Overview

Timeline
- Project start date: 9/1/08
- Project end date: 11/30/14

Budget
- Total Funding Spent*: $1.781M
- Total DOE Project Value: $1.899M
- Total Cost Share: $0.514M

*As of 3/31/14

Barriers
- System weight & volume
- System cost
- Charging/discharging rates
- Thermal management
- Lack of understanding of hydrogen physisorption & chemisorption

Partners
- MeadWestvaco, Charleston, SC
- OsComp, Houston, TX—J. Romanos
- NREL—T. Gennett, P. Parilla
- ORNL—J. Idrobo, R. Olsen
- Missouri U. Science & Technology—D. Waddill
- U. Missouri-Kansas City—P. Rulis
- NIST Center for Neutron Research—R. Paul
Objectives & Relevance

Increase binding energy of $\text{H}_2$ on carbon by functionalization of surface with boron:

- Binding energy of $\text{H}_2$ on graphite: 5 kJ/mol
- Binding energy of $\text{H}_2$ on B-substituted carbon: 10-15 kJ/mol
- Electron donation from $\text{H}_2$ to electron-deficient B
- GCMC simulations of $\text{H}_2$ on 10 wt% boron predict:
  - $\text{H}_2$: adsorbent = 5 total wt% at 298 K, 120 bar,
  - $\text{H}_2$: adsorbent = 12 total wt% at 77 K, 120 bar

Binding energy landscape: 4.8-9.1 kJ/mol (red-blue) on 1-5 wt% B (left-right)
Firlej et al, 2009; Kuchta et al, 2010
Objectives & Relevance

Objectives relative to existing materials

Predicted, 10 wt% B
120 bar, 298 K
U. Missouri Target

Predicted, 10 wt% B
120 bar, 77 K
U. Missouri Target

Undoped U. Missouri materials, 2014 (yellow)
## Approach—Milestones

<table>
<thead>
<tr>
<th>Objectives</th>
<th>Milestones</th>
<th>Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fabricate boron-doped nanoporous carbon (particulate and monoliths) for high-capacity reversible hydrogen storage</strong></td>
<td>• First create undoped high-surface-area materials; then dope with boron (gas phase, B(<em>{10})H(</em>{14})) for high binding energy for H(_2)&lt;br&gt;• Create high-surface-area carbon with minimum pore space, for high volumetric storage capacity&lt;br&gt;• Dope materials with &lt;10 wt% B:(B+C) [Redirection Jan. 2014], for high binding energy for hydrogen&lt;br&gt;• Establish B-doped materials with surface areas (\sim)2700 m(^2)/g, binding energies 10-15 kJ/mol, volumetric storage capacity &gt;40 g/L (material), and gravimetric storage capacity &gt;5.5 wt% (material) at 200 bar and room temperature</td>
<td>80% 100%, 10/2013 80% 60%</td>
</tr>
<tr>
<td><strong>Characterize materials &amp; demonstrate storage performance</strong></td>
<td>• Establish reproducibility of B-doped materials&lt;br&gt;• Establish effective deoxygenation of materials prior to doping&lt;br&gt;• Establish B deposition in monoliths&lt;br&gt;• Establish that boron is completely and uniformly substituted in carbon lattice (sp(^2) B-C bonds)&lt;br&gt;• Establish enhanced binding energy and H(_2) adsorption on B-doped materials at low coverage [Redirection Jan. 2014]&lt;br&gt;• Explore other high-binding-energy carbon materials (alternate approach to high binding energy)&lt;br&gt;• Compute binding energies for relevant pore geometries/chemistries</td>
<td>100%, 12/2013 100%, 01/2014 100%, 05/2013 70% 70% N/A 100%, 01/2014</td>
</tr>
</tbody>
</table>
## Technical Accomplishments

