New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

Randall Snurr, Joseph Hupp, Mercouri Kanatzidis, SonBinh Nguyen
Northwestern University

May, 2012
Overview

Timeline
• Start date: 9/1/2008*
• End date: 8/31/2012
• 80% complete*

Barriers Addressed
• Hydrogen storage
  – Gravimetric target
  – Volumetric target
  – Increased heat of adsorption

Budget
• Total project funding
  – DOE share: $1,295,491
  – Contractor share: $323,875
• FY11 Funding: $300,000
• FY12 Funding: $220,493

Partners
• Juergen Eckert, University of South Florida
• Joe Zhou, Texas A&M
• NREL

* 9/1/2008 is official start date. Initial funding received March 2009.
Relevance

Overall Project Objectives

• Develop new materials to meet DOE volumetric and gravimetric targets for hydrogen storage
  • Metal-organic frameworks (MOFs)
  • Polymer-organic frameworks (POFs) or porous organic polymers (POPs)

• Our view is that room-temperature hydrogen storage sorbents must have **both**
  • High heats of adsorption and
  • High surface area
Objectives for Current Year

• MOFs and POFs
  – Obtain external validation of hydrogen uptake at 77 K in the MOF NU-100: 9.0 wt% and 28 g/L excess measured in our labs last year
  – Develop high surface area materials for cryogenic storage
  – Develop high surface-area materials containing functional groups that can bind hydrogen at room temperature

• Modeling
  – Aid in the development of high surface area materials
  – Screen different cations and cation environments for their ability to bind hydrogen and the resulting storage capacities
  – Assess interplay between high surface area, pore size, and strongly-binding sites on overall performance

Relevance
Approach

Snurr
Computational elucidation, design and modeling

Hupp
Synthesis and characterization of MOFs

Kanatzidis
Synthesis and characterization of POFs

Nguyen
Design and synthesis of SBUs for MOF and POF assembly

External Partners:
• Juergen Eckert, Univ. of South Florida
• Joe Zhou, Texas A&M
• NREL
Approach

1. Enhance heats of adsorption via introduction of cations and strong electric fields
   • “Zwitterionic” MOF
   • Introduction of cations via framework reduction
   • Introduction of cations via linker functionalization
     These techniques were pioneered by members of our team at Northwestern University

2. Enhance H$_2$ capacity by increasing surface area
   • Activation via supercritical drying has been essential
   • This technique is now used by other groups

3. Combine chemistries for high heats of adsorption and high surface areas to increase room temperature hydrogen storage
Status

Go/No-Go Decision: August 2010 → Go
Project End: August 2012

Some Key Milestones Achieved:
• Synthesized POFs with surface areas of >1500 m²/g.
• Achieved 10 kJ/mol heat of adsorption with little or no drop-off at higher coverages (no less than 6 kJ/mol at highest coverage).
• Determined that catenation is generally not beneficial for hydrogen uptake in MOFs without cations.
• Developed model for MOFs containing cations.
• Achieved material gravimetric capacity of >8 wt.% (excess) at 77 K and 100 bar. Result validated at NREL.
Technical Accomplishments: Outline

• Very high surface area materials and cryogenic hydrogen storage
  – Validation of record cryogenic uptake
  – A new MOF designed for cryogenic storage below 35 bar

• Materials with highly-exposed metal cations
  – New synthetic chemistries
  – Computational investigations
  – High-throughput computational screening
Last Year: MOF NU-100

Hydrogen uptake at 77 K

Excess 99.5 mg / g
9 wt%
28 g/L

Total 164 mg / g
14 wt%
45 g/L

Validation of NU-100 at NREL

\[ + \text{Cu(NO}_3\text{)}_2 \rightarrow \text{DMF} \]

\[ \text{N}_2 \text{ Adsorption (cc/g)} \]

\[ 77 \text{ K} \]

\[ \text{Pressure (P/Po)} \]

[Graph showing N\(_2\) Adsorption at 77 K with a comparison between NREL and Northwestern results]
Due to time constraints during the verification process at NREL, approximately 200 mg of NU-100 was activated using a Samdri® PVT-3D supercritical point dryer. Typically, no more than 100 mg of MOF is activated at once. It is believed this extra sample led to the lower surface area observed, as the amount of ethanol within the sample could not be fully exchanged in the amount of time the sample was in the dryer. A slight correction (factor of 1.12) is applied to the nitrogen isotherm taken at NREL in the graph above, showing an overlap in the two isotherm curves.
Validation of NU-100 at NREL

