IV.C.3 Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

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Fiscal Year (FY) 2012 Objectives

- Fabricate high-surface-area, multiply surface-functionalized carbon ("substituted materials") for reversible hydrogen storage with superior storage capacity (strong physisorption).
- Characterize materials and storage performance. Evaluate efficacy of surface functionalization, experimentally and computationally, for fabrication of materials with deep potential wells for hydrogen sorption (high binding energies).
- Optimize gravimetric and volumetric storage capacity by optimizing pore architecture and surface composition ("engineered nanospaces").

Technical Barriers

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

(A) System Weight and Volume

(B) System Cost

(E) Charging/Discharging Rates

(J) Thermal Management

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project aims at the development of surface-engineered carbons, made from corncob or other low-cost raw materials, which simultaneously host high surface areas, created in a multi-step process, and a large fraction of surface sites with high binding energies for hydrogen, created by surface functionalization with boron, iron, and lithium. Targets are surface areas in excess of 4,500 m^2/g, average binding energies in excess of 12 kJ/mol, and porosities below 0.8, toward the design of materials that meet the following 2017 DOE hydrogen storage targets:

- Gravimetric storage capacity: 0.055 kg H_2/kg system
- Volumetric storage capacity: 0.040 kg H_2/liter system

Accomplishments

- Demonstrated that boron substitution of high-surface area carbon raises binding energy (isosteric heat of adsorption) from ~7 kJ/mol to ~17 kJ/mol at zero coverage, and from 6 kJ/mol to 10 kJ/mol at high coverage. Demonstrated reproducibility of the high binding energy on samples from different lots.
- Manufactured boron-substituted carbons by deposition and thermolysis of $B_{10}H_{14}$ on high-surface-area activated carbon, without significant reduction in surface area (~15%), by multiple methods. 1-step doping gave a reduction in total pore volume of ~20%; 5-step doping gave virtually no reduction.
- Measured hydrogen adsorption as a function of boron concentration. Observed systematic increase in adsorption (excess adsorption per surface area) with increasing boron concentration. At room temperature (303 K) and 200 bar, the increase is 40% for B:sample = 8.9 wt% (annealed at 600ºC), and 10% for B:sample = 6.7 wt% (annealed at 1,000ºC).
- Developed experimental estimates of the thickness of adsorbed hydrogen films on boron-free (undoped) carbon at different temperatures. The estimated thickness at room temperature and liquid nitrogen temperature is ~0.6 nm (2012) and ~0.4 nm (2010), respectively, both independent of the gas pressure.
- A 5.3-liter hydrogen sorption tank, densely packed with 1.5 kg of high-performance U. Missouri carbon

(undoped, powder), designed for operation anywhere between room temperature and dry-ice temperature and at 0-100 bar, was put into commission and tested for storage capacity and charge/discharge kinetics. Packing was maximum (random close packing). Storage capacity at 296 K and 100 bar was 0.031 kg H_2/kg carbon (3.0 material wt%).

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Introduction

High-surface-area carbons from corncob, as developed by our team, are outstanding starting materials for the development of functionalized materials which store hydrogen, by strong physisorption, reversibly at high gravimetric and volumetric storage capacity. An earlier carbon exhibited a gravimetric storage capacity of 0.11 kg H_2/kg carbon at 80 K and 50 bar. This project is a systematic effort to achieve comparable results at 300 K, by increasing surface areas from currently ~3,000 m^2/g to ~6,000 m^2/g, and substituting carbon with boron and other elements that increase the binding energy for hydrogen (electron donation from H_2 to electron-deficient B, and other charge-transfer mechanisms). Earlier high surface areas and high binding energies were hosted by sub-nm pores in narrowly spaced "stacks of large graphene sheets." New high-surface-area, boron-substituted materials are manufactured by thermolysis of volatile boron carriers in pores of stacks of graphene sheets. New surface area, created by chemical means (controlled oxidation) in the form of "stacks of small graphene sheets" (large ratio of edge sites to in-plane sites), is expected to be able to add as much as another 3,000 m^2/g. A significant effort of the project goes into conversion of these materials, most of which currently are powders, into monoliths, without loss of surface area and high-binding-energy sites. Monoliths have lower porosity and, as a result, higher volumetric storage capacity than powders.