### Best Performing Carbons (2013-14, reproducible)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Porosity</th>
<th>Max. grav. exc. (wt% material)</th>
<th>Total grav. storage (wt% material)</th>
<th>Total vol. storage (g/L material)</th>
<th>Isosteric heat (kJ / mol) at low/high coverage*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nanoporous Graphene-like Carbons</strong></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>5K-0280 (77 K, 190bar)</td>
<td>2700</td>
<td>0.84</td>
<td>5.9</td>
<td>14</td>
<td>54</td>
<td>N/A, 5.8</td>
</tr>
<tr>
<td>4K-0284 (77 K, 190bar)</td>
<td>2600</td>
<td>0.81</td>
<td>5.6</td>
<td>13</td>
<td>54</td>
<td>N/A, 4.7</td>
</tr>
<tr>
<td><strong>B-Doped Graphene-like Carbons</strong></td>
<td></td>
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<tr>
<td>4K-0246 (B=4%) (77 K, 190bar)</td>
<td>2400</td>
<td>0.81</td>
<td>5.1</td>
<td>12</td>
<td>52</td>
<td>7.5, 5.5</td>
</tr>
<tr>
<td>5K-0215 (B=8%) (77 K, 190bar)</td>
<td>1900</td>
<td>0.79</td>
<td>4.3</td>
<td>11</td>
<td>50</td>
<td>9.7, 6.2</td>
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<tr>
<td><strong>Synthetic Nanoporous Carbons</strong></td>
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<tr>
<td>HS:OB-20 (77 K, 190bar)</td>
<td>940</td>
<td>0.46</td>
<td>2.5</td>
<td>3.5</td>
<td>40</td>
<td>9.4, 6.6</td>
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<tr>
<td>PVDC-0400 (77 K, 190bar)</td>
<td>780</td>
<td>0.49</td>
<td>2.0</td>
<td>3.7</td>
<td>28</td>
<td>10.8, 7.8</td>
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<tr>
<td><strong>Monoliths</strong></td>
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<tr>
<td>4K Monolith (297 K, 100bar)</td>
<td>2100</td>
<td>0.9</td>
<td>2.5</td>
<td>9.5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>BR-0311 (77 K, 190bar)</td>
<td>2300</td>
<td>0.74</td>
<td>4.3</td>
<td>9.0</td>
<td>51</td>
<td>-</td>
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<td><strong>Commercial carbon</strong></td>
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<tr>
<td>MSC-30 (77 K, 190bar)</td>
<td>2700</td>
<td>0.80</td>
<td>5.3</td>
<td>12</td>
<td>53</td>
<td>N/A, 5.0</td>
</tr>
</tbody>
</table>

*Low coverage: <0.01 wt% H₂ absolute ads.; high coverage: >1.5 wt% H₂ absolute ads. (2010 AMR)
B-C phase diagram

Stable B-C structures as a function of B conc. and temperature:

- Single phases or mixtures with variable composition
- Single phases with fixed composition: dashed lines
- U. Missouri-doped materials interpolate between known stoichiometric sp$^2$-B-C compounds
- "Solubility limit" of 2.3 atomic% is not limit for boron substitution
Accomplishments and Progress

Boron doping I—Deposition & decomposition of $B_{10}H_{14}$

• Stationary (no flow) deposition from liquid $B_{10}H_{14}$: can deposit 10 wt% boron on carbon, but may clog pores.
• Stationary deposition from $B_{10}H_{14}$ vapor: reduces pore clogging, but can deposit only up to 1 wt% boron
• Flow deposition from $B_{10}H_{14}$ vapor (carrier gas: Ar) at 150 °C: reduces pore clogging and can deposit 2-5 wt% boron, depending on flow (6-23 cm$^3$/s) and pressure (1.2-2.5 bar total; 0.2-0.3 bar $B_{10}H_{14}$)
• Low flow and low pressure: increase of B conc. 10-fold compared to no flow
Accomplishments and Progress

Boron doping II—Deoxygenation of precursors, XPS spectra

- Residual O in precursor (undoped carbon) competes with C for B: formation of B-O bonds (“boron traps”) instead of B-C bonds
- Remove O by high-temp./chem./… treatment before doping
- O removal reduces surface area (graphitization, loss of high-binding-energy defects)
- Optimum treatment, 800 ºC: 4 at% O and Σ= 2500 m²/g

Boron XPS spectra of doped materials:
- Precursor treated at 600 ºC (2013)
- Precursor treated at 1200 ºC (2014)

- Deoxygenation at 1200 ºC prior to doping reduced B-O bonds from 60% to 10%
- Successful elimination of boron traps while maintaining high surface area
- For resolution of B-C, B-B (not done here), see slide 12
Accomplishments and Progress

