Hydrogen Storage through Nanostructured Porous Organic Polymers (POPs)

Di-Jia Liu\textsuperscript{1}, Shengwen Yuan\textsuperscript{1}, Desiree White\textsuperscript{1}, Alex Mason\textsuperscript{1}, Briana Reprogle\textsuperscript{1}, Zhuo Wang\textsuperscript{2} & Luping Yu\textsuperscript{2}

\textsuperscript{1}Argonne National Laboratory
\textsuperscript{2}The University of Chicago

DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting
Washington, D.C., May 9-13, 2011

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline
- Project start: July 2007
- Project end: October 2011
- % complete: 75%

Barriers
- Barriers addressed
  A. System Weight and Volume
  B. System cost
  C. Efficiency
  D. Durability/Operability

Budget
- Total project funding: $2 Million
  - DOE share: $1.88 Million
  - Contractor share: $120 K
- Funding received in FY2010
  - $ 500 K
- Funding for FY2011
  - $ 400 K

Partners
- Interactions/collaborations
  - Argonne National Laboratory (Lead)
  - U of Chicago (Subcontractor)
  - HSCoE Members
    - NREL
    - UNC
  - Non HSCoE Members
    - U of Hawaii (Sample exchange)
    - GM (Sample exchange)
Objective - Relevance

- To design, synthesize, and evaluate nanostructured porous organic polymers (POPs) as new hydrogen storage adsorbents for transportation applications
- To support polymer materials development with modeling/simulation and advanced structural characterizations

Potential Advantages of POP H₂ Adsorbent & Their Impact on Technology Barriers

- **System Weight and Volume** – POPs are light weight and can be converted to high volumetric density by engineering process such as compression, pelletizing, etc.
- **System Cost** – POPs can be scaled-up for industrial production with the existing infrastructure at competitive cost.
- **Efficiency** – POP-H₂ interaction is based on physi-adsorption/desorption principle with minimum parasitic energy consumption.
- **Durability/Operability** – POPs are stable under the temperature and humidity conditions required for hydrogen storage application.
<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestones</th>
<th>Status Update</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/10</td>
<td>Complete the design, synthesis, and characterization of B-doped POPs</td>
<td><strong>80% Completed.</strong> Surface properties, $H_2$ storage capacities and $\Delta H_{ads}$ were investigated for three new three B-doped POPs. Finding is accepted for publication.</td>
</tr>
<tr>
<td>02/11</td>
<td>Complete the synthesis of an ultra-high surface area aromatic POPs</td>
<td><strong>Completed.</strong> Duplicated a literature report on porous aromatic framework as benchmark comparison for POP capacity and heat of adsorption investigation.</td>
</tr>
<tr>
<td>05/11</td>
<td>Complete adsorption kinetics and charging time investigation for selected POPs</td>
<td><strong>Completed.</strong> Adsorption/desorption kinetics of two representative POPs were studied.</td>
</tr>
<tr>
<td>08/11</td>
<td>Complete $H_2$ storage capacity and heat of adsorption optimization through design/synthesis of new metal-doped POPs</td>
<td><strong>60% completed.</strong> Seven new transition metal doped POPs were prepared. Measurement of surface property, $H_2$ adsorption uptake and isosteric heat of adsorption 50% finished.</td>
</tr>
</tbody>
</table>

The focus of FY2011 is to improve and understand the key factor for isosteric heat of adsorption targeting for ambient temperature storage application.
## Approach - Development Strategy

### New Polymer Exploration (UofC/ANL)
- New POP synthesis through rational design at molecular level
- Structure characterization
- Post synthesis modification

### Characterization & Optimization (ANL)
- \( \text{H}_2 \) storage capacity & heat of adsorption measurement
- Surface property characterization
- Engineering process development

### Modeling & Simulation (ANL)
- \( \text{H}_2 \)-POP interaction study via *ab initio*, DFTB & MD methods
- Advanced characterization

---

- Prepare high surface area & narrow/adjustable pore size polymers through rational design and synthesis
- Incorporate “metallic” feature into polymer through conductive backbone or metal doping
- Improve POP-\( \text{H}_2 \) interaction by incorporating heteroaromatic functional groups
- Develop fundamental understanding through modeling and advanced characterization