77 K

Excess H₂ Adsorption (wt%)

Excess H₂ Adsorption (g/L)

Pressure (P/P₀)

Northwestern
NREL as Measured
NREL Corrected

Northwestern
NREL as measured
NREL Corrected
Validation of NU-100 at NREL

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area (m²/g)</th>
<th>Excess H₂ Uptake at 77 K (wt%)</th>
<th>Excess H₂ Uptake at 77 K (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northwestern</td>
<td>6143</td>
<td>9.0</td>
<td>28.9</td>
</tr>
<tr>
<td>NREL</td>
<td>5360</td>
<td>7.9</td>
<td>24.8</td>
</tr>
<tr>
<td>NREL (Corrected for surface area)</td>
<td>6143*</td>
<td>8.8*</td>
<td>27.8*</td>
</tr>
</tbody>
</table>

*Normalized on the basis of difference in surface area between the Northwestern sample and the NREL sample

These are among the highest (if not the highest) validated values reported to date for excess hydrogen uptake at 77 K.
There is very good agreement between the simulated and experimental isotherms.
“The F125 promises a top speed of 137 miles per hour, 0 to 62 in 4.9 seconds, and 100 kilometers on 0.79 kilograms of hydrogen (or 621 miles on a full tank).”

The F125 reportedly will use MOF-based adsorption for cryogenic H₂ storage. Mercedes’ MOF requirements:
- Maximum pressure of 435 p.s.i. → ~30 bar

*Note the low P*
NU-111: Low-Pressure Cryogenic H₂ Adsorption

- 3,24 net (like NU-100)
- 5,000 ± 80 m²/g
- Excess H₂ uptake peaks at ~35 bar
It is important to include the FH quantum diffraction corrections in the simulations.
Stable to Repetitive Pressure Cycling, Temperature Cycling, Storage, and Shipping

Excess H$_2$ isotherms measured at 303 K at NREL → no change

Measured at NU before and after studies at NREL

Excess H$_2$ isotherms measured at 303 K at NREL
Improved Heats of Adsorption for Room-Temperature Storage

Possible mechanisms to exploit:

• Enhanced London dispersion interactions due to enhanced strut polarizability
• Enhanced adsorption based on increased electric fields in the pores
• Enhanced adsorption due to charge/quadrupole interactions

The major technical and scientific challenge in this area is to increase the heat of adsorption of H$_2$ to ca. 15-25 kJ/mol to enable high loading at ambient temperature.
Improved Heats of Adsorption for Room-Temperature Storage

During the past year, we have tested a variety of synthetic strategies for introducing exposed divalent cations into MOFs and POPs via linker functionalization.

The following 2 slides show 2 examples. More examples are given in the backup slides.

Status:
• Successful metal incorporation
• Heats of adsorption increase upon metal incorporation but are lower than expected, perhaps due to residual solvent molecules blocking access to the metal atoms
Catechol-based POP

\[
\begin{align*}
\text{A} + \text{B} & \rightarrow \text{A}_2\text{B}_1 \text{ quant- yield} \\
& \quad \text{A}_{10}\text{B}_1 \text{ quant- yield} \\
& \quad \text{A}_1\text{B}_2 \text{ quant- yield}
\end{align*}
\]

\[
\begin{align*}
\text{1) } \text{Co}_2(\text{CO})_8 & \quad \text{1,4-Dioxane} \\
& \quad 100 \, ^\circ \text{C} \\
\text{2) } \text{conc. HCl} & \quad \text{A}_{2}\text{B}_1 \text{ quant. yield} \\
& \quad \text{A}_{10}\text{B}_1 \text{ quant. yield} \\
& \quad \text{A}_1\text{B}_2 \text{ quant. yield}
\end{align*}
\]

\[
\begin{align*}
\text{1) } \text{M}^{2+} & \quad \text{THF} \\
& \quad 200 \, ^\circ \text{C} \text{ vacuum} \\
\text{2) } \text{vacuum} & \quad \text{MA}_{2}\text{B}_1 \rightarrow 10.9 \, \text{wt\% Mn} \\
& \quad \text{MA}_{10}\text{B}_1 \rightarrow 21.8 \, \text{wt\% Mn}
\end{align*}
\]

