Developing A Novel Hydrogen Sponge Polymer with Ideal Binding Energy and High Surface Area for Practical Hydrogen Storage

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Overview

**Timeline**
- Project start date: 10/1/2016
- Project end date: 9/30/2019
- % complete: 25%

**Budget**
- Total project funding: $887,266
  - DOE share: $682,715
  - Penn State share: $204,551
- Funding for FY2016-17: $250,000
- Go/no-Go decision: Dec. 2017

**Barriers**
- System weight & volume
- System cost, efficiency, durability
- Charging/discharging rates
- Suitable H₂ binding energy
- High polymer surface area

**Partners**
- HyMARC consortium
  - Sandia National Lab.
  - Lawrence Livermore National Lab.
  - Lawrence Berkeley National Lab.
Research Objectives

- New H₂ sponge (microporous polymer) that can simultaneously exhibit an H₂ binding energy (ΔH) 15-25 kJ/mol, a specific surface area SSA>4000 m²/g, and a material density >0.6 g/cm³.
- Design, synthesis, and evaluation of a new class of B-containing polymers with specific B-moieties and repeating microporous morphology.
- Molecular simulation and advanced structural characterization to support scientific understanding and polymer materials development.

Potential Benefits and the Impact on Technology

- Polymer morphology, free volume, and surface properties can be controlled at molecular level.
- Polymer can be produced in large-scale with low cost, good mechanical properties, and long term stability.
- If successful, this H₂ sponge can achieve gravimetric capacity of 5.5 wt% H₂ and volumetric capacity of 40g H₂/L @ ambient temperature under mild pressure (20-100 bar).
Relevance: 2020 DOE onboard $H_2$ storage targets

<table>
<thead>
<tr>
<th>System</th>
<th>Temp. (°C)</th>
<th>Gravimetric capacity (wt%)</th>
<th>Volumetric capacity (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 Bar Compressed $H_2$ system</td>
<td>Ambient Temp</td>
<td>~4.5</td>
<td>~25</td>
</tr>
<tr>
<td>DOE 2020 targets</td>
<td>Ambient (-40/60)</td>
<td>5.5 (1.8kWh/kg)</td>
<td>40 (1.3 kWh/L)</td>
</tr>
</tbody>
</table>

- Lower pressure operation = less cost at the station
- Fast hydrogen refill (5 kg in 3 to 5 minutes)
- Delivery pressure to fuel cell system (5-12 bar)
- Nominal thermal-management during refueling
- High efficiency (90%)
- Robotic and Durable (1500 cycles)
- Scalable and Low cost
Relevance: Three $H_2$ storage materials

**Physical approach**

**MOF-210**
- SSA: 6240 m$^2$/g
- $\Delta H$: <10 KJ/mol
- Density: 0.25 g/cm$^3$
- Pore size: 2-5 nm
- Pore volume: 3.6 cm$^3$/g

**C Nanohorn**
- SSA: <2000 m$^2$/g
- $\Delta H$: <10 KJ/mol
- Density: 0.75 g/cm$^3$
- Pore size: 1-3.6 nm

**Chemical approach**

- Metal Hydrides: Mg(BH$_4$)$_2$(NH$_3$)$_2$
- Chemical Hydrides: Mg(BH$_4$)$_2$, Ca(BH$_4$)$_2$, LiBH$_4$/MgH$_2$, LiNH$_2$/MgH$_2$, MgH$_2$

$H_2$ Storage Capacity vs. $H_2$ Sorption Temperature (°C)

- MOF-210
- MOF-177
- C aerogel
- MOF-74

$H_2$ Desorption Temperature (°C)

- <10 KJ/mol
- 15-25 KJ/mol
- >30 KJ/mol
**Relevance: Porous organic polymer networks**

Qiu and Zhu at al. Angew Chem Int Ed 2009, 48, 9457

![PAF-1](image)

**PAF-1**
- BET: 6540 m²/g
- H₂ uptake: 7 wt% Total (48 bar/77K)
- Density: 0.315 g/cm³


![PPN-4](image)

**PPN-4**
- BET: 6461 m²/g
- H₂ uptake: 8.34 wt% Total (55 bar/77K)
- ΔH ~4 kJ/mol

- **Porous Polymer Network (PPN) can offer high surface area (>4000 m²/g)**
- **Polymers also offer good mechanical and thermal stability**
- **But low H₂ binding energy (<10 kJ/mol)**
Relevance: Optimal sorbent material

**Binding Energy**

- Bhatia and Myers 2006
- dotted lines $\Delta S = -10R$
- solid lines $\Delta S = -8R$

![Graph showing binding energy vs pressure at 298K, 223K, and 77K](image)

- $\Delta H$: 15-25 kJ/mol

**Bulk Density**

- Argonne National Laboratory
- DOE target

![Graph showing bulk density vs material density and volumetric capacity](image)

