Multiply Surface-Functionalized Nanoporous Carbon for Vehicular Hydrogen Storage

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Overview

Timeline
- Project start date: September 1, 2008
- Project end date: November 30, 2013
- Percent complete: 75%

Budget
- **Total project funding:**
  - DOE share: $1,899K
  - Contractor share: $514K
- **Funding for FY 2011**
  - DOE share: $340K
  - Contractor share: $125K
- **Funding for FY 2012**
  - DOE share: $214K
  - Contractor share: $145K (est.)

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

Partners
- L. Simpson, P. Parilla, K. O’Neill - NREL
- J. Ilavsky - Advanced Photon Source, ANL
- C. Brown, J. Burress - NIST
- L. Firlej - U. Montpellier II, France
- B. Kuchta - U. Marseille, France
- S. Roszak - Wroclaw U. Technology, Poland
- H. Taub - U. Missouri
- M. Stone - ORNL
Objectives & Relevance

Fabricate high-surface-area, multiply surface-functionalized nanoporous carbon, from corncob & other precursors, for reversible H₂ storage (physisorption) with superior storage capacity

- Understand mechanisms & optimize procedures for boron doping of activated carbon

Characterize materials & demonstrate storage performance

- Determine pore-space architecture, nature of functionalized sites, H₂ sorption isotherms (0-200 bar), isosteric heats, & kinetics, at 77-300 K
- Establish effectiveness of boron functionalization by deposition & pyrolysis of (i) B₁₀H₁₄ & (ii) BCl₃
- Establish B-C bonds in B-functionalized materials (FTIR, XPS)
- Establish enhanced binding & adsorption of H₂ on boron-functionalized carbon
- Develop computational predictions of H₂ adsorption for various pore geometries/chemistries

Optimize pore architecture & composition

- Establish optimal precursors for H₂ storage as function of KOH:C ratio & activation temperature
- Compare B-functionalized carbons produced by different synthesis methods
Background

Sorption Landscape

Gravimetric Storage Capacity (g/kg material) vs. Volumetric Storage Capacity (g/L material)

- Powder
- Alane (AlH₃) Complex hydride
- MgH₂
- NaAlH₄
- Chemical hydride
- Methane ~80 bar, 293 K
- MOF: crystal density
- MU AC: intragranular density

Physical adsorption
- Compressed H₂
  - 100 bar, 80 K
Approach

- Raise binding energy of H\textsubscript{2} on carbon by functionalization of surface with boron
  - Firlej et al., 2009; Kuchta et al., 2010: Binding energy of H\textsubscript{2} on carbon: 5 kJ/mol, on B-substituted carbon: 10-15 kJ/mol
  - Computed H\textsubscript{2} ads. isotherms (GCMC) at 10 wt\% B:C: 5 wt\% H\textsubscript{2} at 293 K, 100 bar

- (1) Produce high-surface-area carbon, (2) Dope surface with B (> 2000 m\textsuperscript{2}/g)
  - B\textsubscript{10}H\textsubscript{14} (volatile), incorporate B into lattice by thermal annealing
  - Achieved ~ 10\% B:C: small reduction in surface area, higher isosteric heat of adsorption, higher excess adsorption at room temperature

- 10-liter hydrogen sorption tank
  - Flow measurement & control (transport & sorption kinetics, heat management)

- Surface, pore, and chemical characterization of materials
  - GCMC: adsorption in heterogeneous pores, non-traditional pore geometries, etc.
  - SAXS & N2 sorption: characterization of pore geometries
  - FTIR & XPS: characterization of incorporated boron

- Carbon monoliths for increased hydrogen storage
  - Boron-doped monoliths for optimization of gravimetric & volumetric storage capacity
Technological Accomplishments

**AX-21, U. Missouri:** 3K-600C (0% boron), 3K-H60 (I,B) (7% boron)

**U. Missouri:**
Projected from experimental values

**AX-21:**
Hydrogen storage engineering center of excellence. *Anton. et al.*, 2010-2011. The gravimetric and volumetric storage capacity of material AX-21 decreased by ~62% and ~44% respectively when including the complete storage system.
## Technical Accomplishments