Boron doping III—Uniform boron deposition

TEM, carbon + boron (zero-loss image)
FEI Tecnai F30 G2 Twin, U. Missouri

Energy-filtered TEM: boron only (blue)

Energy-filtered TEM: boron (blue), divided by # layers

Conclusion: B distributed uniformly over >200 nm laterally and ≥3 graphene layers vertically
Boron doping IV—Surface morphology vs B conc. (flow doping)

- Increase in B conc. reduces pore volume and surface area, with largest effect in smallest pores (<15 Å). Porosity decreases to a lesser extent.
- Increase in B conc. reduces $\Sigma$ approximately linearly.
- Reduction of $\Sigma$ reduces $H_2$ grav. excess adsorption in accordance with Chahine’s rule.
- Identical surface excess conc. ($G_{exc}/\Sigma$) indicates identical average $H_2$ binding energy in doped and undoped samples.
Boron doping V—sp$^2$-bonded boron in doped materials

XPS spectra of sample 5K-0215 (deoxyg. & annealed at 1200 ºC)

- Achieved: 1-2 wt% sp$^2$-bonded B (B-C bonds), out of total of 6-14 wt% B
- Best % of sp$^2$-bonded B: annealing at 1200 ºC
- No significant variation of $\Delta H_{\text{ads}}$ at high coverage for varying B$_{\text{B-C}}$% (see also next slide)
- Successful deconvolution of B-C and B-B spectrum by analysis of B-O and C-C spectrum
- Side result: final O is ~50% in C-O and ~50% in B-O

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Sample} & \text{B} & \text{B}_{\text{B-C}} & \frac{\text{B}_{\text{B-C}}}{\text{B}} & \Delta H_{\text{ads, high cov}} \\
\text{(wt%)} & \text{(wt%)} & \% & (kJ/mol) \\
\hline
3K-0211 & 6 & 0.9 & 13 & 5.6 (±0.2) \\
3K-0205 & 10 & 1.1 & 14 & 5.5 (±0.2) \\
3K-0208 & 14 & 1.5 & 13 & 5.4 (±0.2) \\
5K-0215 & 8 & 1.7 & 21 & 6.2 (±0.4) \\
\hline
\end{array}
\]
• Binding energies, $E_B$, from Henry’s law (slide 26) increase linearly with boron wt%: 6.7–9.0 kJ/mol. Demonstrates increase of fraction of high-binding-energy sites.

• Isosteric heats, $\Delta H$, from high H$_2$ coverage (isosteres, slide 26) increase insignificantly with B wt%: 5.5-6.0 kJ/mol. Indicates insignificant increase of average binding energy, $E_{B,av}$.

• For 5K-0215: $\Delta H_{\text{doped}}$ 10-80% higher than $\Delta H_{\text{undoped}}$: high binding energies also from $\Delta H$.

• For 5K-0215: $\Delta H_{\text{doped, zero cov}} = 9.7$ kJ/mol agrees well with $E_B = 9.0$ kJ/mol.
Boron doping VII—H$_2$ adsorption on doped materials

- Screened B-doped materials for high grav. excess ads. per unit surface area
- At 77 K: $G_{\text{exc}}$ at local max. ($p \sim 50$ bar, high coverage)
- At 296 K: $G_{\text{exc}}$ at $p = 10$ bar (“low” coverage)
- Expect $G_{\text{exc}}/\Sigma$ high for high average binding energy, $E_{B,\text{av}}$ (departure from Chahine rule)

- No significant variation of $G_{\text{exc}}/\Sigma$ with increasing boron content
- Reason I: Fraction of high-binding-energy sites too small to raise $E_{B,\text{av}}$ (slide 13)
- Reason II: Not all B in doped material is sp$^2$-bonded, high-$E_B$ boron (slide 12)
Accomplishments and Progress

Does \( B^- \) host higher binding energy than neutral \( B \)?

