IV.C.4 Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

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Overall Objectives

- Fabricate high surface area, multiply surface-functionalized carbon ("substituted materials") for reversible hydrogen storage with superior storage capacity by physisorption.

- Characterize materials and storage performance. Evaluate efficacy of surface functionalization, experimentally and computationally, for fabrication of materials with deep potential wells for hydrogen adsorption, indicating high binding energies.

- Optimize gravimetric and volumetric storage capacity by optimizing pore architecture and surface composition ("engineered nanospaces").

Fiscal Year (FY) 2014 Objectives

- Fabricate boron-doped nanoporous carbon (particulate and monoliths), using decaborane ($B_{10}H_{14}$) as boron carrier, for high-capacity reversible hydrogen storage.

- Establish high surface areas, low void fractions, and boron concentration maps in materials.

- Quantify complete substitution of boron in carbon lattice, enhanced binding energies of hydrogen on doped materials, and enhanced adsorption of hydrogen on doped materials. Establish reproducibility of enhanced performance.

Technical Barriers

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

(A) System Weight and Volume

(B) System Cost

(E) Charging/Discharging Rates

(J) Thermal Management

(O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

Structural and energetic targets are surface-engineered carbons, made from low-cost raw materials, which simultaneously host high surface areas (2,700 m^2/g or higher), high binding energies for hydrogen (12 kJ/mol or higher), and low void fractions (0.70 or less). Progress towards materials that meet DOE performance targets for hydrogen storage (technical targets in the Multi-Year Research, Development, and Demonstration Plan) is summarized in Table 1. Performance of University of Missouri materials at liquid-nitrogen temperature, 77 K, and room temperature, 296 K, is compared with storage targets for vehicles and portable equipment, respectively, because cryogenic tanks are under active consideration by the DOE for vehicles, but are unlikely for portable power supplies.

FY 2014 Accomplishments

- Reproducibly synthesized high-performing precursor and doped carbon powders.

- Developed quantitative X-ray photoelectron spectroscopy (XPS) analysis for simultaneous fitting of spectra.

- Demonstrated the existence of sp^2-bonded boron (high-binding-energy sites, "correctly coordinated boron" [1]).

- Demonstrated that the desired structure (sp^2 B-C bonds) leads to increases in low coverage binding energy as high as 9.2 kJ/mol.

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INTRODUCTION

Graphene-like high surface area carbons, as developed by our team from low-cost raw materials (e.g., corncob), are

TABLE 1. Progress towards meeting 2017 and 2015 DOE targets for hydrogen storage. University of Missouri sorbent is 5K-0280 (undoped carbon powder, [2] and Table 2). Reported gravimetric and volumetric storage capacities are for material, not system. Experimental data for the reported storage capacities, including excess adsorption, are listed in Table 2. Storage material cost is based on $5.20/kg sorbent (raw material and chemicals) and respective gravimetric storage capacity. Referenced targets for portable equipment are for single-use equipment.

Storage Parameter	Onboard Storage for Light-Duty Vehicles, 2017	Storage Material Handling Equipment, 2015	U. Missouri 2014 Status (77 K, 190 bar)
Gravimetric Storage Capacity	0.055 kg H_2/kg system	N/A	0.164 kg H_2/kg sorbent
Volumetric Storage Capacity	0.040 kg H_2/L system	0.030 kg H_2/L system	0.054 kg H_2/L sorbent
Storage Cost	$400/kg H_2 stored	$667/kg H_2 stored	$39/kg H_2 stored (storage material cost)

Storage Parameter	Storage for Low Power Portable Equipment	Storage for Medium Power Portable Equipment	U. Missouri 2014 Status (296 K, 190 bar)
Gravimetric Capacity	0.020 kg H_2/kg system	0.020 kg H_2/kg system	0.046 kg H_2/kg sorbent
Volumetric Capacity	0.030 kg H_2/L system	0.030 kg H_2/L system	0.015 kg H_2/L sorbent
Storage Cost	$3/g H_2 stored	$6.70/g H_2 stored	$0.15/g H_2 stored (storage material cost)