### Boron-doped Carbons from $B_{10}H_{14}$ Deposition: Different Synthesis Methods

<table>
<thead>
<tr>
<th>Sample (B-doped: out of 12 samples synthesized 2011-12)</th>
<th>Precursor</th>
<th>B:C %</th>
<th>$\Sigma N_2$ (m$^2$/g)</th>
<th>$\Phi_{N_2}$</th>
<th>Annealing temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3K 3/3/10-B</td>
<td>Self</td>
<td>0.0</td>
<td>2700</td>
<td>0.77</td>
<td>N/A</td>
</tr>
<tr>
<td>3K 3/3/10-B Outgassed@ 600 °C</td>
<td>Self</td>
<td>0.0</td>
<td>2500</td>
<td>0.76</td>
<td>N/A</td>
</tr>
<tr>
<td>3K-H60 (I,A), 1-step doping</td>
<td>3K 3/3/10-B Outgassed@ 600 °C</td>
<td>8.6</td>
<td>2100</td>
<td>0.74</td>
<td>600°C</td>
</tr>
<tr>
<td>3K-H60 (I,B), 1-step doping</td>
<td>3K 3/3/10-B Outgassed@ 600 °C</td>
<td>6.7</td>
<td>2100</td>
<td>0.72</td>
<td>1000°C</td>
</tr>
<tr>
<td>3K-H79 (I,A), 5-step doping</td>
<td>3K-H78 (I,A)</td>
<td>7.1</td>
<td>2200</td>
<td>0.78</td>
<td>600°C</td>
</tr>
</tbody>
</table>

- Achieved ~ 9% B:C, 1-step doping: no significant reduction in surface area (< 15%)
- Achieved ~ 7% B:C, 5-step doping: no significant reduction in surface area (< 15%)
- 5-step doping gives ~ 20% increase in total pore volume vs. 1-step doping
- Annealing at 1000 °C reduces B content by ~ 20%, with unchanged surface area and pore size distribution, loss of B through further decomposion
Technical Accomplishments

Hydrogen Sorption on B-doped Samples: Cryogenic and Room Temperature

- Systematic increase of H$_2$ with B:C doping ratio: 3K-H60(I,A) > 3K-H60(I,B) at 303 K
- Enhancement at high $T$, $P$: increase in average binding energy
- At 80K: 3K-H60(I,A) was exposed to oxygen before analysis, hence lower uptake than 3K-H60(I,B); but still better than 3K
Technical Accomplishments

Enhanced Isosteric heats for B-doped carbon

\[ \Delta_{ads} H(\theta) = R \frac{T_1 T_2}{T_2 - T_1} \ln \left( \frac{p_2(T_2, \theta)}{p_1(T_1, \theta)} \right), \]

Clausius-Clapeyron equation

- B-doped materials increase binding energy from \(~6\) kJ/mol to \(~10\) kJ/mol
- Enhanced \(\Delta h\), similar to our theoretical predictions (2009-2010)
- Absolute isotherms used [see 2011 AMR]
- 273 K has 80% higher excess adsorption than 303 K; doubling of binding energy results in quadratic increase in adsorption, in Henry's law regime, as temperature decreases
Technical Accomplishments

Decaborane Deposition at Low Vapor Pressure

- Langmuir isotherms at $T=100, 150, 200, 250$ C (blue, red, gold, green)
- ‘X’ marks decaborane vapor pressures at respective temperatures
- Lower (upper) bound on binding energy suggests 10% coverage achievable without pore blockage for $T < 150$ C ($T < T_{\text{decomposition}}$)
- Experimental pressures and temperatures close to computational optimum
During annealing, decaborane will decompose into a plasma of boron ions.

- Large amount of energy required to directly replace a carbon with boron ($\Delta E \approx 600 \text{ kJ/mol}$).
- Activated carbon is comprised of loose flakes of likely defective graphene.

