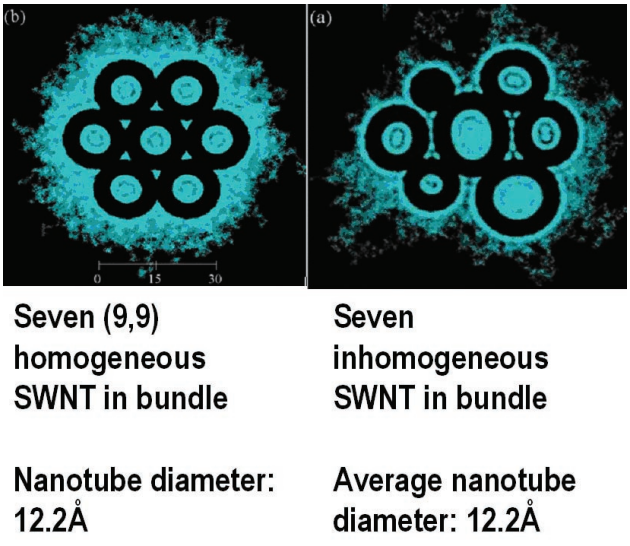

FIGURE 3. Plot of density of hydrogen in various regions in and around the homogeneous and inhomogeneous SWNT bundles during molecular dynamics simulations.

CbHS partners (NREL, ORNL, Penn State). Using the differential pressure adsorption unit, we were able to measure isotherms at near-ambient temperatures on samples as small as 50 mg.

Computational Modeling of Gibbs Excess Adsorption of Hydrogen in Carbon-based Materials

We have developed a new computational approach to model Gibbs excess adsorption on materials. This method is very general and can be easily applied to carbon-based materials of interest within the Center. The key principle is to derive a distribution function that resolves energy contributions of adsorbed hydrogen and gaseous (non-interacting) hydrogen within the simulation. The new method was first applied to bundles of SWNT. We chose this system because our large amount of prior work on modeling of hydrogen adsorption allows us to expect differences in energy as a function of distance from the SWNT surface. In addition, we are interested in simulations of inhomogeneous SWNT bundles (bundles containing more than one type of SWNT), because the experimental SWNT samples used within the CoE are in most cases highly inhomogeneous.

Figure 3 shows the density of hydrogen in various regions in and around the homogeneous and inhomogeneous SWNT bundles during the simulations. The simulations use our previously published curvature-dependent force field model [1,2]. We found that more hydrogen is adsorbed close to the SWNT surfaces in the inhomogeneous bundles because of the higher accessible surface area of these bundles. This is a result of the size mismatch of the nanotubes creating larger interstitial pores (pores between nanotubes) and more bundle groove site area (grooves on external SWNT bundle surface).

Hydrogen Adsorption on Boron- and Nitrogen-doped Carbon Materials

In an effort to discover new materials with higher adsorption energies than pure carbon materials, we have investigated hydrogen adsorption on boron- and nitrogen-doped carbon (stacked graphene sheets) materials using *ab initio* molecular dynamics. While no appreciable hydrogen adsorption energies were calculated for nitrogen-doped graphite, there was a pronounced interaction of hydrogen with boron-doped graphite ($C_{48}B_{16} \cdot 4\ H_2$). We observed that the hydrogen reacts with specific carbon atoms in the graphene sheet to form weak C-H bonds (Figure 4). The heat of adsorption was found to be -17.8 kJ/mol, which is substantially higher than the heat of adsorption in pure carbon using the same computational methodology.

Partner FY 2007 Plans

- Apply computational methods to new materials of interest to CbHS partners:
  - *Ab initio* molecular dynamics study on hydrogen spillover mechanism (potential >7 wt% hydrogen storage).
- Increase collaboration with partners on accurate hydrogen adsorption measurements:

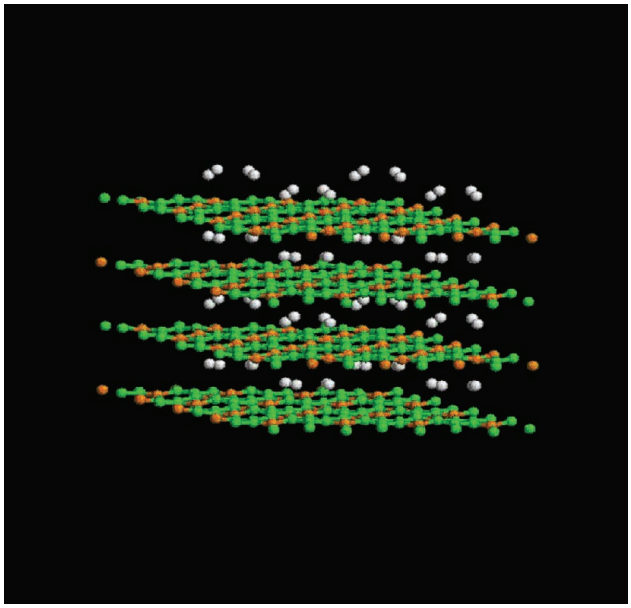

FIGURE 4. Snapshot of hydrogen adsorption on boron-doped graphite ($C_{48}B_{16} \cdot 4\ H_2$) during the molecular dynamics simulations (carbon-green, boron-orange, hydrogen-white).

  - Investigate extending our capability from near-ambient temperatures to cryogenic temperatures (e.g., >7 wt% hydrogen storage in literature using MOF).
  - Complete development of high-temperature pycnometer for correction of helium adsorption effects on hydrogen isotherms (preliminary – up to 25% change in measured capacity for <1 wt% H_2 at 100 atm.).
- Initiate experimental program in FY 2007 on new hydrogen storage materials:
  - Resource dependent.
  - Collaborations expected (e.g., on B-, N-containing carbon materials).

Air Products FY 2006 Publications/Presentations

1. "Tailoring Singlewalled Carbon Nanotubes for Hydrogen Storage," Journal of Materials Research, **20**, 3214 (2005).

2. "Accurate Hydrogen Sorption Measurements via Differential Pressure Analyses" (submitted for publication).

3. "A Low Cost Sorption Experiment Designed for the Support of H_2 Storage Materials Development" (submitted for publication).

4. "On the Effective Capacity of Finite Bundles of Single Walled Carbon Nanotubes for Hydrogen Adsorption" (submitted for publication).

5. "Advanced Hydrogen Sorption Measurement Techniques: Application to Tailored Singlewalled Carbon Nanotubes": Materials Research Society Fall Meeting, 11/05, Invited Presentation.

6. "Enabling Discovery of Materials With Higher Heat of Adsorption": FreedomCAR tech team review meeting, 3/06.

7. "Enabling Discovery of Materials With a Suitable Heat of H_2 Adsorption": DOE Hydrogen Program Annual Merit Review, 5/06.

References

1. M. K. Kostov, H. Cheng, A. C. Cooper, and G. P. Pez, Phys. Rev. Lett. **89**, 146105 (2002).

2. H. Cheng, A. C. Cooper, G. P. Pez, M. K. Kostov, P. Piotrowski, and S. J. Stuart, J. Phys. Chem. **109**, 3780 (2005).