NA - not applicable

outstanding starting materials for functionalized materials that store hydrogen by adsorption at high gravimetric and volumetric storage capacity. A recent carbon exhibited a gravimetric storage capacity of 0.164 kg H_2/kg carbon and 0.054 kg H_2/L carbon at 77 K and 190 bar (Table 1). This project is a systematic effort to achieve comparable results at 300 K, by maintaining current surface areas, ~2,700 m^2g, and substituting carbon with boron and other chemistries to increase the binding energy for hydrogen (electron donation from H_2 to electron-deficient B, and other charge-transfer mechanisms). In the DOE Hydrogen Sorption Center of Excellence, one of the program final recommendations stated [1]: "*...it became clear that only correctly coordinated boron substituted in graphitic carbon is a viable route to improved hydrogen storage for substituted carbon materials... the Center recommends that researchers should develop substituted/heterogeneous materials that can be used to enhance dihydrogen isosteric heats of adsorption in the range of 10–25 kJ/mol ... Development efforts should focus on creating materials with the appropriate chemical and electronic structures, sufficient composition, and high specific-surface areas....*" High binding energies are also hosted by sub-nanometer pores in narrowly spaced stacks of graphene sheets. Boron-substituted materials are manufactured by thermolysis of volatile $B_{10}H_{14}$ in pores of stacks of graphene sheets. A significant effort of the project goes into conversion of these materials, most of which 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, enthalpies of adsorption (isosteric heats), and binding energies. 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 structure data.

RESULTS

In 2013-14, approximately 150 new carbon samples were prepared as high-surface-area, graphene-like carbon and precursors for boron-doped materials, using varied KOH:C ratios, affecting the pore structures and defect ratios of the precursor. The carbons were fully characterized and tested for reproducibility of material composition and performance. The best performing materials are summarized in Table 2. Precursor carbons were boron-doped by decomposition of $B_{10}H_{14}$ according to temperature and pressure protocols described in [2]. Hydrogen adsorption properties of doped materials were analyzed at low and high pressures, and at cryogenic and room temperatures. Linear isotherms at low pressure and 77 K and 87 K (Figure 1a) gave binding energies, E_B (depth of the adsorption potential), which could be compared with new theoretical estimates of the energy from quantum-chemical computations (Figure 1b). The agreement between experimental binding energies of B-doped carbons, 6.5–9.2 kJ/mol, and computed binding energies, 7.4-12 kJ/mol, was excellent. Binding energies from Henry's law were determined from ratios of gravimetric excess adsorption at temperatures T_1 and T_2,

$$G_{ex}(p,T_1)/G_{ex}(p,T_2) = \chi(T_1)/\chi(T_2) = (T_2/T_1)^{1/2} \cdot \exp\{E_B(T_2-T_1)/[(T_1T_2)R]\} \qquad (1)$$

evaluated for the Langmuir model in the limit of zero pressure, with Langmuir constant $\chi(T)$ [3]. They were found

TABLE 2. Best performing, reproducible U. Missouri carbons 2013-14 (undoped, doped, powders, and monoliths) at liquid-nitrogen temperature (77 K) and room temperature (296 K), high-lighted in yellow. Performance metrics are: gravimetric storage capacity, G_{st}; volumetric storage capacity, V_{st}; binding energy, E_B; and enthalpy of adsorption, ΔH. Specific surface areas, Σ, and void fractions, ϕ, are from N_2 adsorption at 77 K. Gravimetric and volumetric storage capacities are calculated from experimental gravimetric excess adsorption, G_{ex}, and void fraction according to Ref. [4], Eqs. (1, 2). Void fraction is related to bulk density by $\rho_{bulk} = (1 - \phi)\,\rho_{skel}$, where the skeletal density is 2.0 g/cm^3 for University of Missouri carbons. The reported maximum values of gravimetric excess adsorption, Max. G_{ex}, are for the pressure interval 0-190 bar. The maximum occurs at 40-50 bar for 77 K, and at 190 bar for 296 K.