If a defect is already present, carbon structure readily incorporates boron ($\Delta E \approx -1000 \text{ kJ/mol}$).
Technical Accomplishments

Small Angle X-ray Scattering

- Boron doping has minimal effect at large length scales
- $q < 3 \times 10^{-3}$ Å$^{-1}$: surface fractal network with $D_s \approx 2.5$
- $q > 0.3$ Å$^{-1}$: modeled with Guinier fit to determine radius of gyration

<table>
<thead>
<tr>
<th>Model</th>
<th>3K-600C</th>
<th>3K-H60 (I,A)</th>
<th>3K-H60 (I,B)</th>
<th>3K-H63 (I,A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron content (%)</td>
<td>0 %</td>
<td>9 %</td>
<td>7 %</td>
<td>21 %</td>
</tr>
<tr>
<td>Radius of gyration</td>
<td>6 Å</td>
<td>7 Å</td>
<td>7 Å</td>
<td>10 Å</td>
</tr>
<tr>
<td>Side length square cross section pore, from $R_G$</td>
<td>14 Å</td>
<td>18 Å</td>
<td>17 Å</td>
<td>25 Å</td>
</tr>
<tr>
<td>Ave pore width (SAXS, knee)</td>
<td>23 Å</td>
<td>28 Å</td>
<td>26 Å</td>
<td>36 Å</td>
</tr>
<tr>
<td>Ave pore width ($N_2$ sorption)</td>
<td>18 Å</td>
<td>29 Å</td>
<td>28 Å</td>
<td>N/A</td>
</tr>
</tbody>
</table>

- Radius of gyration and resulting average pore widths increase linearly with boron content
- Consistent with reduction in pore volumes of narrowest pores
Technical Accomplishments

X-ray photoelectron spectroscopy

- ~50% of the boron in sample is bound to a carbon.
- Main carbon peak resolved into two component peaks with energies characteristic of C-B and C-C bonds.
- 26% of carbon being in a C-B bond is consistent with ~8% boron where boron has displaced a carbon in hexagonal lattice.

XPS results consistent with boron incorporated into lattice
- Room to improve remaining ~50% of boron
Technical Accomplishments

Fourier Transform Infrared Spectroscopy

- FTIR was used in transmission mode to identify the nature of the boron bonds in boron doped activated carbon.
- FTIR observation of line at 1022 cm\(^{-1}\) characteristic of B-C bonds (A. P. Cote, et al., "Science,"
- First time that the existence of B-C bonds in boron-doped carbons (vapor deposition) has been observed
Technical Accomplishments

Fourier Transform Infrared Spectroscopy

FTIR (2011)
Consistent with XPS (2012)

- Sample post-treatment successful in removing surface oxidation as evidenced by elimination of O-H bending and C-O stretch modes at ~1650 cm$^{-1}$ & ~1050 cm$^{-1}$, respectively

O-H bending
C-O stretch

Before heat treatment

After heat treatment

Sample post-treatment successful in removing surface oxidation as evidenced by elimination of O-H bending and C-O stretch modes at ~1650 cm$^{-1}$ & ~1050 cm$^{-1}$, respectively
Technical Accomplishments

10-liter Hydrogen Sorption Instrument

- 10-liter system capable of non-equilibrium measurements (pressure temperature, flow rate)
- Gives information about heat management and sample/tank kinetics

Capacity: 10.6 L
Pressure: 0-100 bar
Temp.: 194-303 K
Flow rate range: (0-400 Ln/min H₂)
Technical Accomplishments

10-liter Hydrogen Sorption Instrument

- 10-liter system validated, including sorbent homogeneity
- Gravimetric storage (total) capacity of bulk material is higher than that of individual carbon grains because porosity is higher

\[
V_{ST} = G_{ex} \left(1 - \phi\right) \rho_{skel} + \phi \rho_{gas}
\]

\[
G_{ST} = \frac{V_{ST}}{(1 - \phi) \rho_{skel}}
\]

\[
G_{ST} = G_{ex} + \frac{\rho_{H_2} \phi}{(1 - \phi) \rho_{skel}}
\]

\[
\phi_{intragranular} = \frac{V_{pore}}{V_{pore} + V_{skel}} < \phi_{tank} = 1 - \frac{V_{skel}}{V_{tank}}
\]
Here are the technical accomplishments:

