IV.C.1m Enhanced Hydrogen Dipole Physisorption

Channing Ahn

California Institute of Technology
1200 E. California Blvd., MS 138-78
Pasadena, CA 91125
Phone: (626) 395-2174; Fax: (626) 795-6132
E-mail: cca@caltech.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

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Objectives

- Synthesis, analysis, and quantification of surface excess isotherm behavior in high surface area carbon and modified framework structures.
- Establishment of the principle of enhanced dipole physisorption.
- Evaluation of the efficacy of carbon and other high surface area systems as commercially viable hydrogen storage sorbents.
- Overcome specific thermodynamic limitations to hydrogen physisorption, by deepening the potential well for physisorption.

Technical Barriers

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

(A) System Weight and Volume
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(Q) Reproducibility of Performance

Technical Targets

Data are typically reported as surface excess gravimetric densities that reflect the amount of hydrogen sorbed due to the presence of the sorbent. Gas law contributions are not considered as part of this analysis as these depend on the surface area and skeletal density of the sorbent. Inclusion of such a number will typically add ~30% to the values noted below. The contribution to the system weights from the tanks and insulation are not considered in our values whereas the 2010 targets for gravimetric and volumetric capacity are targeted on the system's basis of 6 wt% and 0.045 kg/L, respectively.

The best materials we have synthesized/studied to date have a specific energy of 1.91 kWh/kg and a volumetric density of 1.28 kWh/L, measured at 77 K.

Accomplishments

- Measurement and correlation of gravimetric density with surface area in carbon aerogels with surface areas up to 3,200 m^2/gm.
- Measurement of Oak Ridge National Laboratory nanohorn samples of up to 1,500 m^2/gm that show hysteresis effects, traditionally associated with capillary condensation.
- Synthesis of framework structures including MOF-74 that shows higher than expected uptake on the basis of surface area, and MIL-53 that also shows adsorption/desorption hysteresis.

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Approach

High surface area will be amongst the criteria for high gravimetric density storage. We have been using well-developed volumetric techniques [1] in order to measure isotherm behavior at 77 K and room temperature. This work has enabled us to validate behavior noted by other investigators wherein gravimetric density scales with surface area [2] in a wide range of carbons. Using the rule of thumb where 1 wt% hydrogen is adsorbed for every 500 m^2/gm of surface area of sorbent, we have been working with Hydrogen Sorption-Center of Excellence partner Ted Baumann of Lawrence Livermore National Laboratory (LLNL), who has been using a range of carbonization temperatures and processing techniques in synthesizing carbon aerogels and he has synthesized the highest surface area carbon aerogel yet made. These materials can be made in monolithic form, potentially giving them packing density advantages over that of traditional high surface area carbons such as activated carbon. We also note that traditional high surface area approaches will require a microstructure dominated by micropore volumes wherein pore sizes are typically <2 nm.

We have also been synthesizing high surface area organic framework structures and have been concentrating on those systems that show high adsorption enthalpies, or affinities for molecular hydrogen that will enable us to consider systems capable of operating at temperatures greater than 77 K. Characteristic of such systems are those materials that have exposed d-series metals.

Results

Figura 1a shows isotherm traces from a series of aerogels from LLNL, with increasingly higher surface area materials showing higher maxima of the surface excess sorption plot. Figure 1b shows the result of the overall trend of maximum surface excess value vs. Brunauer-Emmett-Teller (BET) surface area. The value of 3,200m^2/gm represents the maximum value that is likely achievable as the theoretical limit of the surface area of a graphene sheet is 2,600 m^2/gm. The additional surface area presumably consists of edge terminations to the armchair or zig-zag graphene structure. The values that are presented here are comparable to isotherms seen in the highest surface area activated carbons.

Figure 2a shows a comparison of isotherm traces, over a large pressure range, of framework structures that we have synthesized. Note that while there is a difference of nearly a factor of two in BET surface area between MIL-100 and MOF-74, the surface excess capacity of these systems is nearly identical. This offers some insight into the possibility that correctly designed systems can go beyond the surface area trends seen in typical carbons as the MOF-74 shows sorption maxima that are ~50% greater than expected. Figure 2b on the right shows a blow-up of the left plot, showing a high isotherm slope, typical of high sorption enthalpy materials.

Figure 3 shows the isosteric enthalpy of adsorption for MOF-74 determined at 77 and 87 K and as expected in systems of the type, initially high heats (in this case 8.5 kJ/mole) begin to fall off as specific high energy sites are filled, leaving weaker sites as H$_2$ loading increases. Results like this are critical in evaluating the ultimate requirements of engineering systems that may employ sorbents of this type.

