Advanced Boron and Metal Loaded High Porosity Carbons

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Project ID # ST080

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Overview

Timeline
• Project start: 2/1/05
• Project end: 06/30/10
• % complete: 100%

Budget
• Total funding for PSU team
  – DOE share: $1,485,000
  – Contractor share: 371,250
• FY09: $444,000
• FY10: $0

Partners
• Dispersed throughout HSCoE: NIST(neutron), NREL (TPD), Air Products (vol. ads.), UNC (NMR)
• M Dresselhaus (MIT)
• Carbolex, Inc.

Barriers
A: System Wt. & Vol: Hydrogen volumetric (1.5 KWh/L) and gravimetric (6 wt%) storage density goals for 2010
B: Absorbents: Hydrogen binding energy 10 – 20 KJ/mol and SSA > 2000 m²/g
C: System Cost: High-volume low-cost synthesis routes (via pyrolysis, molecular reaction and arc)
D: Energy Efficiency: Moderate temperature operation (via enhanced binding energy)
E: Charge/Discharge Rate: via Mixed micro/mesopore structures through precursor design
F: Thermal Management: via designed moderate binding energies of physisorption
G: Improved Understanding: via calculations in coupling with fundamental measurements on well-characterized, well-ordered systems
Three complementary approaches to prepare B-substituted carbon (BC\textsubscript{x}) materials

- **B-containing Polymer Precursors and Pyrolysis (Chung)**
  - New precursors to prepare BC\textsubscript{x} with high B content, acidity and SSA
  - **Accomplishment:** 15% substitutional B in BC\textsubscript{x} structure. Data show the incorporation of B in C doubles the H\textsubscript{2} binding energy and adsorption capacity. BC\textsubscript{x} shows enhanced dispersion of Pt nanoparticles for spill-over study. Developing new route to prepare the well-defined B-framework that could further enhance B acidity, content, exposure, and SSA.

- **Molecular Reaction and Pyrolysis (Foley)**
  - Combinations of precursors to control complex pyrolytic decomposition
  - **Accomplishment:** Synthesis of BC\textsubscript{x} coated carbon templates that show increase of H\textsubscript{2} binding energy and adsorption capacity

- **Electric arc vaporization from M-B-C Electrodes (Eklund)**
  - Non-equilibrium high-energy conditions
  - **Accomplishment:** Production of highly ordered uniform high SSA B-doped carbon nanotubes with boron doping up to 3% which shows enhancement of H\textsubscript{2} binding energy by inelastic neutron scattering. Production of Al-B-nanocarbon particles from Al-B-C electrodes.
Objectives and Approaches

Achieving DOE 2010 H₂ storage goal with 60 mg H₂/g (gravimetric) and 45 g H₂/L (volumetric) by developing advanced H₂ adsorption Materials with moderate binding energy (10-20 KJ/mol) and high SSA (> 2000 m²/g)

Synthesis of Microporous Boron Substitutional Carbon Materials (BCₓ) and its derivatives, closely coupled to adsorption measurements and first-principles materials theory

Boron Features
- Lightness of boron
- Abundant
- Enhancing H₂ interaction
- Tunable acidity
- Stabilizing atomic metal
Project Activities and Schedule

Year 06
- Studying three synthesis routes (polymer precursor, molecular reaction and electric arc vaporization) to prepare B-substitution C (BC_x) materials.
- Synthesizing and Characterizing new BC_x materials with B content up to 7% and SSA 1000 m2/g, and their H2 adsorption.

Year 07
- Theoretical prediction of M/BC_x materials M (Pt, Pd, etc.)
- GO decision for the program
- Optimizing the methods to prepare the desirable BC_x materials with B content (>10%) including BC_3 coated aerogels.
- Identifying (experiments and calculation) the most suitable H_2 binding sites (binding energy 10 -20 KJ/mol H_2)

Year 08
- Investigating new synthetic routes to prepare metal dispersion (M-intercalation) in BC_x materials for spill-over study.
- Exploring new synthesis route for the well-defined B-Framework.
- Developing well-defined B-Framework with strong B acidity and high H2 binding energy > 20 KJ/mol.
- Studying storage mechanism for spill-over and direct H-M binding in M/C, M/BC_x materials M (Pt, Pd, etc.)