	Sample	Σ (m^2/g)	ϕ	Max. G_{ex} (wt%)	G_{st} (wt%)	V_{st} (g/L)	ΔH, E_B (kJ / mol)
Nanoporous Graphene-like Carbons	5K-0280 (77 K, 190 bar) (296 K, 190 bar)	2,700	0.84	5.9 0.9	14 4.4	54 15	5.8, N/A
	4K-0284 (77 K, 190 bar) (296 K, 190 bar)	2,600	0.81	5.6 1.0	13 3.9	54 15	4.7, N/A
B-Doped Graphene-like Carbons	4K-0246 (B=4%) (77 K, 190 bar) (296 K, 190 bar)	2,400	0.81	5.1 0.9	12 3.8	52 15	5.5, 7.5
	5K-0215 (B=8%) (77 K, 190 bar) (296 K, 190 bar)	1,900	0.79	4.3 0.7	11 3.3	50 14	6.2, 9.2
Synthetic Nanoporous Carbons	HS;0B-20 (77 K, 190 bar)	940	0.46	2.5	3.5	40	6.6, 9.4
	PVDC-0400 (77 K, 190 bar)	780	0.49	2.0	3.7	28	7.8, 10.8
Monoliths	4K Monolith (297 K, 100 bar)	2,100		0.9	2.5	9.5	-
	BR-0311 (77 K, 190 bar) (296 K, 190 bar)	2,300	0.74	4.3 0.9	9.0 2.9	51 15	5.6, N/A
Commercial Carbon	MSC-30 (77 K, 190 bar) (296 K, 190 bar)	2,700	0.80	5.3 0.9	12 3.6	53 15	5.0, N/A

to increase with increasing boron concentration, while isosteric heats ΔH as a function of boron concentration exhibited only insignificant variation (Figure 2a). This demonstrates that B-doped samples typically host a whole distribution of binding energies and that different metrics, such as E_B and ΔH, probe different components of the distribution.

To better understand the chemistry of $B_{10}H_{14}$ decomposition and the resulting environment of boron in the carbon matrix, the process was monitored by XPS. Boron XPS spectra exhibited a strong dependence on B concentration: at low concentration the spectrum consists only of a B-O peak, with residual oxygen from undoped, incompletely deoxygenated carbon precursor, and no measureable B-B or B-C. At higher concentration, the B-O peak splits into a B-B and a sp^2-bonded B-C peak ("correctly coordinated" boron atoms), allowing us to estimate the concentration of B-O, B-B, B-C, and C-O from an analysis

of three simultaneous spectra—B, C, O (Figure 3). From the B-C spectrum we obtained the concentration of sp^2-bonded boron. While the concentration of sp^2-bonded boron is low in the investigated samples, with approximately one sp^2-bonded boron atom per total of 5-7 boron atoms (Figure 3, left), the binding energy is already at 9.2 kJ/mol at 1.7 wt% sp^2-bonded boron (Figure 2, right). This suggests that improved deposition and annealing methods in samples yet to be investigated, are likely to generate high binding energies, E_B = 11-12 kJ/mol, both on individual adsorption sites and for the average binding energy, $E_{B,av}$.

