2007 DOE Hydrogen Program

Advanced Boron and Metal Loaded High Porosity Carbons

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Project ID: ST # 8

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Overview

Timeline
• Project start: 2/1/05
• Project end: 1/31/10
• % complete: 40%

Budget
• Total project funding
  – 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)
• M Dresselhaus (MIT)
• Carbolex, Inc

Barriers addressed
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
Objectives/Approaches

Achieving DOE 2010 $H_2$ storage goal (6 wt%) by developing advanced $H_2$ adsorption materials with high binding energy (10-30 kJ/mol) and high SSA (> 2000 m$^2$/g)

FY06
- Developing methods to prepare porous 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 B content (>10%) and SSA (>2000 m$^2$/g).
- Investigating routes to prepare atomic metal dispersion (M-intercalation) in B/C materials.
- Studying structure-property relationship.
- Theoretical prediction of M/B/C materials.

Substitutional B in C
- Lightness of Boron
- Enhancing $H_2$ interaction
- No serious structural distortions
- Catalyzing carbonization
- Stabilizing atomic metal
Boron substitutions of the carbon framework have shown the raise of binding energy to $H_2$ into the range of theoretical prediction.

We have predicted that boron doping stabilizes atomically dispersed metals (Sc, Mg, Ti, Pd, Be...) against aggregation, a necessary condition to expose orbitals for reversible hydrogen binding.

(Vince Crespi)
Three complementary approaches to prepare B-substituted carbon (B/C) materials

• 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$_2$ binding energy by inelastic neutron scattering. Production of Al-B-nanocarbon particles (~20 nm dia) from Al-B-C electrodes.

• Molecular Reaction / Pyrolysis *(Foley)*
  – Combinations of precursors to control complex pyrolytic decomposition
  – **Accomplishment:** Synthesis of highly porous materials with a controlled mixture of micropores (for large storage) and mesopores (for rapid transport)

• B-Containing Precursors (Polymers) / Pyrolysis *(Chung)*
  – Ability to design precursors with high B contents and high SSA
  – **Accomplishment:** 8% boron incorporation into sp$^2$ carbon frameworks. *Data show the increase of H$_2$ binding energy (~10 KJ/mol) and doubles H$_2$ absorption capacity.*
Synthesis of Nanoparticle Carbides by Electric arc vaporization

- Crystalline metal-boro-carbides produced.
- Research Reactor capacity ~100 g/hr (scalable).

(Peter Eklund)
Al-B-C Nanoparticles (20-100 nm diameter)

TEM-EDS

HRTEM

XRD

Crystalline Al-B-Carbides are produced by Electric arc vaporization

(Peter Eklund)
It is known that Cl₂ will vapor transport not only the metal atoms, but also boron from bulk carbides.

We are exploring non-equilibrium conditions that lead to preferential metal removal leading to a porous boro-carbon with residual metal sites—the residual metal should also be active for H₂ chemisorption.

Encouraging experiments are in progress.

(Peter Eklund)
Synthesis of B/C Materials by Molecular Reaction/Pyrolysis

\[ \text{TEAB} \rightarrow \text{CH}_2\text{OBH}_2 + \text{N(C}_2\text{H}_5)_3 + \text{C}_2\text{H}_6(g) + \text{H}_2(g) \]

Mix PFA and FA (2:1)

- 80 °C \(\rightarrow\) 1h
- Add TEAB in PFA/FA (0.5)

Add PEG 6k (1)

- 60 °C \(\rightarrow\)
- Add PEG 6k (1)

Pyrolyze at 800 °C for 8h (1)

Activate with CO\(_2\) at 900 °C for 4h (2)

- BET surface area = 980 m\(^2\)/g.
- B:C (atomic%) for sample before activation was 1:60 and after activation was 1:20 respectively

(Hank Foley)
### Hydrogen storage measurements

<table>
<thead>
<tr>
<th>Measurement at NREL</th>
<th>TEAB-1</th>
<th>TEAB-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2 BET SSA, as received</td>
<td>35 m²/g</td>
<td>~950 m²/g</td>
</tr>
<tr>
<td>Sieverts RT H₂ Uptake at ~2 bar, as received</td>
<td>&lt;0.01 wt%</td>
<td>0.025 wt%</td>
</tr>
<tr>
<td>Sieverts 77 K H₂ Uptake at ~2 bar, as received</td>
<td>0.2 wt%</td>
<td>1.5 wt%</td>
</tr>
<tr>
<td>Sieverts 77 K H₂ Uptake at ~2 bar, after 200°C vacuum degas</td>
<td></td>
<td>2.0 wt%</td>
</tr>
<tr>
<td>N2 BET SSA, after 200°C vacuum degas</td>
<td></td>
<td>1071 m²/g</td>
</tr>
</tbody>
</table>

TEAB-1 and TEAB-2 are the B/C materials before and after CO₂ activation at 900°C for 3 hs.