- Bulk material density: $>0.6 \text{ g/cm}^3$

Practical $\text{H}_2$ storage at ambient temperature and pressure $<100$ bar
Relevance: Increase $H_2$ binding energy

NREL led $H_2$ Sorption Center of Excellence (HSCoE) 2005-10
**Relevance: Synthesis of BC$_x$ by Precursors**

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Pyrolysis temp. (°C)</th>
<th>BC$_x$ (B wt%)</th>
<th>d-Spacing (nm)</th>
<th>La (nm)</th>
<th>Lc (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>600</td>
<td>BC$_{12}$ (7.7)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A-2</td>
<td>800</td>
<td>BC$_{13}$ (6.4)</td>
<td>0.367</td>
<td>3.70</td>
<td>1.10</td>
</tr>
<tr>
<td>A-3</td>
<td>1100</td>
<td>BC$_{21}$ (4.2)</td>
<td>0.356</td>
<td>3.73</td>
<td>1.23</td>
</tr>
<tr>
<td>A-4</td>
<td>1400</td>
<td>BC$_{25}$ (3.5)</td>
<td>0.353</td>
<td>4.87</td>
<td>1.61</td>
</tr>
<tr>
<td>A-5</td>
<td>1500</td>
<td>BC$_{28}$ (2.6)</td>
<td>0.347</td>
<td>5.04</td>
<td>1.64</td>
</tr>
<tr>
<td>A-6</td>
<td>1800</td>
<td>BC$_{40}$ (2.2)</td>
<td>0.339</td>
<td>6.04</td>
<td>2.77</td>
</tr>
</tbody>
</table>

- **Pyrolysis temp. (°C)**: Temperatures at which pyrolysis was performed.
- **BC$_x$ (B wt%)**: Weight percentage of boron in the synthesized BC$_x$.
- **d-Spacing (nm)**: Distance between layers in nanometers.
- **La (nm)**: Length in nanometers.
- **Lc (nm)**: Width in nanometers.

*Images and diagrams show the synthesis process and resulting materials.*

*References:*

1. Carbon 1996, 34, 595
2. Carbon 1996, 34, 1181
3. Carbon 1997, 35, 641
6. Carbon 2010, 48, 2526
Relevance: $H_2$ adsorption isotherms in $BC_{12}$

<table>
<thead>
<tr>
<th>Run no.</th>
<th>N$_2$ sorption at 77 K</th>
<th>CO$_2$ sorption at 273 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface area (m$^2$/g)</td>
<td>Pore vol. (cm$^3$/g)</td>
</tr>
<tr>
<td>A-1</td>
<td>780</td>
<td>0.38 (0.43)*</td>
</tr>
</tbody>
</table>

Volumetric measurement

Gravimetric measurement

$^1$H NMR (H$_2$ at 295 K and 10 Mpa)

Clausius-Clapeyron equation estimates the initial isosteric heat of adsorption is 12.47 kJ/mol and maintains a high level (10.8 kJ/mol for 0.62 wt % H$_2$ uptake).

Peaks B and C are associated with H$_2$ in two different types of confined regions. The Langmuir fit of peak C isotherm yields a H$_2$ binding energy of 11.4 kJ/mol.

Carbon 2010, 48, 2526-2537

JACS 2008, 130, 6668

### Approach: New sorbent targets

<table>
<thead>
<tr>
<th>System</th>
<th>SSA (m²/g)</th>
<th>Density (g/cm³)</th>
<th>Pore volume (cm³/g)</th>
<th>H₂ binding energy (kJ/mol)</th>
<th>Pres./Temp. (bar)/(K)</th>
<th>Gravimetric capacity (wt%)</th>
<th>Volumetric capacity (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF 210</td>
<td>6240</td>
<td>0.25</td>
<td>3.6</td>
<td>&lt;10</td>
<td>60/77</td>
<td>8.6</td>
<td>24</td>
</tr>
<tr>
<td>Porous Polymer</td>
<td>&gt;4000</td>
<td>&lt;1.0</td>
<td>&lt;10</td>
<td>90/77</td>
<td>&gt;7.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porous BC₁₂</td>
<td>1500</td>
<td>0.98</td>
<td>0.43</td>
<td>10-12</td>
<td>60/77</td>
<td>3.3</td>
<td>34</td>
</tr>
<tr>
<td>DOE and B-polymer targets</td>
<td>&gt;4000</td>
<td>&gt;0.6</td>
<td>&lt;0.7</td>
<td>15-25</td>
<td>&lt;100 / 273</td>
<td>5.5</td>
<td>40</td>
</tr>
</tbody>
</table>

New sorbent shall simultaneously exhibit H₂ binding energy 15-25 kJ/mol, SSA >4000 m²/g, material density >0.7 g/cm³.
Approach: Two New B-containing Polymer Networks