Conclusions and Future Directions

- Sorbents for non-dissociative hydrogen storage offer higher storage densities than compressed gas storage alone. To this end we have collaborated with LLNL, measuring and analyzing the sorption properties of carbon aerogels and note that these materials display properties similar to those of activated carbons but with the advantage of conformability during synthesis. Having established the surface area dependence, we plan to concentrate
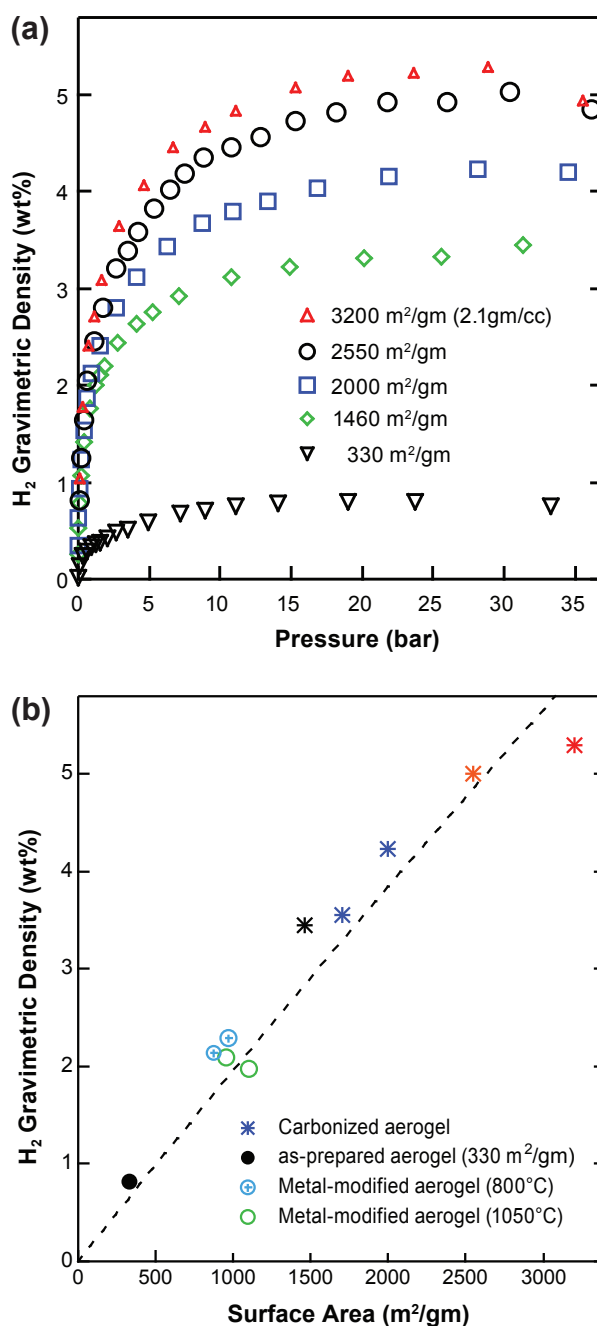

FIGURE 1. (a) The figure shows isotherm traces for a range of aerogels with different surface areas. (b) The figure shows maximum value of surface excess sorption vs. surface area. The dotted trace is the "rule of thumb" of 1 wt%/500 m^2/gm of surface area that is typical of most carbons.

on reducing pore sizes to the micropore regime in order to improve the volumetric density.

- Our synthesis of high surface area framework structures has established important behavior in the MOF-74 compound wherein higher than expected gravimetric densities can be seen as a function of surface area, over that of typical carbons.
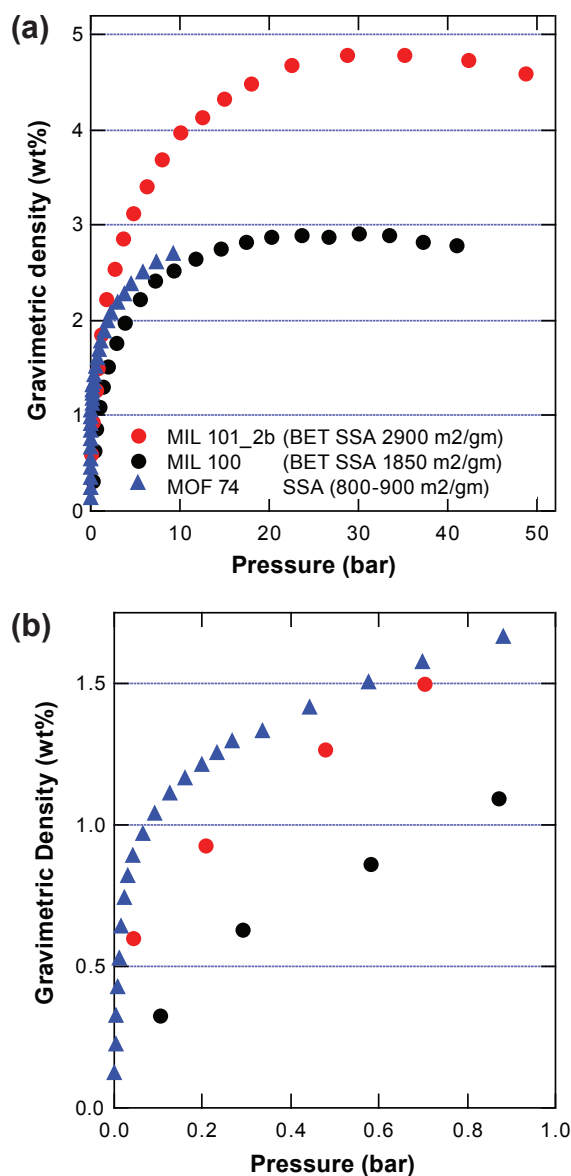
(a)