---

- Over 100 POPs in three categories, aromatic, heteroaromatic and metal doped systems with high surface areas and narrow pore size distribution were designed and prepared
- Hydrogen uptake capacities of 0.055 (kg\( \text{H}_2 \)/kg\(_{\text{ads}} \)) and 0.022 (kg\( \text{H}_2 \)/L\(_{\text{ads}} \)), and the isosteric heat of adsorption of \(~10 \text{ kJ/mol}\) were achieved
- The correlations between surface property, \( \text{H}_2 \) storage capacity and adsorption enthalpy were found through combined experiment/simulation effort for better understanding on \( \text{H}_2 \)-POP interaction
Technical Approach - Summary on Hydrogen Storage via Aromatic POPs

- Over 50 aromatic POPs were prepared, high BET surface (> 3200 m²/g) and tunable pore sizes (7Å to 10Å) achieved.
- H₂ uptakes up to 5.5% at 77K and 0.5% at RT were achieved, heat of adsorptions are usually limited at ~6 kJ/mol.
- High SSA leads to higher gravimetric hydrogen uptake at 77 K, but not necessarily higher volumetric uptake.
Technical Approach - Summary on Hydrogen Storage via Heteroaromatic POPs

- Over 30 heteroaromatic POPs were prepared containing B, N, S, etc., high BET surface (> 1000 m²/g) and narrow pore sizes (~8Å) achieved.
- H₂ uptakes ~ 3% at 77K and the heat of adsorptions > 9 kJ/mol were achieved.
- Improvement of ∆H_ads is element-dependent, for example, S and N → ∆H_ads ↓, B → ∆H_ads ↑.

Nitrogen Sulfur Oxygen Boron

...with high SSA and narrow pore distribution...

...were synthesized using various monomers and crosslinking schemes...

...and element-sensitive H₂ adsorption enthalpy...

...verified by computational modeling.
Technical Approach - Summary on Hydrogen Storage via Metal Doped POPs

POPs with different TM-ligand coordinations were prepared ... for direct hydrogen storage evaluation ...

...or through thermal activation to generate coordinatively unsaturated site...

...to increase uptake capacity and heat of adsorption.

- Over 25 transition metal (Fe, Co, Ni...) doped POPs were prepared with BET surface (~2000 m²/g) and narrow pore sizes (~8Å) achieved
- H₂ uptakes of ~ 4% at 77K and the heat of adsorptions as high as ~ 10 kJ/mol were achieved
- Incorporating TMts clearly improves the isosteric heat of adsorption. New metals (Ti, Mg, V, etc.) and possibly new coordination chemistry need to be explored to enhance ΔH_{ads} in the 15 ~20 kJ/mol range
FY2011 Technical Accomplishment 1 - Design & Synthesis of High Surface Area Carborane-containing POPs

Rationale

- Computational modeling studies from HSCoE suggest non-dissociative binding energy of 19.2 kJ/mol between H₂ and boron doped carbon cluster (Kim, et. al. *Phys. Rev. Lett.* 2006)

- Isotherm and spectroscopic studies from HSCoE found enhanced $\Delta H_{ads}$ over B-doped graphitic carbon (T. Chung, et. al. *JACS* 2008, A. Kleinhammes, et. al. *JPCC* 2010)

- High surface area B-doped polymer can serve as precursor of high SSA adsorbent via further activation

Synthetic Scheme - An Example

HSCoE Studies on H₂ in BC₃ system

$\Delta H_{ads} = 12\sim13$ kJ/mol observed by Chung’s group

Desired B-C framework

Chung – Penn State, HSCoE
FY2011 Technical Accomplishment 1 - Surface Properties & H₂ Storage Capacity of Carborane-containing POPs

BPOP-1, BET SSA = 422 m²/g
BPOP-2, BET SSA = 864 m²/g
BPOP-3, BET SSA = 1037 m²/g

All has narrow Pore distributions...

