Advanced Boron and Metal Loaded High Porosity Carbons

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Project ID#: STP 11

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Overview

Timeline
- Project start: 2/1/05
- Project end: 1/31/10
- % complete: 60%

Budget
- Total funding for PSU team
  - DOE share: $1.2M
  - Contractor share: $0.3M
- FY06 $ 225,000
- FY07 $ 333,000

Partners
- Dispersed throughout HSCoE: NIST (neutron), NREL (TPD), Air Products (vol. ads.), UNC (NMR)

Barriers
A: System Wt & Vol: Hydrogen volumetric (1.5 kWh/L) and gravimetric (6wt%) storage density goals for 2010
B: System Cost: High-volume low-cost synthesis routes (via pyrolysis, arc)
C: Energy Efficiency: Low pressure, moderate temperature operation (via enhanced binding energy through chemical modification)
E: Charge/discharge rate: via Mixed micro/mesopore structures through precursor design
J: Thermal management: via designed moderate binding energies of mixed physi/chemi-sorption
P: Improved understanding: via calculations in close coupling with fundamental measurements on well-characterized, well-ordered systems
Project Objectives and Approaches

6 wt% H₂ storage goal by increasing binding energy (10-30 kJ/mol) and SSA (> 2000 m²/g)

Micro-porous
B Substitution C (B/C) Materials

Microporous Metal Intercalation M/B/C Materials

B in C Structures
- Lightness of Boron
- Enhancing H₂ interaction
- No serious structural distortions
- Catalyzing carbonization
- Stabilizing atomic metal
Project Activities and Schedule

**FY06**
- Developing synthesis routes and processes to prepare B/C (B-substitution) materials.
- Characterizing new B/C materials and structure-property-$H_2$ adsorption relationship.

**FY07**
- Synthesizing the desirable B/C materials with high B content and high SSA, and their $H_2$ adsorption.
- Investigating synthesis routes to prepare atomic metal dispersion (M-intercalation) in B/C materials.

**FY08**
- Synthesizing the desirable B/C and M/B/C materials with B content (>10 mol%), M content (>3 mol%), and SSA (>2000 m$^2$/g).
- Studying structure-property relationship.
Technical Accomplishments

Synthesis of B/C Materials by B-containing Precursors

- Simple process
- Large scale production
- Varying pyrolysis temp.
- Control Crystal structure
- Control B content (up to 10%)

CBF

\[
\begin{align*}
\text{B/C/Cl} &= 1/12/1 \\
\end{align*}
\]

PBDE

\[
\begin{align*}
\text{B/C/Cl} &= 1/10/3 \\
\end{align*}
\]

PBDA

\[
\begin{align*}
\text{B/C/Cl} &= 1/10/1 \\
\end{align*}
\]

- Conjugated B-C bonds
- Reactive B-Cl for stabilization
Technical Accomplishments

Synthesis of Micro-porous C/B Material

Li⁺ C≡C―Cl―C≡C^+Li

BCl₃

C[Cl C≡C―C≡C_B]_x

(± LiCl)

B/C = 1/10

Δ

Micro-porous B/C

<table>
<thead>
<tr>
<th>Pyrolysis temp. (°C)</th>
<th>B content^a (wt%)</th>
<th>B content^b (wt%)</th>
<th>Surface area^c (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>7.2</td>
<td>7.6</td>
<td>780</td>
</tr>
<tr>
<td>800</td>
<td>5.7</td>
<td>7.1</td>
<td>528</td>
</tr>
<tr>
<td>1500</td>
<td>3.8</td>
<td>3.0</td>
<td>33</td>
</tr>
</tbody>
</table>

^a. Prompt Gamma-ray Activation Analysis (NIST).
^b. ¹¹B MAS-NMR measurement (UNC).
^c. BET method using N₂ gas at liquid N₂.
Technical Accomplishments

**Solid State 11B MAS-NMR spectra of B/C materials**

PBDA precursor

(a) 150, (b) 600, (c) 800, (d) 1000 °C

CBF precursor

200 °C

400 °C

800 °C

1500 °C

B-Graphite

B-CNT

Yue Wu (UNC) and Mike Chung
Technical Accomplishments

XRD Patterns of C/B materials

<table>
<thead>
<tr>
<th>Pyrolysis Temp.</th>
<th>D-Spacing (002) (Å)</th>
<th>Boron Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td>3.461</td>
<td>7.65%</td>
</tr>
<tr>
<td>1500°C</td>
<td>3.411</td>
<td>7.58%</td>
</tr>
<tr>
<td>(PGAA, NIST)</td>
<td></td>
<td>(PGAA, NIST)</td>
</tr>
<tr>
<td>1800°C</td>
<td>3.383</td>
<td>7.42%</td>
</tr>
<tr>
<td>2100°C</td>
<td>3.363</td>
<td>6.96%</td>
</tr>
<tr>
<td>2300°C</td>
<td>3.347</td>
<td>3.46%</td>
</tr>
</tbody>
</table>
Technical Accomplishments