Approach

The approach is an integrated fabrication, characterization, and computational effort. Structural characterization includes determination of surface areas, pore-size distributions, and pore shapes. Storage characterization includes measurements of hydrogen sorption isotherms and isosteric heats. Computational work includes adsorption potentials and simulations of adsorbed films for thermodynamic analysis of experimental isotherms. Comparison of computed and experimental isotherms validates theoretical adsorption potentials and experimental structural data.

Results

Increase of binding energy and hydrogen uptake on boron-doped samples

High-surface-area boron-substituted ("doped") carbons were prepared by using as precursor (boron-free carbon) the U. Missouri sample 3K-600C, coating the precursor with a monolayer or less of decaborane, $B_{10}H_{14}$ (liquid/vapor deposition), thermal decomposition of the adduct, and annealing of the decomposition product [1]. Sample 3K-600C is our best-performing undoped carbon, with 30% and 20% higher gravimetric excess hydrogen adsorption than the commercial carbon MSC-30 (Maxsorb, Kansai Coke and Chemicals, Ltd) at 100 bar and 80 K and 303 K, respectively [2]. Representative results for doped samples are collected in Table 1 and Figure 1. They demonstrate that the doping method developed preserves much of the structural integrity of the precursor: reduction of surface area upon doping is ~15% or less (Table 1); reduction of volume in pores <2.0 nm is about 20%; and reduction in the total pore volume is about 0-20% (Figure 1). Sample 3K-H79 (I,A), which gave negligible reduction in total pore volume, suggests that multiple doping by small amounts is better than single doping by a large amount. The increase in binding energy and hydrogen uptake on boron-doped samples, as predicted by theory [3], can be observed in three different ways:

(i) The hydrogen excess adsorption per unit surface area ("areal excess adsorption") systematically increases with increasing boron concentration (Figure 2, bottom). At 303 K and 200 bar, the increase relative to the undoped precursor is 10% and 40% at boron concentration 6.7 and 8.9 wt%, respectively. The top performer, 3K-H60 (I,A), outperforms the undoped precursor even at the level of gravimetric excess adsorption (Figure 2, top), illustrating that the higher binding energy in the doped sample can more than make

TABLE 1. Preparation of boron-doped carbons. Brunauer-Emmett-Teller (BET) surface areas (Σ) and void fractions (porosity, ϕ) are from N_2 adsorption at 77 K. Boron concentrations (B:sample) were measured by prompt gamma neutron activation analysis at the University of Missouri Research Reactor. Annealing at 1,000°C [3K-H60 (I,B)] reduced the boron content by ~25% relative to annealing at 600°C [3K-H60 (I,A)], with unknown decomposition products, but unchanged surface area and pore-size distribution.

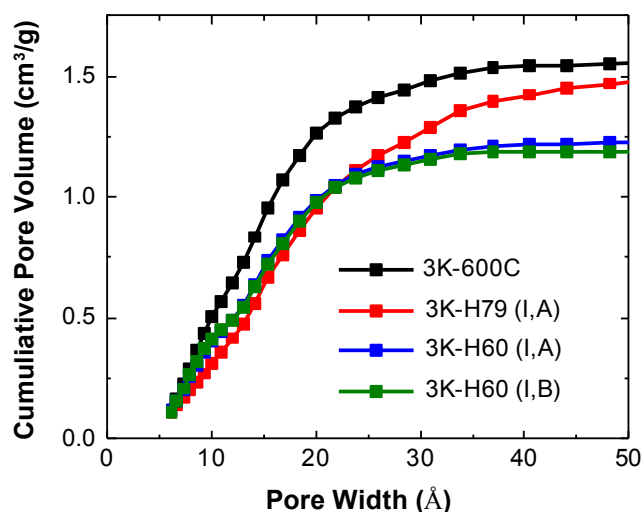| Sample	Precursor	Annealing temp.	B conc. (wt%)	BC_x	Σ (m^2/g)	ϕ
3K-600C	Not applicable (N/A)	N/A	0.0	BC_∞	2,500	0.76
3K-H60 (I,A), 1-step doping	3K-600C	600°C	8.9	$BC_{9.21}$	2,100	0.74
3K-H60 (I,B), 1-step doping	3K-600C	1,000°C	6.7	$BC_{12.5}$	2,100	0.72
3K-H79 (I,A), 5-step doping	3K-H78 (I,A)	600°C	7.1	$BC_{11.8}$	2,200	0.78