Condensation Mechanism

(A)

Addition Mechanism

(B)

R Spacers:

Organoborane moiety with suitable acidity (correlative $^{11}$B chemical shift to H$_2$ binding energy)
Accomplishments - Condensation mechanism; 2,6-divinyl-9,10-methoxyboraanthracene monomer

Incremental Surface Area vs. Pore width (C-A)

Surface area and micro-pore volume

Bulk density = 0.95 g/cm³

(A)
Accomplishments: Addition mechanism; B-containing poly(butylstyrene) (B-PBS)

**Chemical Reaction**

\[
\text{Syndio-specific metallocene catalyst} \rightarrow \text{B-PBS}
\]

**Thermal Stability**

- \(200 \, ^\circ\text{C}\)
- \(230 \, ^\circ\text{C}\)
- \(270 \, ^\circ\text{C}\)
- \(>300 \, ^\circ\text{C}\)
Accomplishments: FTIR spectrum of B-PBS polymer
Accomplishments: MAS $^{11}$B NMR spectrum of B-PBS polymer

Solid state Boron NMR

MAS $^{11}$B NMR spectrum of B-PBS polymer
Accomplishments: Pore Structure of B-PBS polymers

**B-PBS-300**
- Surface Area: 800 m²/g
- Micropore Volume: 0.48 cm³/g
- Density: 1 g/cm³

**B-PBS-230**
- Surface Area: 1,150 m²/g
- Micropore Volume: 0.75 cm³/g
- Density: 1 g/cm³
Accomplishments: $H_2$ Adsorption Isotherm

$H_2$ adsorption was measured at Sandia National Labs (Dr. Vitalie Stavila)

- B-PBS-230
  - $1,150 \text{ m}^2/\text{g}$

At:
- $0 \degree \text{C}$
- $25 \degree \text{C}$

$H_2$ adsorption was measured at Sandia National Labs (Dr. Vitalie Stavila)
Summary

• Design and Synthesis of two new classes of microporous B-containing polymers.

• Structure characterization by FTIR, $^1$H, $^{11}$B, and $^{13}$C NMR spectroscopies, SEM, micropores and surface area.

• Collaboration with HyMARC core team for H$_2$ adsorption isotherm measurements.
Proposed future work

- Broadening B-polymer compositions
- Refining reaction conditions to control microporous morphology
- Titan TEM-EDS and FE-SEM electron microscopies to observe the microporous morphology with the elemental map.
- Correlating B chemical shifts (B-acidity) to H₂ binding energy (ΔH) and sorption-desorption cycles.
## Collaboration with HyMARC / HySCORE teams

<table>
<thead>
<tr>
<th>Partner</th>
<th>Project Roles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandia National Lab.</td>
<td>H₂ adsorption isotherm measurements up to 200 bar H₂ pressure and various temperatures, also the stability tests up to 1000 bar H₂ pressure and various temperatures.</td>
</tr>
<tr>
<td>Lawrence Livermore National Lab.</td>
<td>Computer simulation of B-polymer networks to understand morphology (pore size, pore volume, surface area, density, etc.) and surface energy for H₂ adsorption</td>
</tr>
<tr>
<td>National Renewable Energy Lab.</td>
<td>H₂ adsorption isotherm measurements / Verification of our experimental results</td>
</tr>
</tbody>
</table>
### Future Work (cont.)

<table>
<thead>
<tr>
<th>Phase 1</th>
<th>Key Milestones &amp; Deliverables</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/1/2016</td>
<td>• Synthesis routes to prepare B-monomers, B-polymers, and the corresponding B-networks.</td>
</tr>
<tr>
<td></td>
<td>• Collaborating with HyMARC to examine B-network structures, SSA, H(_2) binding energy and adsorption capacity.</td>
</tr>
<tr>
<td>12/31/2017</td>
<td>• A B-polymer network with SSA&gt;3000 m(^2)/g, an average H(<em>2) binding energy (E</em>{\text{ads}})&gt;15 kJ/mol, H(_2) adsorption capacity 5 wt% excess (Go/No-Go criteria).</td>
</tr>
<tr>
<td>12/31/2017</td>
<td><strong>Go/No-Go decision</strong></td>
</tr>
<tr>
<td>Phase 2</td>
<td>• Expanding B-polymer Networks by varying R spacer between B-moieties.</td>
</tr>
<tr>
<td>1/1/2018</td>
<td>• Collaborating with HyMARC to understand free volume and H(_2) binding energy.</td>
</tr>
<tr>
<td>9/30/2019</td>
<td>• Understanding the structure-property relationship by a systematical study.</td>
</tr>
<tr>
<td></td>
<td>• Achieving the DOE 2020 H(_2) Storage Target.</td>
</tr>
</tbody>
</table>