Evolution of B/C Structure during Pyrolysis

600 °C

1000 °C

>1500 °C

B/C materials with various B site structures that are controlled by pyrolysis temperatures
Technical Accomplishments

Hydrogen Uptake in Micro-porous B/C (SSA: 780 m²/g)

- Initial heat of adsorption for the B/C material is 12.47 kJ/mol
- About 2 times H₂ adsorption capacity (vs. C having similar SSA)
Technical Accomplishments

$^1H$ NMR spectrum of $H_2$ Gas in Porous B/C Material

Peak 1 and peak 2&3 depend linearly on pressure as expected for free $H_2$ gas. Peak 4 shows nonlinear pressure dependence. Using the Langmuir equation, an estimate of binding energy $E_{ads} = 11$ kJ/mol.

Boron significantly enhances $H_2$ binding energy

Yue Wu (UNC) and Mike Chung
Technical Accomplishments

Metal-loading in B/C Materials

Graphitic C

\[ \text{H}_2\text{PtCl}_6 \] in Water

\[ \text{NaBH}_4 \] chemical reduction

\textbf{Pt(0) particles in C material}

B/C material

\[ \text{Cp}^*_2\text{ZrCl}_2 \] Homogeneous Toluene solution

Washing then Drying

\( \Delta \) 600 °C

\textbf{Zr/B/C Material}
Technical Accomplishments

**Comparison of Metal Loading onto C and B/C Materials**

<table>
<thead>
<tr>
<th>Metal Containing Reagents</th>
<th>Activated C (200 mg, 600 m²/g)</th>
<th>B/C Material (200 mg, 500 m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After metal loading (mg)</td>
<td>After metal loading (mg)</td>
</tr>
<tr>
<td>H₂PtCl₆&lt;sup&gt;a&lt;/sup&gt;</td>
<td>230</td>
<td>234</td>
</tr>
<tr>
<td>Cp₂TiCl₂&lt;sup&gt;b&lt;/sup&gt;</td>
<td>200</td>
<td>309</td>
</tr>
<tr>
<td>Cp*₂ZrCl₂&lt;sup&gt;b&lt;/sup&gt;</td>
<td>205</td>
<td>222</td>
</tr>
<tr>
<td>[(η⁵-Cp*)SiMe₂(η¹-NCMe₃)]TiCl₂&lt;sup&gt;b&lt;/sup&gt;</td>
<td>203</td>
<td>272</td>
</tr>
</tbody>
</table>

- a. Loading in surfactant/water emulsion
- b. Loading in toluene solvent (without surfactant)

**Substitutional B in C structure enhances metal intercalation**
Technical Accomplishments

High resolution TEM Image of Zr/B/C Material

B/C Material with Cp\*2ZrCl2 $\xrightarrow{\Delta 600 \, ^{\circ}C}$ Zr/B/C Material

Wave-like B/C structure

Uniform Zr particles (size < 2nm)

Intercalating uniform metal nanoparticles without surfactant
Technical Accomplishments

H₂ adsorption at 77K

- B/C-Zr (400)
- B/C-Pt cluster (600)
  = B/C
- B/C-Zr (600)
- B/C-Ti (400)
- B/C-Ti (600)
Summary

• Micro-porous B/C Materials (B ~8%, SSA ~800 m²/g) has been prepared by B-precursor and pyrolysis

• B/C Structure Changes with Pyrolysis Temp
  B moiety gradually immerses in graphitic structure

• B/C Shows H₂ Binding Energy (~12 KJ/mol) and Double Adsorption Capacity (vs. C)

• New M/B/C Materials Have Been Prepared with Intercalated Nano-Metal Particles
Future Work

Year 08

• **Increase Surface Area of B/C Materials**
  
  H$_2$ adsorption could reach 6 wt% if B/C material would contain > 10% B and >2000 m$^2$/g

• **Increase Binding Energy of M/B/C Materials**
  
  H$_2$ adsorption at ambient temperature requires higher binding energy (15-30 KJ/mole)

  Finding right M species

  Well-dispersed metal atoms or neat atomic particles

• **Spill-over on M/B/C Materials**