FIGURE 1. Cumulative pore-size distribution of doped materials and undoped precursor in Table 1. Sample 3K-H79 (I,A), from 5-step doping, with ~1.4 wt% boron added per step, exhibits the smallest loss in surface area and largest retention of total pore volume.

up for a lower surface area. Areal excess adsorption is a direct measure of the binding energy because it depends only on how strongly the surface adsorbs hydrogen, but not on pore volume and surface area of the sample. If high-binding-energy sites were present only as a small fraction of all surface sites, the areal excess adsorption isotherm of the doped surface would rise over the isotherm of undoped surface at low pressure (high-binding-energy sites are filled first), but then approach the isotherm of the undoped surface at higher pressures. Figure 2 shows that this is not the case; instead the isotherm of the doped surface rises above the isotherm of the undoped surface at *high pressures*, signaling the presence of high binding energies on a majority of surface sites (high *average* binding energy).

(ii) Isosteric heats of adsorption (enthalpy of adsorption), ΔH, of hydrogen on boron-doped and undoped samples were determined, from Clausius-Clapeyron analysis of adsorption isotherms at 273 K and 303 K (Figure 3). The boron-doped sample gave $\Delta H \sim 17$ kJ/mol at zero coverage and $\Delta H \sim 10$ kJ/mol at high coverage (Figure 3, bottom), exhibiting that the surface hosts a small fraction of sites with binding energies as high as 17 kJ/mol, and a majority of sites with binding energy of 10 kJ/mol (*average* binding energy). The undoped sample gave $\Delta H \sim 7$ kJ/mol at zero coverage and $\Delta H \sim 6$ kJ/mol at high coverage, and corresponding high and average binding energies. (Estimates of binding energies are equated to ΔH values in this report; more accurate estimates involve addition of zero-point and thermal energies [4].) This demonstrates that the U. Missouri boron-doping procedure successfully raises the binding energy, from ~6 kJ/mol to ~10 kJ/mol, uniformly across a majority of surface sites—in excellent agreement with theory, which predicts, on undoped/
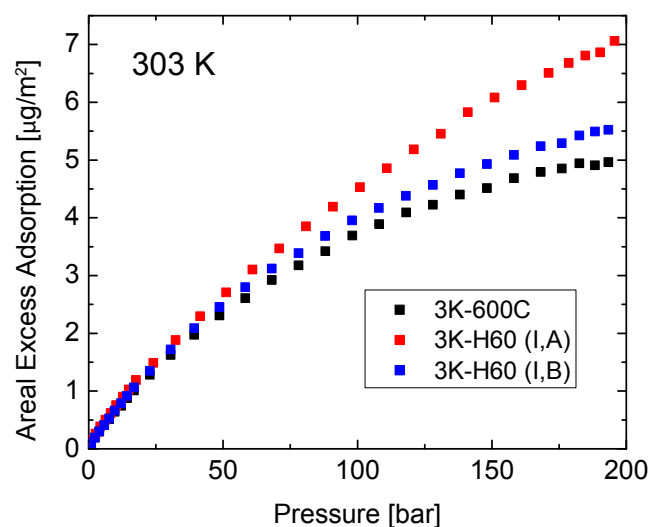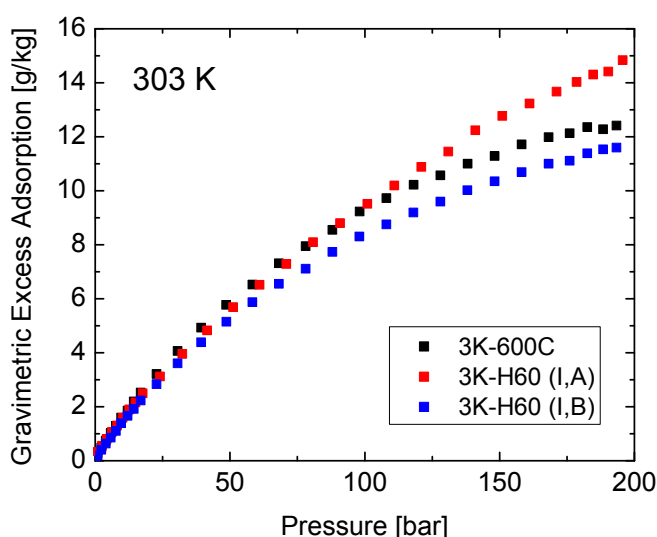