Year 09
- Developing new processing routes to deposit BC_x materials on high surface area templates
- Studying the interaction of hydrogen with BC_x materials using various characterization techniques including DRIFTS and NMR
- Preparing BC_x materials with a combination of high B content (> 15%), acidity, exposure and surface area (SSA > 1000 m2/g)
- Developing means to stabilize highly dispersed metals on BC_x supports.

Year 10
- Developing new concepts in storage exploiting electron-deficient frameworks, topological constraints
Synthesis of $\text{BC}_x$ with Porous Structure by B-Polymer Precursor

- Strong B-C Bonds
- Reactive B-Cl groups
- Ready [2+4] cyclo-addition

$\text{BC}_x$ microstructure and porosity are dependent on pyrolysis temperature

J. Am. Chem. Soc. 2008, 130, 6668
**BC$_x$ Molecular Structure**

**MAS$^{11}$B NMR**

- **BC11 (600°C)**
  - 7.7% B content
- **BC34 (1500°C)**
  - 3.1% B content

**TEM Micrographs**

- **BC11 (600°C)**
- **BC34 (1500°C)**

**Pore size distribution**

- **LiCl template**
- **NaCl template**

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**Carbon (29 March 2010)**

<table>
<thead>
<tr>
<th>Template</th>
<th>N$_2$ sorption at 77K</th>
<th>CO$_2$ sorption at 273K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface area$^a$ (m$^2$/g)</td>
<td>Micropore volume$^b$ (cm$^3$/g)</td>
</tr>
<tr>
<td>LiCl</td>
<td>780</td>
<td>0.38</td>
</tr>
<tr>
<td>LiCl</td>
<td>528</td>
<td>0.10</td>
</tr>
<tr>
<td>NaCl</td>
<td>634</td>
<td>0.34</td>
</tr>
<tr>
<td>NaCl</td>
<td>405</td>
<td>0.16</td>
</tr>
</tbody>
</table>

- $^a$ Calculated by BET equation
- $^b$ Estimated by BJH method
- $^c$ Estimated by D-R method
H₂ Adsorption in Porous BC₁₀ and BC₁₂

**BC₁₀ (SSA=609 m²/g)**

**BC₁₂ (SSA=780 m²/g)**

> Despite low surface area, the samples show significantly higher H₂ adsorption capacity per surface area
Synthesis of BC$_x$ by CVD process

$$2BCl_3 + C_6H_6 \rightarrow 2BC_3 + 6HCl$$

<table>
<thead>
<tr>
<th>B Concentration</th>
<th>B:C Ratio</th>
<th>$d_{002}$; Lattice Spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS$^1$</td>
<td>XPS</td>
<td>XPS</td>
</tr>
<tr>
<td>17</td>
<td>1:3</td>
<td>15.9</td>
</tr>
<tr>
<td>$^{11}$B NMR</td>
<td>$^{11}$B NMR</td>
<td>1:4.6</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>XRD</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>TEM</td>
</tr>
</tbody>
</table>

- BC$_x$ films synthesized by chemical vapor deposition are turbostratic in nature with little or no accessible porosity
- Presence of 16 – 17 at% substitutional boron confirmed by XPS (surface) and B-NMR (bulk) techniques
- Downfield shift in B-NMR peaks confirm the presence of trigonally bonded carbon
Two peaks at 3200 and 1190 cm⁻¹ appear as BCx is exposed to 5% H₂/Ar gas mixture and the peak intensity increases with time of exposure.

The peaks start to disappear when the sample is purged with helium indicating reversible desorption of hydrogen.

The peaks may be due to formation of B-H str. (1190 cm⁻¹). Further study is underway to understand the origin of these peaks using high pressure DRIFTS accessory.
Depositing $\text{BC}_x$ on mesoporous silica template

- Dramatic collapse in surface area with heat treatment at 900°C

- Presence of substitutional boron confirmed by solid state B-NMR

- Downselected the use of mesoporous silica template for $\text{BC}_x$ deposition due to pore collapsing issues upon heat treatment

- Hydrogen uptake was very low due to low accessible surface area, however initial heat of adsorption of $\text{BC}_x$ coated aerogels under controlled synthesis conditions were ~ 11KJ/mol, three times higher than the silica aerogel supports.
Studies of BC\textsubscript{x} deposition on commercially available mesoporous activated carbons

- BC\textsubscript{x} deposition showed slight increase in the heat of adsorption of microporous carbons, however the uptake is limited due to micropore clogging.
- BC\textsubscript{x} deposition on mesoporous carbon accomplished without significant pore clogging and accessible surface area of 800 m\textsuperscript{2}/g.
- Studies underway to measure the effect on hydrogen adsorption on mesoporous activated carbons.