Mn-POP shows higher Qst than non-metallated POP, at both low and high loadings

Weston et al. Chem. Mater. 2012, ASAP
Melamine-based POP

Mn-POP shows slightly higher Qst than non-metallated POP, but only at low loading
Computational Screening

• Functionalizing linkers with highly exposed Mg$^{2+}$ sites is predicted to improve H$_2$ uptake at room temperature.

\[ \Delta \text{wt}\% (P_{H_2}) = \text{wt}\% (P_{H_2}) - \text{wt}\% (2 \text{ bar}) \]

\[ \Delta \text{gH}_2 \text{ L}^{-1} (P_{H_2}) = \text{gH}_2 \text{ L}^{-1} (P_{H_2}) - \text{gH}_2 \text{ L}^{-1} (2 \text{ bar}) \]

• What is the best combination of metal type, metal loading, pore size, surface area, etc. to maximize gravimetric and volumetric deliverable capacity?

\[ \Delta \text{wt}\% (P_{H_2}) = \text{wt}\% (P_{H_2}) - \text{wt}\% (2 \text{ bar}) \]

\[ \Delta \text{gH}_2 \text{ L}^{-1} (P_{H_2}) = \text{gH}_2 \text{ L}^{-1} (P_{H_2}) - \text{gH}_2 \text{ L}^{-1} (2 \text{ bar}) \]

• In previous work,* we fit quantum mechanical energies (MP2 level) to a force field for use in grand canonical Monte Carlo (GCMC) simulations. We can use the GCMC simulations to answer these questions.

Predicted $\text{H}_2$ Absolute Capacity

Higher degree of functionalization leads to increased absolute $\text{H}_2$ uptake and outperforms the unfunctionalized MOFs.

<table>
<thead>
<tr>
<th>MOF</th>
<th>SA (m$^2$/g)</th>
<th>Largest Pore (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NU-100</td>
<td>5813</td>
<td>27.4</td>
</tr>
<tr>
<td>UiO-68</td>
<td>4082</td>
<td>15.8</td>
</tr>
</tbody>
</table>

$\text{H}_2$ Adsorption Isotherms from GCMC Simulations (243 K)
The deliverable gravimetric capacity does not necessarily increase with higher degree of functionalization.

**Predicted H$_2$ Deliverable Capacity**

H$_2$ Adsorption Isotherms from GCMC Simulation (243 K)
Predicted H₂ Deliverable Capacity

The deliverable volumetric capacity does not necessarily increase with higher degree of functionalization.

H₂ Adsorption Isotherms from GCMC Simulation (243 K)
High-Throughput Computational Screening of MOFs

Crystal generator for hypothetical MOFs
• Comprehensively enumerates all possible structures from a library of building blocks
• Creates a large database of hypothetical MOFs

High-Throughput Computational Screening of MOFs

- First demonstration was for methane storage in another project*
- Now add Mg-functionalized linkers for hydrogen storage

- Linkers can have varying degrees of functionalization
- Currently performing GCMC simulations for > 16,000 MOFs
  - H₂ adsorption at 243 K
  - Deliverable capacity: 100 bar – 2 bar absolute adsorption

Preliminary results:
• Deliverable gravimetric capacity increases with void faction
• Deliverable volumetric capacity has a maximum around 0.75 void fraction
High-Throughput Computational Screening of MOFs

Preliminary results for optimum density of Mg alkoxide groups
Collaborations

• NREL
  – Lin Simpson, Philip Parilla
  – Validation of high pressure sorption measurements

• University of South Florida
  – Juergen Eckert
  – Neutron scattering
  – Manuscript in preparation

• Texas A&M University
  – Joe Zhou
  – Combined modeling and experimental development of a high surface area MOF (joint paper published*)
  – Assistance with supercritical activation

Future Work

Planned work:

• Continue efforts to increase heats of adsorption via metal incorporation in MOFs and POFs
• Continue to measure H$_2$ uptake and heats in new materials
• Measure high-pressure, room-temperature isotherms in most promising materials
• Determine optimal combination of heat of adsorption, surface area, pore size, etc. via high-throughput computational screening
• Model diffusion in cation-containing MOFs
• Model “out-of-the-box” ideas
Summary

• We are developing new materials to meet DOE hydrogen storage targets. The new concept is to introduce cations into MOFs and POFs to **improve heats of adsorption** (which will improve room temperature storage) along with **high surface areas** (which are needed for high hydrogen capacity).