FIGURE 2. Hydrogen sorption at room temperature for materials in Table 1, as a function of boron concentration. Top: gravimetric excess adsorption. Bottom: areal excess adsorption (gravimetric excess adsorption divided by BET surface area; compares excess adsorption on identical surface areas). The higher the areal excess adsorption at a given pressure and temperature, the higher is the binding energy. Thus, the samples ordered from high to low binding energy are: 3K-H60 (I,A) > 3K-H60 (I,B) > 3K-600C. The corresponding boron concentrations are: 8.9 > 6.7 > 0.0 wt%.

doped graphene sheets, an increase from 5 kJ/mol (0 wt% B) to 10-12 kJ/mol (10 wt% B) [3].

(iii) As the temperature is lowered from 303 K to 273 K, gravimetric excess adsorption in Figure 3, top, increases by about 90% for the boron-doped sample and about 45% for the undoped sample, both at high pressure (200 bar) and low pressure (50 bar). These increases are consistent with that the binding energy of the doped material, E_d, is approximately twice the binding energy of the undoped material, E_u. The analysis is as follows. For given E_d, E_u, and temperatures
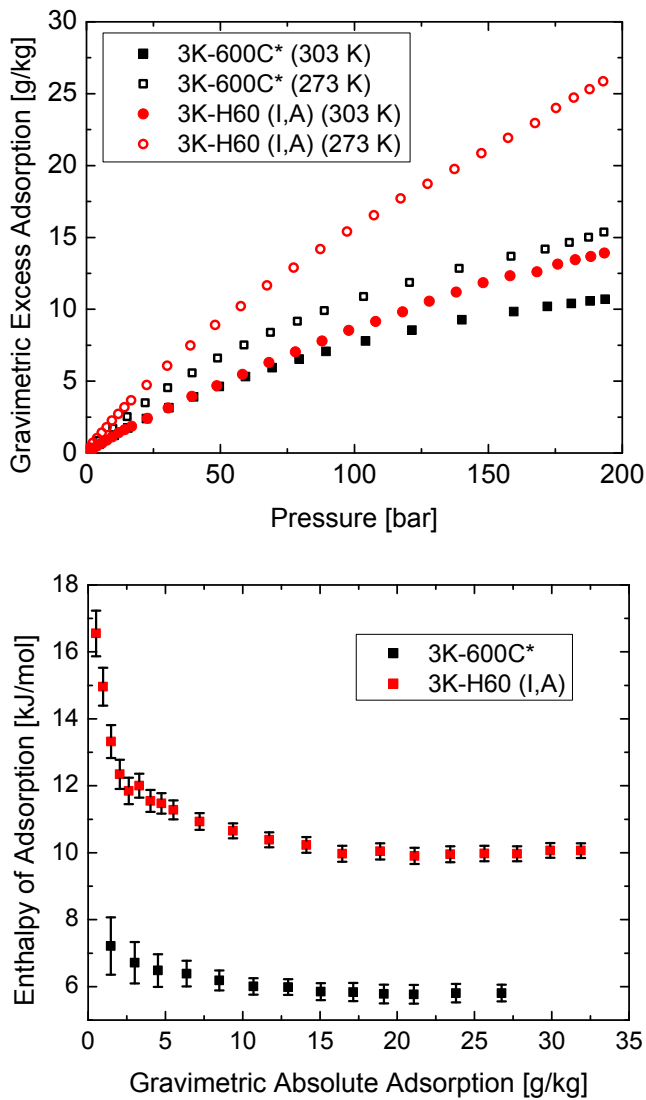
$$R_d/R_u \approx \exp[(E_d - E_u)(T_1^{-1} - T_2^{-1})/R] \approx (T_1/T_2)^{1/2} R_u \qquad (3)$$