CONCLUSIONS AND FUTURE DIRECTIONS

- Quantitative XPS analysis demonstrates that the total amount of sp^2-bonded boron increases approximately linearly with total boron.
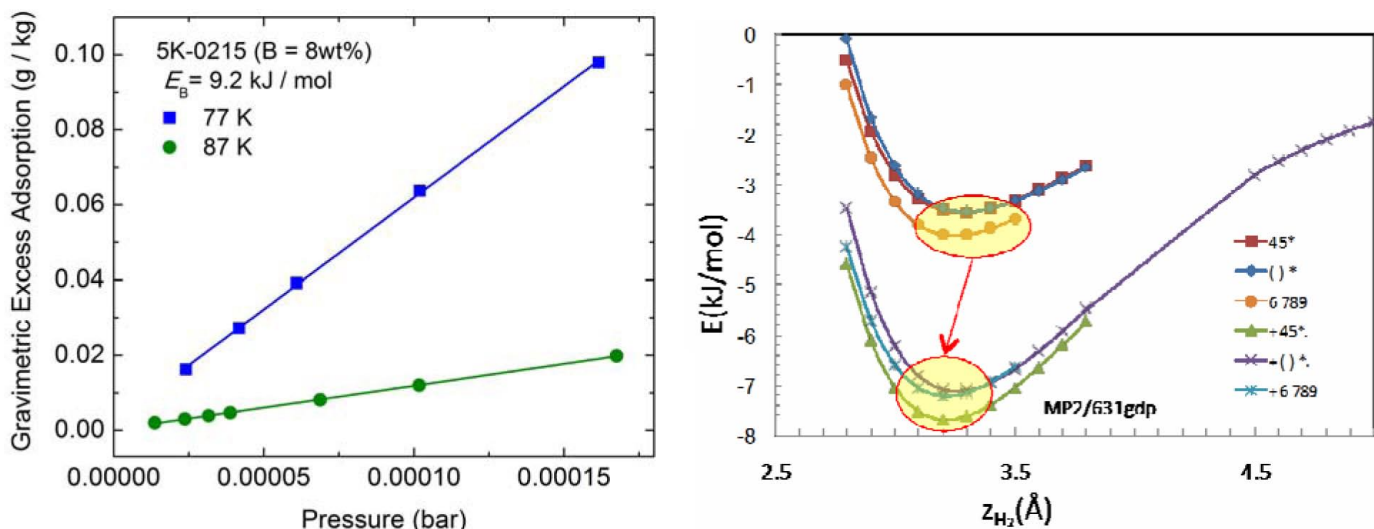
FIGURE 1. *Left:* Adsorption increases linearly with increasing pressure at sufficiently low pressure (Henry's law), here for sample 5K-0215 and p = 0–0.15 mbar. The slope of the isotherm grows exponentially with the binding energy E_B. For fixed binding energy, the ratio of the slopes at two different temperatures gives E_B, Eq. (1), here E_B = 9.2.kJ/mol. The linear behavior of the isotherm and the value of the slope were highly repeatable for all samples, also on different instruments. *Right:* Binding energy of graphene with one carbon atom substituted by anionic boron, B⁻, and an unspecified cation, from ab initio calculations of the potential energy of a H_2 molecule as a function of distance from the boron atom. For a single B atom, E_B = 7.8 kJ/mol, and rises to E_B = 11-12 kJ/mol for B~10 wt%. About 50% of the enhanced binding energy is attributable to the negative charge distribution near B⁻.
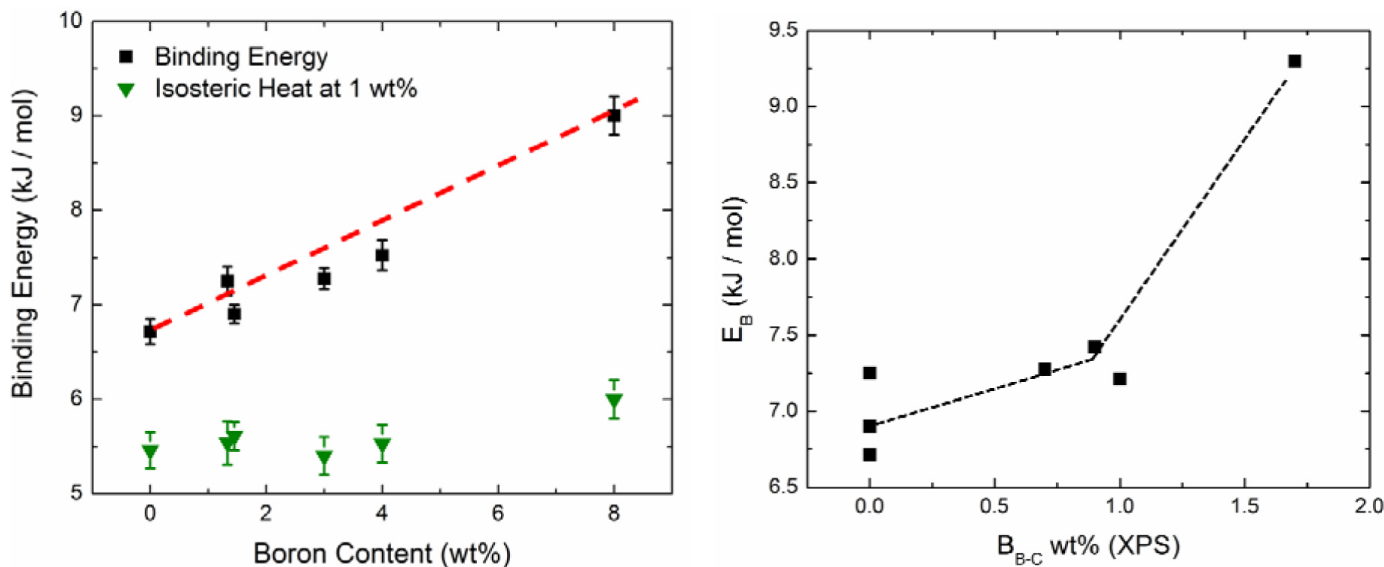