Pore concentrated @ 7~8 Å by NLDFT analysis

...And robust thermal stability

TGA shows no thermal degradation up to 500 °C
FY2011 Technical Accomplishment 1 - Improving $\Delta H_{ads}$ through B-doped POPs

$H_2$ adsorption isotherms at different $T$

<table>
<thead>
<tr>
<th></th>
<th>BET SSA (m$^2$/g)</th>
<th>Langr. SSA (m$^2$/g)</th>
<th>Tot Pore Vol (cm$^3$/g)</th>
<th>$\mu$-pore Volume (cm$^3$/g)</th>
<th>Pore Diameter (nm)</th>
<th>$H_2$ Gr. Uptake @ 77K (kg$<em>{H_2}$/kg$</em>{ads+H_2}$)</th>
<th>B/C ratio</th>
<th>$\Delta H_{ads}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPOP-1</td>
<td>422</td>
<td>592</td>
<td>0.14</td>
<td>0.04</td>
<td>0.68</td>
<td>0.014</td>
<td>1/1.8</td>
<td>10.2</td>
</tr>
<tr>
<td>BPOP-2</td>
<td>864</td>
<td>1164</td>
<td>0.57</td>
<td>0.30</td>
<td>0.76</td>
<td>0.021</td>
<td>1/1.6</td>
<td>9.0</td>
</tr>
<tr>
<td>BPOP-3</td>
<td>1037</td>
<td>1497</td>
<td>1.12</td>
<td>0.33</td>
<td>0.77</td>
<td>0.028</td>
<td>1/3.0</td>
<td>8.2</td>
</tr>
</tbody>
</table>

- $\Delta H_{ads}$ improves with higher B content in POPs, but it decays quickly with increase of hydrogen loading
- Carborane POPs will be evaluated as precursors of adsorbents with improved $\Delta H_{ads}$ through further activation

$\Delta H_{ads}$ as function of hydrogen uptakes

$\Delta H_{ads}$ was calculated based on isotherm measurements at 195 K and 298 K.
FY 2011 Technical Accomplishment 2 - Design & Synthesis of TM/Polyporphyrin POPs

**Rationale**

- Unsaturated transition metal/hydrogen interaction could form H$_2$\cdot\cdot\cdot$TM$ bond, leading to improved heat of adsorption ($\Delta H_{ads}$) without dissociation (Kubas interaction)
- Computational modelings suggest enhanced $\Delta H_{ads}$ can be achieved by decorating TM in graphene plane (M. Yoon et. al. ORNL) or macrocyclic plane (Kim & Zhang NREL/RPI)
- ANL/UC team successfully prepared and characterized several TM doped POPs with high surface area and narrow pore size distribution

**Synthetic Scheme: Fe-Co/Por**

Fe-Co/Por, BET SSA = 1571 m$^2$/g

**HSCoE theoretical studies on H$_2$ over TM doped surfaces**

Suitable ranges of $\Delta H_{ads}$ for storage are suggested through non-dissociative binding of H$_2$/square-planar TM coordination site
FY 2011 Technical Accomplishment 2 - Design & Synthesis of TM/Polyporphyrin POPs

**Synthetic Scheme: Ni – Polyporphyrins (Ni-Por)**

Ni/Por-1, BET SSA: 1704 m²/g

Ni/Por-2, BET SSA: 572 m²/g

Ni/Por-3, BET SSA: 1033 m²/g

Ni/Por-4, BET SSA: 624 m²/g
FY 2011 Technical Accomplishment 2 - Improving H₂ Storage Capacity & Heat of Adsorption over TM/Polyporphyrin POPs

### H₂ adsorption isotherms for Ni/Por-1 at different T

- **T = 77 K**
- **T = 195 K**
- **T = 298 K**

### Comparison of ∆Hₜₐ₅ as function of H₂ uptakes

- Ni Por-1
- Fe-Co-Por

<table>
<thead>
<tr>
<th></th>
<th>BET SSA (m²/g)</th>
<th>Langr. SSA (m²/g)</th>
<th>Tot Pore Vol (cm³/g)</th>
<th>µ-pore Volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
<th>H₂ Gr. Uptake @ 77K (kgH₂/kg_ads+H₂)</th>
<th>∆Hₜₐ₅ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Por-1</td>
<td>1704</td>
<td>2291</td>
<td>0.91</td>
<td>0.66</td>
<td>0.80</td>
<td>0.034</td>
<td>8.0</td>
</tr>
<tr>
<td>Fe-Co/Por</td>
<td>1571</td>
<td>2098</td>
<td>0.97</td>
<td>0.63</td>
<td>0.80</td>
<td>0.033</td>
<td>7.4</td>
</tr>
</tbody>
</table>