$$R_d \approx (T_1/T_2)^{1/2}(R_u)^2 \qquad \text{if } E_d = 2E_u \qquad (4)$$

In Eqs. (1, 2), gravimetric excess adsorption is approximated by absolute adsorption, valid at low pressure; absolute adsorption is calculated from the Langmuir isotherm for mobile adsorption with Langmuir constants $\chi(E_d, T)$ and $\chi(E_u, T)$, respectively, evaluated at low pressure and high temperature, and evaluated with $\alpha(T_1) = \alpha(T_2)$ for the footprint area of one hydrogen molecule [5]; and R is the gas constant. Equation (3) follows from (1, 2), where in the second part $E_d = 2E_u$ has been used. This gives the "doubling of the binding energy" relation (4). Experimentally, $R_d = 1.89$ and $R_u = 1.43$ at 50 bar (Figure 3, top). Theoretically, $R_d \approx 1.94$ from $R_u = 1.43$ and (4). The remarkable agreement of the experimental and theoretical value for R_d shows that a doubling of the binding energy, from ~5 kJ/mol to ~10 kJ/mol according to (ii), indeed accounts for the observed increase of 90% on the doped sample.

Hydrogen storage on undoped carbon in 5.3-liter tank

A 5.3-liter hydrogen sorption tank, constructed by the University of Missouri and Midwest Research Institute under a Defense Logistics Agency contract [6], was filled with undoped high-performance U. Missouri carbon and tested for storage capacity and charge/discharge kinetics, including temperature evolution during, at room temperature (Figure 4). To the best of our knowledge, this is the first fully operational sorption-based hydrogen tank in the U.S., allowing comparison of projected storage capacity (based on adsorption of hydrogen on small, typically a few 100 mg, samples in the laboratory) and actual storage capacity, measured by a flow meter on a tank holding of the order of a kilogram of sorbent. This amounts to a scale-up by a factor of 10^4. The agreement between projected storage capacity ("tank capacity from 300 mg sample") and actual storage capacity ("total hydrogen in tank from flow meter"), both in terms of gravimetric storage capacity, is better than within 1%, across the entire pressure range (Figure 4b). The agreement demonstrates that the 1.5 kg carbon has outstanding sample homogeneity. Storage capacities at 296 K and 100 bar from Figure 4b are: 0.031 kg H_2/kg carbon (3.0 material wt%), 0.047 kg H_2 (whole tank), and 0.0088 kg H_2/liter internal tank volume. To the best of our knowledge, these values are unprecedented for sorption at room temperature.

How densely was the carbon powder packed in the tank? The answer is obtained from the relation between the void fraction in the tank and the void fraction in individual sorbent particles, with packing fraction f (fraction of tank volume that is occupied by particles):

$$\phi_{tank} = (1 - f) + f \cdot \phi_{cryst} \qquad (5)$$

FIGURE 3. Isosteric heat of adsorption (bottom) from adsorption isotherms at 273 K and 303 K (top). The isosteric heats refer to the temperature $[(273 \text{ K}) \cdot (303 \text{ K})]^{1/2} = 288$ K. Gravimetric excess adsorption was converted into absolute adsorption ("coverage"), using a hydrogen film thickness of 0.6 nm (smallest film thickness such that the calculated ΔH does not rise at high coverage); gas pressure at constant coverage (isosteric variation of film) was calculated from interpolated absolute adsorption; and the Clausius-Clapeyron equation was evaluated with so-determined pressures at constant coverage [4]. Plotted isosteric heats are the average over four different interpolation models for absolute adsorption, and error bars represent the variation from the different models. The boron-doped sample 3K-H60 (I,A) is from Table 1; the undoped sample 3K-600C* is from a remanufactured lot of the precursor 3K-600C in Table 1. A remanufactured lot of 3K-H60 (I,A) gives an isosteric heat curve similar to the one here, with $\Delta H \sim 10$ kJ/mol at high coverage.