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At room temperature, high pressure hydrogen uptake values (0.5 wt% at 100 bar) are similar to activated carbon that has twice the surface area of TEAB-2

*(Hank Foley)*
Synthesis of B/C Materials by Using B-containing Precursors

Precursor Design

- Aromatic (conjugated) framework
- Strong B-C Bond and Reactive B-Cl bonds for intermolecular and intra-cyclization reactions

Economic process for producing large scale material, with the control of B content, crystal structure, morphology (SSA, pore size and distribution)

(Mike Chung)
Peak 1 and peak 2&3 depend linearly on pressure as expected for free H₂ gas. Peak 4 shows nonlinear pressure dependence. Using the Langmuir equation, an estimate of binding energy $E_{ads} = 9.2 \text{ kJ/mol} (> 3 \text{ times higher than C})$.

**Boron significantly enhances H₂ binding energy**

Yue Wu (UNC) and Mike Chung
Pore Size Distribution in B/C Material (III)
(B content = 5.7%; Surface area = 528 m²/g)

B content measured by PGAA, NIST

About 1/3 of the incorporated B atoms are available for interaction

(Mike Chung)
### Hydrogen Uptake in B/C Material (III) (NREL)

<table>
<thead>
<tr>
<th>Measurement</th>
<th>PBDA (BC-800)</th>
<th>PBDA (BC-1500)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2} BET SSA, as received</td>
<td>528 m\textsuperscript{2}/g</td>
<td>33 m\textsuperscript{2}/g</td>
</tr>
<tr>
<td>Sieverts RT H\textsubscript{2} Uptake at ~2 bar, as received</td>
<td>0.02 wt%</td>
<td>0.004 wt%</td>
</tr>
<tr>
<td>Sieverts 77 K H\textsubscript{2} Uptake at ~2 bar, as received</td>
<td>1.4 wt%</td>
<td>0.07 wt%</td>
</tr>
<tr>
<td>TPD from 77 K to 800\textdegree C</td>
<td>Physisorption only</td>
<td>Physisorption only</td>
</tr>
<tr>
<td>BET after 800\textdegree C degas</td>
<td>619 m\textsuperscript{2}/g</td>
<td></td>
</tr>
<tr>
<td>Sieverts 77 K H\textsubscript{2} Uptake at ~2 bar, After 800\textdegree C degas</td>
<td>1.6 wt%</td>
<td></td>
</tr>
</tbody>
</table>

**B/C material (vs. C with a similar SSA) shows >50% increase in H\textsubscript{2} uptake at 2 bar**

Ahn et al, Chem. Mat. 18, 6085, 2006

(Mike Chung)
Hydrogen Uptake in new B/C Material (IV)
(B content = 6.5%; Surface area = 780 m²/g)

- The corresponding C material with a similar surface area only adsorbs < 2% H₂ at 77K and 30 bar.
- Reversible Adsorption-Desorption cycles by pressure

B/C material (vs. C with a similar SSA) doubles H₂ adsorption at 77K

(Mike Chung)
Summary: Penn State Effort

- **Relevance:** Increase reversible hydrogen BE by developing new storage materials through chemical modification of carbon frameworks.

- **Approach:** Three complementary synthesis techniques closely coupled to adsorption measurements and first-principles materials theory.

- **Technical accomplishments:**
  - All three synthesis routes produce boron-substituted sp² carbon (B/C) materials.
  - B/C materials have been prepared with up to 8% substitutional B elements and SSA ~1000 m²/g.
  - B/C material increases H₂ binding energy (~10 kJ/mol) and doubles absorption capacity.
  - Calculations show that higher boron content in higher-curvature geometries have higher binding energy (~30 kJ/mol) and boron stabilizes atomically dispersed metals on the carbon framework.

- **Collaborations:** NREL, NIST, UNC, AirProducts, Carbolex
Future Work

Plan for the rest of FY07

- Continuing the development of new B/C materials with more reactive B species, B content (>10%) and surface area (>2000 m²/g), which further increase storage capacity at high temperatures.
- Studying the correlation between B species (structure, morphology) and H₂ Binding Energy.
- Investigating synthesis protocols for metal dispersion onto B/C materials to further increase binding energy and raise the operating temperature.

Plan for FY08

- Pushing B content to >20% and surface area > 2000 m²/g in various forms of B/C materials to further increase binding energy and determine (T,P) needed for 6 wt% reversible H₂ storage.
- Developing the desirable Metal-Boro-Carbon materials (specific metal, composition, and morphology) and investigate bi-functional (B & metal) H-storage.
**Summary Table**

Comparison of Hydrogen Storage in Various Material Systems

<table>
<thead>
<tr>
<th>Material</th>
<th>Binding Energy (KJ/mol)</th>
<th>H₂ Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Wt (%)</td>
</tr>
<tr>
<td>C material (1000 m²/g SSA)</td>
<td>~ 3</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>B/C material (IV) (6.5% B content; 780 m²/g SSA)</td>
<td>&gt; 10</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.2</td>
</tr>
<tr>
<td>M-B-C Material (calculation)</td>
<td>30-80</td>
<td>&gt; 5</td>
</tr>
</tbody>
</table>

Our intent is to optimize the material to meet the 2010 goals with higher boron concentrations, greater surface areas, and metal dispersion for bi-functional (physical/chemical) adsorption & storage.