(b)

FIGURE 2. (a) The figure shows isotherms comparison of several framework structures that we have synthesized. (b) The figure shows a blow-up of the low pressure region showing a higher slope in the Henry's Law region, indicating a high differential enthalpy of adsorption at zero coverage.

- Our overall work has seen differential enthalpies of adsorption at zero coverage that range from 4 to 8.5 kJ/mole, with the highest values seen in the MOF-74 compound. We expect that this model system will provide insights into improving gravimetric densities and sorption enthalpies in order to reach DOE targets.
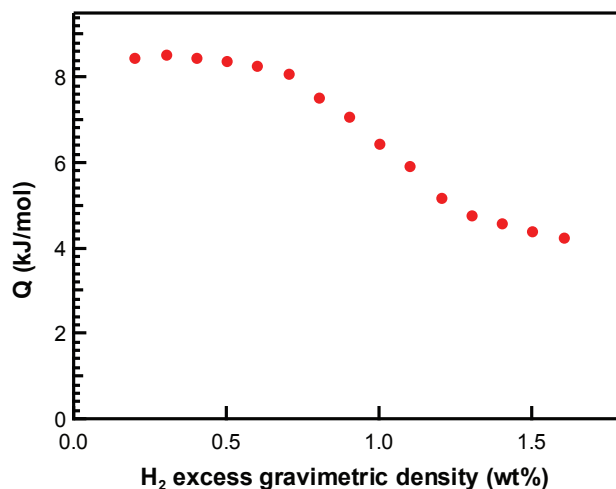

FIGURE 3. A plot of the isosteric enthalpy of adsorption determined at 77 and 87 K showing the initially high 8.5 kJ/mole value, eventually decreasing as high sorption sites become filled as a function of loading.

FY 2007 Publications/Presentations

1. "H$_2$ Physisorption in Carbons and Metal Organic Frameworks," C. C. Ahn, invited presentation, MH2006, Maui (October 2006).

2. "The Tailoring of Single-Walled Carbon Nanohorns for Hydrogen Storage," Hui Hu, Bin Zhao, Alexander Puretzky, David Styers-Barnett, Christopher Rouleau, David Geohegan, Yun Liu, Craig Brown, Dan Neumann, Houria Kabbour, Channing Ahn, John Zielinski, Charles Coe, Alan Cooper, Lin Simpson, Anne Dillon, Philip Parilla and Michael Heben, Fall MRS Symposium Z5: Hydrogen Storage Technologies: Carbon and Nanotubes, Boston, (November 2006).

3. "Hydrogen Sorption Properties of MIL-53, 100 and 101 Compounds: Correlation with the Surface Area and the Microporosity," Houria Kabbour, Anne Dailly and Channing C. Ahn, Fall MRS Symposium Z6, Hydrogen Storage Technologies: Carbon and MOFS, Boston, (November 2006).

4. "Toward New Candidates for Hydrogen Storage: High-Surface-Area Carbon Aerogels," Houria Kabbour, Theodore F. Baumann, Joe H. Satcher, Jr., Angelique Saulnier and Channing C. Ahn, Chem. Mater. 18 (26), 6085 (December 2006).

References

1. R. C. Bowman, Jr., C. H. Luo, C. C. Ahn, C. K. Witham, B. Fultz, *J. Alloys Compd.* 217, 185, (1995).

2. "Characterization and optimization of adsorbents for hydrogen storage," R. Chahine and T.K. Bose, in Hydrogen Energy Progress XI (3 Vols.), Proceedings of the 11th WHEC, Veziroglu TN, Winter C-J, Baselt JP, Kreysa G., eds. P 1259, Oxford: Pergamon Press, 1996.