- Yes—neg. charge creates larger polarization of \( H_2 \)
- \( H_2 \) on B-doped C: anionic B-doped C shows enhancement 4-5 \( \rightarrow \) 7-8 kJ/mol.
- 50% of the enhancement attributable to electrostatic field due to charge distribution near B

*Calculated using MP2/631gdp method: “2nd Order Moller-Plesset” 631gdp is the basis set
Accomplishments and Progress

Validation of U. Missouri data by NREL: synthetic carbon HS;0B-20

\[ G_{\text{ex}} = \left( \frac{V_{\text{film}}}{m_{\text{solid}}} \right) \left[ \rho_{\text{film}} - \rho_{\text{gas}} \right] \]

\[ G_{\text{ex}} = \left( \frac{V_{\text{film}}}{m_{\text{solid}}} \right) \left[ \rho_{\text{film}, \text{sat}} - \rho_{\text{gas}} \right] \]

\[ V_{\text{film}} = \text{const}, \quad \rho_{\text{film}, \text{sat}} = \text{const} \]

- HS;0B-20 = high-\( E_B \) material via 7 Å pores
- \( \Delta H = 8-11 \text{ kJ/mol} \)

- Film density over 50% higher than liq. H\(_2\) (71 g/L)
- Film volume ≠ total pore volume!
• **FY13 Reviewer Comment:** Focus on understanding the nature of the boron doping and its impact on enhanced hydrogen storage is important; abilities of these materials to achieve DOE targets was not apparent. This should be a focus of any future work.

• **Response:** Development of a boron doped material with binding energy > 10 kJ/mol would lead to materials which meet 2017 DOE onboard storage targets (0.055 kg H$_2$/kg system and 0.04 kg H$_2$/L system) (see slides 3 & 4).

• **FY13 Reviewer Comment:** There are still unresolved questions regarding the most basic features of the materials, such as what the composition and local structure. If the fundamentals of the material are still not understood, it is unclear why researchers would scale up to monoliths

• **Response:** The presence of sp2 B-C bonds and their concentration, and B-B bonds and their concentration is reported in slide 9. Uniformity of B concentration in C has been established in slide 10. Doping of monoliths has been discontinued in favor of systematic studies of B-doping of powder materials (DOE redirection January/2014)

• **FY13 Reviewer Comment:** Incorrect assumptions about the core possibilities associated with boron-doping levels in a carbon matrix (e.g., 20% brings one to boron-carbide)

• **Response:** There is ample experimental evidence in the literature for high B concentrations in sp$^2$ B-C substitutional compounds (up to 25% in BC$_3$). Boron-carbide starts at 80%, not 20% (see slide 7).
<table>
<thead>
<tr>
<th>Institution/Collaborators</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NREL (Federal laboratory):</strong> P. Parilla, T. Gennett</td>
<td>Validation of H₂ sorption isotherms</td>
</tr>
<tr>
<td><strong>NIST Center for Neutron Research (Federal laboratory):</strong> R. Paul</td>
<td>PGAA on boron-doped carbons</td>
</tr>
<tr>
<td><strong>ORNL (Federal laboratory):</strong> R. Olsen, J. Idrobo</td>
<td>High-density H₂ films, Ultrahigh-resolution TEM and EELS</td>
</tr>
<tr>
<td><strong>U. Missouri (University):</strong> M. Greenlief, T. White, W. Ritts, H. Foley</td>
<td>XPS analysis, Energy-filtered TEM and EELS, Boron-doped nanoporous carbons</td>
</tr>
<tr>
<td><strong>Missouri U. of Science &amp; Technology (University):</strong> D. Waddill</td>
<td>XPS analysis</td>
</tr>
<tr>
<td><strong>U. Missouri-Kansas City (University):</strong> P. Rulis</td>
<td>Modeling of XPS and EELS spectra</td>
</tr>
<tr>
<td><strong>OsComp (Industry):</strong> J. Romanos</td>
<td>Monolith fabrication, high-density H₂ films</td>
</tr>
<tr>
<td><strong>MeadWestvaco (Industry):</strong> B.-P. Holbrook</td>
<td>Industrial scale production of nanoporous carbon</td>
</tr>
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</table>
Proposed Future Work (Plans Through 11/2014)

• Utilize computational analysis to quantify perturbations to the 1s electron orbitals in sp² B-C bonds. This will increase our understanding of the B-C bonds present in our materials via XPS data.

• Collect NMR data on boron doped nanoporous carbons to further establish the presence of sp² boron carbon bonds.

• Optimize vapor deposition/decomposition of B₁₀H₁₄ and annealing of B to insure boron is uniformly deposited and incorporated into carbon lattice.

• Establish maximum boron content that yields increase in isosteric heat at low coverage.