$T_1 < T_2$, the respective ratios R_d, R_u of gravimetric excess adsorption at T_1 to gravimetric excess adsorption at T_2 are approximately:

$$R_d \approx \chi(E_d, T_1)/\chi(E_d, T_2) = (T_2/T_1)^{1/2} \exp[E_d(T_1^{-1} - T_2^{-1})/R] \qquad (1)$$

$$R_u \approx \chi(E_u, T_1)/\chi(E_u, T_2) = (T_2/T_1)^{1/2} \exp[E_u(T_1^{-1} - T_2^{-1})/R)] \qquad (2)$$
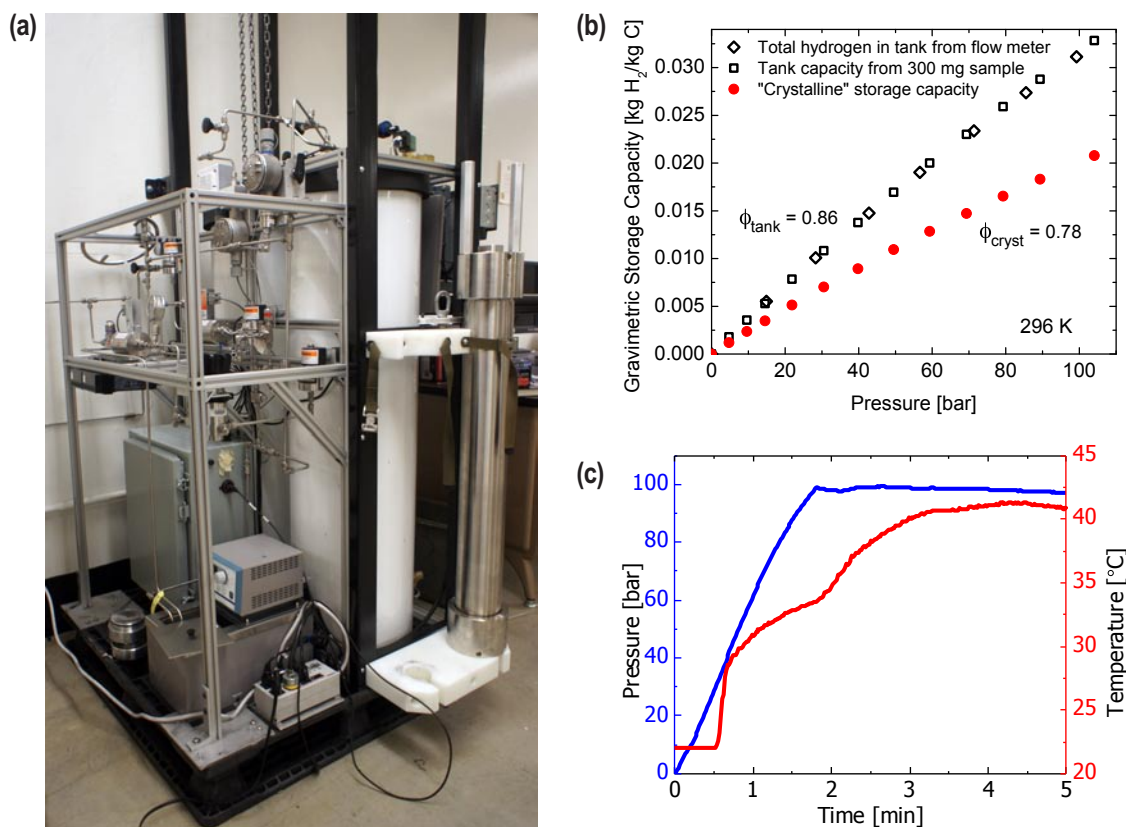
FIGURE 4. (a) Two cylindrical 5.3-liter tanks, designed to operate individually or as joint 10.6-liter tank, between room temperature and dry-ice temperature and pressure 0-100 bar. One of the tanks was filled with 1.5 kg of carbon powder, similar to 3K-600C (Table 1), but degassed at 120ºC instead of 600ºC. Degassing was done in situ. Surface area (Σ) and void fraction (ϕ_{cryst}) of the carbon was 2,700 m^2/g and 0.78, from N$_2$ adsorption at 77 K. We refer to the void fraction in individual sorbent particles as "crystalline" in analogy to the void fraction in metal-organic frameworks and other porous solids, and in contradistinction to the void fraction after packing of sorbent particles in a bed or tank, ϕ_{tank}. (b) Gravimetric storage capacity of the tank at 296 K, (i) measured by flow meter; (ii) calculated from gravimetric excess adsorption, G_{ex}, measured on a 300-mg sample, and the tank void fraction, ϕ_{tank}; (iii) calculated from G_{ex} and void fraction ϕ_{cryst} ("crystalline" storage capacity). Gravimetric storage capacity from G_{ex} and ϕ was calculated as $G_{ex} + (\rho_{gas}/\rho_{skel})\phi/(1-\phi)$ with $\rho_{skel} = 2.0$ g/cm^3 [7]. The tank void fraction was $\phi_{tank} = 1 - m_{sorbent}/(\rho_{skel}V_{tank}) = 0.86$. (c) Pressure and temperature evolution in the tank during a fast-fill cycle.