- Transition metal (Ni, Co, and Fe) addition improves ∆Hₜₐ₅, mechanism needs to be studied
- Other promising metals (Ti, V, Mg, etc.) need to be explored with different doping method
FY 2011 Technical Accomplishment 3 - Design & Synthesis of TM/POPs Coordinated through Hydroxyquinoline

**Rationale**

- POPs crosslinked through TM-hydroxyquinoline bonds are very stable towards humidity and other contaminants
- Coordination geometry between TMs and ligand (square-planar vs. tetrahedral) may shed light on hydrogen-metal interaction

**Synthetic Scheme: Metal Coordinated Hydroxyquinoline**

- Co/HQ-1, BET SSA: 580 m²/g; Ni/HQ-1, BET SSA: 596 m²/g
- Other TM/HQ POPs was also prepared with high SSAs
- The tetrahedral (Co) metal-ligand coordination led to POP with a slightly larger pore size than that with square-planar (Ni) ligation
**FY 2011 Technical Accomplishment 3 - Surface Properties, H₂ Storage Capacity & ΔH_{ads} of TM/HQ-1s**

**H₂ adsorption isotherms of Co/HQ-1 at different T**

**Comparison of ΔH_{ads} as function of H₂ uptakes**

Co-hydroxyquinoline POP produced a higher isosteric heat of adsorption (9.9 kJ/mol) than its nickel counterpart, suggesting a possible metal dependent H₂-TM/POP interaction.

<table>
<thead>
<tr>
<th></th>
<th>BET SSA (m²/g)</th>
<th>Langr. SSA (m²/g)</th>
<th>Tot. Pore Vol. (cm³/g)</th>
<th>µ-pore Volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
<th>H₂ Gr. Uptake @ 77K (kg_H₂/kg_{Ads+H₂})</th>
<th>ΔH_{ads} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/HQ-1</td>
<td>596</td>
<td>807</td>
<td>0.59</td>
<td>0.22</td>
<td>0.82</td>
<td>0.017</td>
<td>8.0</td>
</tr>
<tr>
<td>Co/HQ-1</td>
<td>580</td>
<td>786</td>
<td>0.58</td>
<td>0.22</td>
<td>0.87</td>
<td>0.017</td>
<td>9.9</td>
</tr>
</tbody>
</table>
The temporal profiles between adsorption and desorption are nearly identical.

The system reaches equilibrium in a faster pace at ambient temperature than 77 K, all within 20 seconds.
### Summary Table