Micropore clogging resulting in loss of surface area with increase in deposition time.

H\textsubscript{2} adsorption measurements done at 77K, 1bar.

No evidence of closed porosity or pore clogging.
**BC_\text{x} on MCM-48 templated carbons**

**XRD of synthesized templated carbons show long range ordering of mesopores as seen from the presence of peaks at 1.6° and 2.7° respectively**

- **SA of BC_x coated carbon ~ 900 m²/g**

- **Initial Heat of adsorption almost doubled with BC_x coated templated carbon as compared to MCM-48 template**

**All H_2 adsorption measurements done at 77K, 1bar**
- Carbon nanospheres in the order of 500 nm in diameter with large extrinsic surface area was synthesized.
- Activated carbon nanospheres with large extrinsic surface area show initial hydrogen heat of adsorption of ~ 10 KJ/mol.
- Currently exploring the use of these carbons as templates for BC$_x$ deposition.
Theory: Metal dispersion & New frameworks

When metals are dispersed onto BC$_x$ sheets, they preferentially stick to the B-rich regions. Using percolation theory and first-principles calculations, we have estimated the activation barrier against metal atom aggregation across a range of B concentrations. (At the higher B concentrations, the metal is actually thermodynamically stable against aggregation).

<table>
<thead>
<tr>
<th>B concentration</th>
<th>Barrier against Ti aggregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>3.8 eV</td>
</tr>
<tr>
<td>10%</td>
<td>2.4 eV</td>
</tr>
<tr>
<td>20%</td>
<td>1.3 eV</td>
</tr>
</tbody>
</table>

In additional work, we have demonstrated that novel BN-based framework compounds can reversibly release H$_2$ without irreversible collapse into a BN end-state.
Metal nanoparticles decorated BC$_x$ (FE-SEM Micrographs)

Pd/BC$_{12}$ (Pd: 1.65 wt%)                         Pt/BC$_{12}$ (Pt: 0.7 wt%)

SSA: 650 m$^2$/g                               SSA: 644 m$^2$/g

(Starting BC$_{12}$: 650 m$^2$/g)

Nano Letters (submitted)
Platinum nanoparticles were better dispersed on BC$_x$ support as compared to carbon support of similar surface area.
Comparison of Hydrogen adsorption
Pt-BC\textsubscript{12} (0.7 wt\% Pt), BC\textsubscript{12} and C

(SSA=650 m\textsuperscript{2}/g)

Evidence of increased hydrogen adsorption capacity on Pt/BC\textsubscript{12} as compared to BC\textsubscript{12} and porous carbon of similar surface area
Future Work

Plan for the rest of FY10

• *Increasing surface area of BC$_x$ materials*
  Continuing the development of BC$_x$ materials to achieve a combination of high B content, acidity and exposure and surface area (> 2000 m$^2$/g) using templated approach, which could further increase H$_2$ storage capacity at ambient temperature

• *Probe the interaction of hydrogen with BC$_x$ materials*
  Characterize interaction of hydrogen with BC$_x$ coated carbons using DRIFTS and NMR
Summary

- **Relevance:** Increase reversible hydrogen binding energy by developing new storage materials through B-substitutional carbon (BC_x) structures.
- **Approach:** Three complementary synthesis techniques closely coupled to adsorption measurements and first-principles materials theory.
- **Technical Accomplishments:**
  - Developed new synthetic approaches to deposit BC_x films with 16 at% boron content onto high surface area supports.
  - Showed increased heat of adsorption for BC_x coated templates.
  - Theory work predicted better metal dispersion on BC_x material with high boron content.
  - Pt/BC_{12} with SSA=650 m^2/g has increased hydrogen adsorption capacity of 0.6wt% at 298K, 85 bar as compared to BC_{12}.
  - Studying interaction of hydrogen with BC_x using spectroscopic techniques.