The values $\phi_{tank} = 0.86$ and $\phi_{cryst} = 0.78$ in Figure 4 yield $f = 0.64$. This is, within experimental uncertainty, equal to the theoretical maximum, $f = 0.63$, for random close packing of spherical particles of identical size. The only way to achieve a higher packing fraction would be to convert the powder into monoliths, ideally with $f = 1$, which would give $\phi_{tank} = \phi_{cryst}$, a mass of 2.3 kg carbon in the tank, and the following storage capacities at 296 K and 100 bar: 0.021 kg H$_2$/kg carbon (Figure 4b), 0.049 kg H$_2$ (whole tank), and 0.0092 kg H$_2$/liter internal tank volume. This illustrates that a decrease in ϕ_{tank} leads to a drop in gravimetric storage capacity (because more sorbent fits into the tank) and a rise in volumetric storage capacity (because the tank holds less nonadsorbed gas) [7]. In the present case, the drop is large and the rise is small because the tank, as is, resides on the flat part of the volumetric-vs.-gravimetric storage capacity curve in Ref. [7].

The kinetic data, Figure 4c, shows that the tank can be filled in ~3 minutes (end of temperature rise). Gravimetric storage capacity as a function of time (not shown) showed that the tank was 95% full in 3.3 minutes. The temperature inside the tank (center of the cylinder) rose from initially 22ºC to a maximum of 41ºC (Figure 4c), due to heat of adiabatic compression and heat of adsorption (no attempt was made to measure the two effects separately). The cusp in the pressure and temperature curve at 2 min is the result of that the hydrogen flow was stopped when the pressure reached 100 bar. As the flow of room-temperature gas, acting as a coolant, stopped, the temperature began to rise more rapidly. During the interval 2.5-3.3 min, the hydrogen flow resumed at a low rate to maintain the target pressure of 100 bar. At 3.3 min, the flow was stopped permanently, which gave rise to a second, less pronounced cusp in the temperature curve. The overall temperature profile suggests that heat transfer

via convection in the gas phase is faster than heat transfer via heat conduction through the sorbent and tank walls.

Conclusions and Future Directions

- Established increase in binding energy of molecular hydrogen on boron-doped carbon, by a factor of two on average surface sites and a factor of three on exceptional surface sites, and established correspondingly enhanced adsorption of hydrogen, by 40%, on such surfaces at room temperature, relative to undoped surfaces.

- Demonstrated record-breaking performance of a kg-scale hydrogen tank, based on adsorption of hydrogen on undoped carbon at room temperature, with gravimetric storage capacity of over 50% and volumetric storage capacity of over 20% of the 2017 DOE hydrogen storage targets, both relative to material.