**H₂ storage capacities for selected POPs by Argonne – UofC Team in FY2011**

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET SSA (m²/g)</th>
<th>Gr. Uptake (77K, 40 bars) (kg H₂/kg adsorbent+H₂ads)</th>
<th>Vol. Uptake a (77K, 40 bars) (kg H₂/kg adsorbent+H₂ads)</th>
<th>Gr. Uptake (RT, 70 bars) (kg H₂/kg adsorbent+H₂ads)</th>
<th>Vol. Uptake (RT, 70 bars) (kg H₂/kg adsorbent+H₂ads)</th>
<th>μ-Pore /Total Pore (cm³/g / cm³/g)</th>
<th>Skeleton Vol. b (cm³/g)</th>
<th>ΔH_ads (kJ/mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAF-1 (A)</td>
<td>3143</td>
<td>0.055</td>
<td>0.020</td>
<td>0.0053</td>
<td>0.0018</td>
<td>1.08/2.08</td>
<td>0.82</td>
<td>6.5</td>
</tr>
<tr>
<td>PTA-3 (H)</td>
<td>870</td>
<td>0.029</td>
<td>0.021</td>
<td>0.0024</td>
<td>0.0017</td>
<td>0.40/0.66</td>
<td>0.80</td>
<td>6.6</td>
</tr>
<tr>
<td>BPOP-1 (H)</td>
<td>422</td>
<td>0.013</td>
<td>0.014</td>
<td>0.0016</td>
<td>0.0017</td>
<td>0.04/0.14</td>
<td>0.81</td>
<td>10.2</td>
</tr>
<tr>
<td>BPOP-2 (H)</td>
<td>864</td>
<td>0.021</td>
<td>0.014</td>
<td>0.0018</td>
<td>0.0012</td>
<td>0.30/0.57</td>
<td>0.94</td>
<td>9.0</td>
</tr>
<tr>
<td>BPOP-3 (H)</td>
<td>1037</td>
<td>0.027</td>
<td>0.016</td>
<td>0.0030</td>
<td>0.0015</td>
<td>0.33/1.12</td>
<td>0.87</td>
<td>8.2</td>
</tr>
<tr>
<td>Ni/Por-1 (M)</td>
<td>1704</td>
<td>0.035</td>
<td>0.021</td>
<td>0.0038</td>
<td>0.0022</td>
<td>0.66/0.91</td>
<td>0.85</td>
<td>8.0</td>
</tr>
<tr>
<td>Fe-Co/Por (M)</td>
<td>1571</td>
<td>0.034</td>
<td>0.022</td>
<td>0.0041</td>
<td>0.0026</td>
<td>0.63/0.97</td>
<td>0.65</td>
<td>7.4</td>
</tr>
<tr>
<td>Ni/HQ-1 (M)</td>
<td>596</td>
<td>0.017</td>
<td>0.015</td>
<td>0.0019</td>
<td>0.0017</td>
<td>0.22/0.59</td>
<td>0.56</td>
<td>8.0</td>
</tr>
<tr>
<td>Co/HQ-1 (M)</td>
<td>580</td>
<td>0.017</td>
<td>0.016</td>
<td>0.0019</td>
<td>0.0017</td>
<td>0.22/0.58</td>
<td>0.53</td>
<td>9.9</td>
</tr>
</tbody>
</table>

A - Aromatic POP; H - Heteroaromatic POP; M - Metal doped POP

a. Volumetric capacity is calculated based on the measured skeleton density plus total pore volume density.
b. Skeleton volume is measured using helium as calibration gas.
c. Rate of ΔH_ads (kJ/mol) change as function of gravimetric uptake Cg (%) at ambient temperature near the zero coverage point.

- System with the highest gravimetric capacity does not necessarily have the highest volumetric capacity
- Transition metal and boron doping can improve adsorption enthalpy
Collaboration

Partnership within and outside of Hydrogen Sorption Center of Excellence

- Teaming between Argonne National Laboratory (prime) and The University of Chicago (subcontractor)
- Members of DOE HSCoE under the clusters of “Engineered Nanospace” (RC1) and “Substituted Materials” (RC2)
- Collaboration with UNC (HSCoE member) on $^1$H NMR experiment
- Collaboration with NREL (HSCoE member) on measurement validation
- Information exchange with ORNL (HSCoE member) and RPI on computational modeling and simulation

Technology Transfer through HSCoE

- Valuable inputs on our adsorption apparatus test validation
- New ideas and direction, examples include B and metal doped polymers
- Collaboration opportunities in polymer characterization, examples include NMR study
- Up-to-date information on new developments in sorption based materials
Future Work

- Complete the investigation on TM exchanged polyporphyrin POPs
- Complete the investigation on improving heat of adsorption for B-doped POP via activation
- Evaluate potential application of other emerging technologies to sorption based hydrogen storage and recommend further research direction to DOE
- Prepare final project report

FUTURE DIRECTION

- POP is becoming a great platform as hydrogen adsorbent due to its high surface area and narrow pore (vs. carbon) and excellent chemical stability (vs. MOF)
- Unmodified aromatic POPs will unlikely reach desired $H_2$ adsorption enthalpy for room temperature application even with increased surface area or adjustable porosity
- To achieve near-ambient temperature application, the surface of POP needs to be modified by incorporating metal or other elements promoting $H_2$ binding
- New surface modification techniques, departing from the conventional synthetic approaches, have the potential to produce high binding energy sites predicted by theory
- POPs with tailored surface property and chemical composition can also serve as precursor of fabricating new adsorbent after additional chemical/physical processing