• We have synthesized a variety of new MOFs
  – Functional groups can be tailored to increase the $\text{H}_2$ heat of adsorption
  – Achieved 11 kJ/mol heat of adsorption at low loading (zwitterionic MOF)
  – Achieved 14 wt% and 45 g/L (absolute) at cryogenic temperatures (NU-100 MOF)

• We have synthesized a variety of new POFs
  – Functional groups can be tailored to increase the $\text{H}_2$ heat of adsorption
  – Achieved 1500 m$^2$/g
  – Achieved 9 kJ/mol heat of adsorption at low loading

• We have developed useful models for functionalized MOFs
  – Alkaline earth and transition metal alkoxide groups are promising targets
  – Modeling can be used to design MOFs on the computer before their synthesis
  – High-throughput computational screening looks very promising
## Summary

<table>
<thead>
<tr>
<th></th>
<th>March 2011</th>
<th>March 2012</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface Area (m²/g)</strong></td>
<td>6143</td>
<td>6143</td>
</tr>
<tr>
<td><strong>Isosteric Heat of Adsorption at Low Loading (kJ/mol)</strong></td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td><strong>Excess H₂ Uptake at 77 K and 70 bar (wt%)</strong></td>
<td>9.0 Measured in our labs</td>
<td>7.9 Validated at NREL</td>
</tr>
<tr>
<td><strong>Excess H₂ Uptake at 77 K and 70 bar (g/L)</strong></td>
<td>28 Measured in our labs</td>
<td>25 Validated at NREL</td>
</tr>
<tr>
<td><strong>Modeling</strong></td>
<td>Screening dozens of MOFs</td>
<td>Screening &gt;16,000 MOFs</td>
</tr>
</tbody>
</table>
Technical Backup Slides
Snapshots of H$_2$ in NU-111 from GCMC Simulations at 77 K

A
1 bar

B
10 bar

C
100 bar

$H_2$ uptake (mg/g)

- NU-111 Excess
- NU-111 Absolute

Pressure (bar)

1 bar 10 bar 100 bar
POFs with –OH functional groups

- Microporous POFs with –OH functional groups
- Heat of H₂ adsorption is 8.3 kJ/mol at low coverage
- Na⁺ exchanged POF exhibits heat of H₂ adsorption of 9 kJ/mol at low coverage
Metalation of POFs

- Metalation of POF with acetate salts
- Content of metal ~ 4-8% wt.
- All metalated POFs are microporous

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal content (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POF Mn</td>
<td>7.7</td>
</tr>
<tr>
<td>POF Co</td>
<td>4.5</td>
</tr>
<tr>
<td>POF Ni</td>
<td>4.4</td>
</tr>
<tr>
<td>POF Cu</td>
<td>8.1</td>
</tr>
</tbody>
</table>
Heat of H₂ Adsorption of Me-POF

- Metalated POFs with Mn, Co and Cu show heat of H₂ adsorption at low coverage in the range ~9 kJ/mol.
- Co-POF exhibits high heat of adsorption, which is stable over the whole adsorption range.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat of H₂ adsorption (kJ/mol)</th>
<th>Total uptake of H₂ (% wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POF Mn</td>
<td>8.9 – 6.1</td>
<td>0.78</td>
</tr>
<tr>
<td>POF Co</td>
<td>9.0 – 7.9</td>
<td>0.92</td>
</tr>
<tr>
<td>POF Ni</td>
<td>8.3 – 6.3</td>
<td>1.02</td>
</tr>
<tr>
<td>POF Cu</td>
<td>8.8 – 7.2</td>
<td>0.75</td>
</tr>
<tr>
<td>POF</td>
<td>8.3 – 6.9</td>
<td>1.25</td>
</tr>
</tbody>
</table>