- Future work: Overall goal: manufacture, characterize, and optimize B-doped carbon monoliths, by direct deposition of $B_{10}H_{14}$ into/onto carbon monoliths, for achievement, at room temperature, of 2017 DOE hydrogen storage targets. In support of this agenda: (a) Optimize B-doping—with precursor 3K-600C—in the region B:sample 0-10 wt% for maximum areal excess adsorption of H_2 at room temperature, under variation of B-delivery (1-step vs. 5-step doping), annealing (600-1,000ºC), and removal of B via high-temperature reaction with H_2. (b) Investigate—with precursor 3K-600C and optimal path from (a)—the region B:sample 10-20 wt%. Find saturation limit, i.e., lowest B concentration above which further boron does not improve H_2 adsorption. (c) Produce and characterize B-doped samples—with precursors different from 3K-600C, but optimal path from (a, b)—in high-performance region of B concentration. Precursors: U. Missouri monoliths and powders 2.5K, 3.5K, 4K, 5K [1]. (d) Perform H_2 storage and associated kinetic measurements on B-doped monoliths under oxygen-free conditions in U. Missouri 0.5-liter hydrogen test fixture [1]. (e) Monitor quality of doped materials by (i) isosteric heat determinations at room temperature; (ii) determination of binding energies from Henry-law analysis of low-pressure room-temperature adsorption isotherms; (iii) Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and nuclear magnetic resonance spectroscopy under oxygen-free conditions; (iv) computational simulations on select B-doped structures. (f) Investigate low-temperature performance (77 K) of select B-doped materials.

FY 2012 Publications/Presentations

1. J. Romanos, "Nanospace Engineering of Porous Carbon for Gas Storage." Ph.D. Dissertation, University of Missouri (2012)

M. Beckner, "Hydrogen Adsorption Studies of Engineered and Chemically Modified Activated Carbons." Ph.D. Dissertation, University of Missouri (2012).

2. J. Romanos, M. Beckner, T. Rash, L. Firlej, B. Kuchta, P. Yu, G. Suppes, C. Wexler, and P. Pfeifer, "Nanospace Engineering of KOH Activated Carbon." Nanotechnology **23**, 015401 (2012).

3. B. Kuchta, L. Firlej, A. Mohammadhosseini, P. Boulet, M.W. Beckner, J. Romanos, and P. Pfeifer, "Hypothetical High-Surface-Area Carbons with Exceptional Hydrogen Storage Capacities: Open Carbon Frameworks." *J. Am. Chem. Soc.* **134**, 15130-15137 (2012).

4. J. Romanos, M. Beckner, D. Stalla, A. Tekeei, G. Suppes, S. Jalisatgi, M. Lee, F. Hawthorne, J. D. Robertson, L. Firlej, B. Kuchta C. Wexler, P. Yu, P. Pfeifer, "Infrared Study of Boron-Carbon Chemical Bonds in Boron Doped Activated Carbon." *Carbon*, under review (2012).

5. R.J. Olsen, M. Beckner, J. Romanos, P. Lewellyn, B. Kuchta, P. Pfeifer, and C. Wexler, "Experimental Determination of Adsorbed Film Volumes." *Adsorption*, under review (2012).

6. P. Pfeifer, C. Wexler, P. Yu, G. Suppes, F. Hawthorne, S. Jalisatgi, M. Lee, D. Robertson, and S. Chakraborti, "Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage." *2012 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation,* Arlington, VA, May 13-17, 2012.

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3. L. Firlej, S. Roszack, B. Kuchta, P. Pfeifer, and C. Wexler, *J. Chem. Phys.* **131**, 164701 (2009).

4. P. Pfeifer *et al.*, In: *DOE Hydrogen Program, FY 2010 Annual Progress Report*, ed. by S. Satyapal (U.S. Department of Energy, Washington, DC, 2011), p. 474-480.

5. J. Burress *et al.*, *Nanotechnology* **20**, 204026 (2009).

6. Defense Logistics Agency, Contract NSWC-N00164-08-C-GS37 (2008-11).

7. P. Pfeifer *et al.*, In: *DOE Hydrogen Program, FY 2009 Annual Progress Report*, ed. by S. Satyapal (U.S. Department of Energy, Washington, DC, 2009), p. 646-651.