- Able to fill the tank to 95% capacity in 3.3 minutes, 303 K; no heat exchanger
- Gravimetric storage capacity will increase 5% with improved outgassing procedure
Technical Accomplishments

Mixing procedure:
- Adsorbent
- Binder

Compaction:
- Melted binder

Pyrolysis:

Multi-variable optimization:
- Powder precursor
- Activation temperature
- Activation agent concentration
- Binder material
- Binder mass concentration
- Mixing procedure
- Compaction time
- Compaction pressure
- Compaction temperature
- Pyrolysis time
- Pyrolysis temperature

Final monolith composition:
- 80-85 % AC adsorbent: 2600 m²/g
- 15-20 % carbon from binder: 700 m²/g
Technical Accomplishments

Optimization of Carbon Monoliths

- Optimal gravimetric monolith: high surface area and high density
- Optimal volumetric monolith: high surface area and low density

- Assumption: No dependence between excess adsorption and porosity

- Surface area optimized for various synthesis parameters
  - $T =$ Compaction temperature
  - $S =$ Binder:carbon ratio
  - $P =$ Carbon precursor
  - $H =$ Pyrolysis temperature

- Optimal monolith will be boron-doped & tested for hydrogen uptake
Technical Achievements (Summary)

- B can be incorporated into high-surface area nanoporous carbon
- Raises the binding energy and enhances excess adsorption
- Precursor monoliths optimized for surface area and await doping
Collaborations

- **Midwest Research Institute** (Subcontractor): design & construction of instrument for large-scale, automated B-doping

- **NREL** (Federal): L. Simpson, P. Parilla, K. O’Neill—Validation of H₂ uptake


- **NIST** (Federal): Y. Liu, G. Brown, J. Burress—small-angle neutron scattering with in-situ, adsorbed H₂


- **Wroclaw U. Technology**, Poland (Academic): S. Roszak—adsorption potentials for H₂ sorption on B-doped materials from ab initio quantum-chemical computations

- **ORNL** (Federal): M. Stone, R. Olsen—incoherent inelastic neutron scattering with in-situ, adsorbed H₂


- **U. Missouri** (Academic): M. Greenlief—XPS analysis
Future Work: Plans for 2012/13

- Characterize granular materials & demonstrate storage performance
  - Study boron-carbon bonds with micro-Raman spectroscopy & solid-state NMR
  - In-situ Raman spectroscopy of B-C bonds & mass spectroscopy of volatile reaction products during decaborane decomposition & annealing
  - Investigate advantages of multi-step doping over single step doping
  - Investigate new boron-doping methods: (i) high-temperature dissolution of boron into high-surface-area carbon; (ii) boron-carbide-derived high-surface-area materials

- Manufacture and test monolithic materials
  - Manufacture boron-doped monoliths
  - Test performance of monoliths (3.5”diameter) in 10-liter hydrogen tank during charging/discharging (temperature/pressure as a function of time; thermal management)
Manufactured B-substituted carbon under O$_2$-free conditions by thermolysis of B$_{10}$H$_{14}$, with B:C = 7-10 wt%, without compromising high surface areas (≥ 2000 m$^2$/g)

Demonstrated that B:C = 8.6 wt% raises areal excess adsorption at 303 K & 200 bar by 30% relative to undoped material, indicates increase in average binding energy, not solely highest binding energy

Demonstrated that B:C = 8.6 wt% (annealed at 1000 C) raises areal excess adsorption at 80 K & 200 bar by 20% relative to undoped material

Demonstrated that B-doped carbon has a significantly higher isosteric heat of adsorption (10-12 kJ/mol) vs. undoped material (5-6 kJ/mol)

Established existence of B-C bonds in B-doped carbons, made from B$_{10}$H$_{14}$, using FTIR and XPS

Understood the energetics and mechanisms of boron deposition and doping of carbon using B$_{10}$H$_{14}$

Put into operation a large-scale H$_2$ sorption tank for non-equilibrium flow and thermal management measurements