FIGURE 2. *Left:* Binding energies, from Henry's law (Figure 1a), increase linearly with increasing boron concentration: E_B = 6.7-9.2 kJ/mol. Isosteric heats, ΔH, from high H_2 coverage, 1.0 wt%, and isosteres from four different temperatures, increase insignificantly with B wt%: 5.5-6.0 kJ/mol. This indicates an insignificant increase of average binding energy, $E_{B,av}$. The two results are entirely consistent because Henry's law probes binding energies in the limit of zero coverage (highest binding energies present in the material), while ΔH at high coverage is sensitive only to the average binding energy, $E_{B,av}$, which may be low because only a few boron atoms may be present, or only a few "correctly coordinated" boron atoms —sp²-bonded boron (B-C bonds, high-binding-energy sites) are present. *Right:* XPS analysis of sp²-bonded boron (Figure 3) indicates that only 0.0-1.7 wt% sp²-bonded boron is present on the samples analyzed. Equivalently, only up to 1 out 5 boron atoms present in the sample is sp²-bonded. The graph of E_B vs. B_{B-C} wt% (right) shows that E_B = 9.2 kJ/mol is already reached at 1.7 B_{B-C} wt%.
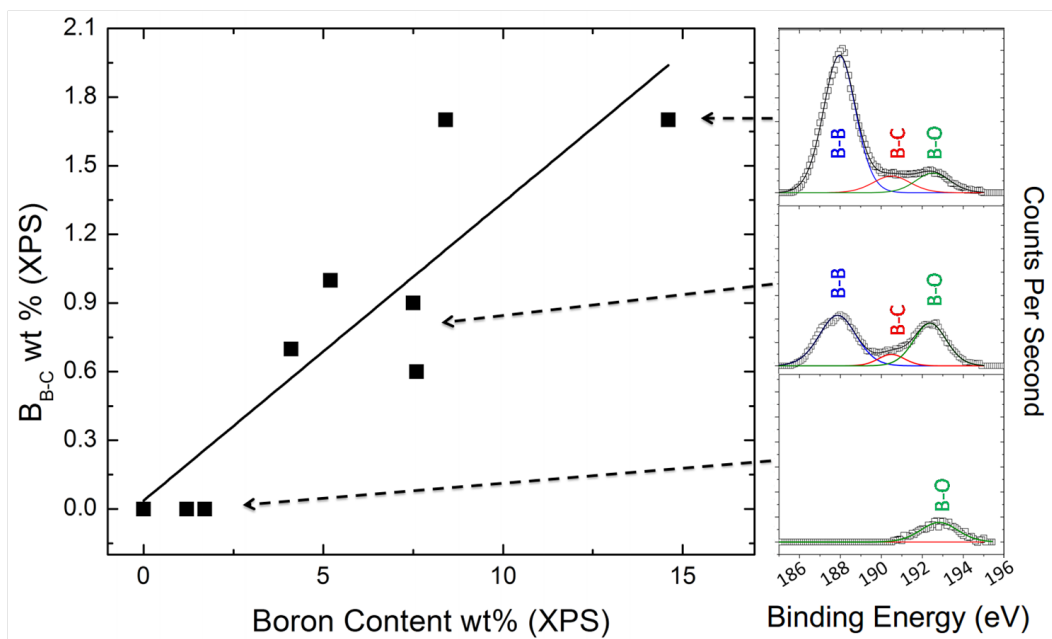
FIGURE 3. *Left:* Concentration of sp²-bonded boron (B-C bonds, high-binding-energy sites) in different samples as a function of total boron concentration in the samples. XPS spectra for boron, carbon, and oxygen were simultaneously fit to determine amounts of sp²-bonded boron in doped carbon samples. The concentration of sp²-bonded boron increases with increasing total boron content. *Bottom Right:* Boron spectrum for sample 4K-0244. This spectrum is representative of all samples with boron content <2 wt%. In this range, the decomposition of $B_{10}H_{14}$ readily forms B-O bonds. No B-C bonds are observed. *Middle Right:* Boron spectrum for sample 3K-0211. This spectrum is representative of samples with 2 <B wt% <7. In this range, peak splitting is observed as B-B and B-C bonds emerge in addition to the formation of B-O bonds. *Top Right:* Boron spectrum for sample 3K-0208. This spectrum is representative of samples with B wt% >7. The B-B peak is most prominent in this spectrum due to the larger quantity of total boron in the sample. Further, the area under the B-C peak increased to be approximately equal to that under the B-O peak, indicating a larger amount of sp²-bonded boron (1.7 wt%) in the sample. The spectra are normalized such that the area under the combined B-B, B-C, and B-O peaks corresponds to the total B concentration present in each sample.