• Establish that increases in isosteric heat from boron doping enhance hydrogen uptake.
## Project Summary

<table>
<thead>
<tr>
<th>Relevance</th>
<th>The boron-doped carbons developed in this project have the potential to meet the 2017 onboard hydrogen storage goals established by the DOE by creating adsorbents with high binding energies and high surface areas.</th>
</tr>
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<tbody>
<tr>
<td>Approach</td>
<td>We first create undoped high-surface-area materials; then dope with boron by deposition and decomposition of decaborane into elemental boron and hydrogen, followed by incorporation of boron atoms into the carbon lattice.</td>
</tr>
<tr>
<td>Technical Accomplishments</td>
<td>Established protocols for reproducible incorporation of 1-15 wt% boron into high-surface carbons, with a ratio of B-C to B-B bonds of 0.25-0.33. Established presence of binding energies of 5-10 kJ/mol for B:(B+C) = 0-8 wt%, and 7-11 kJ/mol for undoped synthetic carbons, both at low H₂ coverage.</td>
</tr>
<tr>
<td>Proposed Future Work</td>
<td>Improve B incorporation into carbon, with a larger ratio of B-C to B-B bonds, for achievement of ≥10 kJ/mol binding energy at low and high H₂ coverage.</td>
</tr>
</tbody>
</table>
Technical Back-Up Slides
Boron-doping instrumentation

2-step stationary (1. deposition, 2. pyrolysis; DB/C mixed), x/10-4/13

1-step stationary (combined deposition/pyrolysis; DB/C mixed), 5/13-present

2-step continuous-flow (1. deposition, 2. pyrolysis; DB/C separate), 12/13-present
Step 1:
C + B_{10}H_{14}(liq/gas)

Step 2:
Pyrolysis of B_{10}H_{14} & annealing of B
$T$, $p$-profile for 1-step stationary doping

C + B$_{10}$H$_{14}$(liq/gas)

Pyrolysis of B$_{10}$H$_{14}$ & annealing of B
$T, \rho$-profile for 2-step continuous-flow doping

Step 1:
$C + B_{10}H_{14}($gas$)$

Step 2:
Pyrolysis of $B_{10}H_{14}$ & annealing of B
Binding energies from Henry’s law, isosteric heats from isosteres

Henry’s Law Method:
• Most methods of determining $E_B$ proceed via $\Delta H$ and depend on film thickness ($t_f$) assumptions.
• $E_B$ from Henry’s law are independent of film thickness.
• Langmuir model of mobile adsorption (L.P. limit)
• $E_B$ calc. from $k_H$ using isotherms at two different temperatures:
• Resembles Clausius Clapeyron Equation
• Most methods of determining

$$\frac{m_{\text{abs}}}{m_s} = \left(\sum N_A^{\text{gas}}\right) \frac{\theta(p, T)}{\alpha(T)}$$

$$\frac{m_{\text{ads}}(p, T)}{m_s} = k_H(T)p$$

$$E_B = N_A k \left(\frac{T_1 T_2}{T_1 - T_2}\right) \ln \left[\frac{k_H(T_1)}{k_H(T_2)} \sqrt{\frac{T_1}{T_2}}\right]$$

Method of Isosteres:
• Convert to Absolute Adsorption
• Solve for pressure at constant coverage
• Using rearrangement of C.C. equation
• $\Delta H$ solved from slope
• Assumes negligible changes in $\Delta H$ with temp.
• Choose $V_{\text{film}}$ so that isostere matches $E_B$ from Henry’s

$$\frac{m_{\text{abs}}}{m_s} = \frac{m_{\text{exc}}}{m_s} + \rho_{\text{gas}}(p, T)V_{\text{film}}$$

$$\frac{\Delta_{\text{ads}} H(\theta)}{R} = -R \left[\ln\left(\frac{\theta(T)}{\theta(T_1)}\right) - \ln\left(\frac{\theta(T_2)}{\theta(T_2)}\right)\right]$$

$$\ln[P(T)] = \frac{\Delta_{\text{ads}} H(\theta)}{R} \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Slope of the adsorption function is the Henry’s law constant. Henry’s law is observed here

$$k_H(T) = \frac{\chi(T, E_B) m \Sigma}{\alpha(T)}$$