- Binding energies were shown to increase both with increasing total boron content and with increasing sp²-bonded boron, in quantitative agreement with the binding energy calculations in Figure 1. The increase with increasing sp²-bonded boron appears to be non-linear, with a rapid rise observed between 1 and 2 wt% sp²-bonded boron (Figure 2, right) and expected saturation at 11-12 kJ/mol around 10 wt% sp²-bonded boron. This demonstrates that B-doping of nano-engineered carbon by vapor deposition and pyrolysis of decaborane has the capability of delivering materials with surface areas in excess of 2,000 m²/g [2], average binding energies in excess of 10 kJ/mol, and accordingly enhanced gravimetric and volumetric storage capacities.

- Test higher annealing temperatures for possibly higher (% of sp²-bonded boron)/(% of total boron).

- Conduct solid-state nuclear magnetic resonance work (¹¹B spectra) of boron-doped materials and compare with XPS.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

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3. P. Pfeifer, A. Gillespie, E. Dohnke, and Y.Soo, "Hydrogen densities greater than liquid hydrogen at 77 K in engineered carbon nanospaces." In: *Materials Challenges in Alternative & Renewable Energy, Conference Program* (American Ceramic Society, Columbus, OH, 2014), MCARE-166-2014, p. 36.

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3. J. Burress, M. Kraus, M. Beckner, R. Cepel, G. Suppes, C. Wexler, and P. Pfeifer, *Nanotechnology* 20, 204026 (2009).

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