Hydrogen Storage through Nanostructured Polymeric Materials

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Overview

Timeline

- Project start: July 2007
- Project end: June 2012
- % complete: 40%

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 FY08
  - $ 516 K (operation)
  - $100 K (equipment)
- Funding for FY09
  - $ 800 K

Partners

- Interactions/collaborations
  - Argonne National Laboratory (Lead)
  - U of Chicago (Subcontractor)
  - HSCoE Members
    - U of N. Carolina (1H NMR)
    - NIST (Neutron)
    - Air Products (Sample exchange)
**Objective**

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

**Potential Advantages of Polymeric H₂ Adsorbent & Their Impacts to Technology Barriers**

- **System Weight and Volume** – Polymers are light weight and can be converted to high volumetric density by engineering process such as compression, pelletizing, etc.
- **System Cost** – Polymer can be scaled-up for industrial production with the existing infrastructure at competitive cost.
- **Efficiency** – Polymeric adsorbent is based on physi-adsorption/desorption principle with minimum parasitic energy consumption.
- **Durability/Operability** – Polymeric materials are stable under the temperature and humidity conditions required for hydrogen storage application.
**Milestones**

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestones</th>
<th>Status Update</th>
</tr>
</thead>
<tbody>
<tr>
<td>05/08</td>
<td>Complete the surface property and hydrogen storage capacity measurement of the benchmark materials</td>
<td><strong>Completed.</strong> Several published materials including MOF and polymers were duplicated and tested.</td>
</tr>
<tr>
<td>08/08</td>
<td>Initiate theoretical simulation of the interactions between hydrogen and model polymer systems</td>
<td><strong>Completed.</strong> Preliminary modeling on conjugated polymer and metal doped systems were completed at Argonne.</td>
</tr>
<tr>
<td>08/08</td>
<td>Complete design and synthesize two or more new porous polymer materials with targeted hydrogen uptake capacity of 3% at 77 K and 1% at 298 K</td>
<td><strong>Completed.</strong> Three classes of polymers with over 50 different structures and synthesis schemes were prepared and characterized. H\textsubscript{2} updates of 5.1% at 77K and 0.5% at RT were achieved, a major improvement over FY08 results.</td>
</tr>
<tr>
<td>05/09</td>
<td>Complete surface area and hydrogen uptake measurements for the first batch of metal-doped porous polymers</td>
<td><strong>60% completed.</strong> BET, H\textsubscript{2} uptake and (\Delta H_{ads}) studies of the representative samples are completed. Measurement is underway for other samples</td>
</tr>
<tr>
<td>08/09</td>
<td>Complete quantum chemical study at MP2/DFT level of hydrogen adsorption on polymer model with transition metal sites</td>
<td><strong>50% completed.</strong> The modeling on doped metal system is finished. Work on synthesized system will start soon.</td>
</tr>
<tr>
<td>09/09</td>
<td>Complete the improvement for the new polymers to reach H\textsubscript{2} adsorption capacity of 1.5 wt.% at the ambient temperature &amp; 100 bars</td>
<td><strong>20% completed.</strong> Focus is now on polymers with variable pore size, metal and other non-C element incorporation. Other modification methods are under evaluation.</td>
</tr>
</tbody>
</table>

We significantly expanded synthesis effort leading to > 50 new polymers produced with nearly doubled surface area and H\textsubscript{2} storage capacity over last AMR report!
Approach

**New Polymer Exploration (UofC/ANL)**
- New polymer synthesis through rational design at molecular level
- Molecular structure characterization

**Measurement & Optimization (ANL)**
- H₂ storage capacity measurement
- Surface structure characterization
- Synthesis method improvement

**Modeling & Characterization (ANL/HSCoE)**
- H₂-polymer interaction study via *ab initio*, DFTB & MD methods
- Advanced characterization through NMR, neutron, x-ray, etc.

- Preparing 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 polymer-H₂ interaction by incorporating functional groups with hetero (non-C) elements
- Develop fundamental understanding through modeling and advanced characterization

*An example of ANL/UofC polymer with conductive backbone incorporated with different elements*
Progress Update – Porous Polymers Prepared from Aromatic Monomers

- A variety of monomers and synthesis methods were used to fine-tune the surface area and porosity, including contorted monomers, Friedel-Crafts reaction, etc.
- Over 20 porous polymers with different 3-D structures were prepared with simple aromatic building blocks.
- Studies on correlation between surface properties & H₂ adsorption capacity/energy is underway.

3-D structures of selected aromatic polymers prepared at Argonne and U of Chicago

High surface area (1000 M²/g ~ 1800 M²/g) & narrow pore size (6Å to 10Å) were achieved!
Progress Update – Design, Synthesis & Surface Properties of Porous Polymers from Aromatic Monomers

Majority of polymers showed narrow pore size distribution following our design principle. Systematically controlling pore dimension for better H₂ trapping is underway.

**Progress Update – $H_2$ Storage Capacity Measurements**

Excess $H_2$ adsorption measurements at 77K and 87K*

- Adsorption reaches saturation at relatively high equilibrium pressure.
- Desorption is completely reversible down to 2 bar.

*Solid symbol – adsorption: Hollow symbol – desorption
Progress Update – Isosteric Heat of Adsorption Derived from Experiment & Theory: A Case Study

$\Delta H_{\text{ads}}$ from experiment

$\Delta H_{\text{ads}}$ from theory

<table>
<thead>
<tr>
<th># H$_2$/unit cell</th>
<th>Gr. uptake (%)</th>
<th>$\Delta H_{\text{ads}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.4</td>
<td>6.77</td>
</tr>
<tr>
<td>11</td>
<td>2.2</td>
<td>6.53</td>
</tr>
<tr>
<td>21</td>
<td>4.2</td>
<td>5.29</td>
</tr>
</tbody>
</table>

DFT calculations (PW91)

- Experimentally determined $\Delta H_{\text{ads}}$ demonstrated dependence on H$_2$ coverage.
- DFT calculation correctly predicted the same trend.
**Progress Update – Theoretical Investigation of H₂-Polymer Interaction**

Polymer structure optimization and interaction with H₂

Partial radial distribution function (RDF) of H₂ in adsorbent

- Optimized 3-D structure through DFT duplicated the experimental pore size.
- RDF calculation revealed the interatomic distance changes between H₂ & adsorbent.
- Further study will include the prediction of H₂ packing limit.
Progress Update – Porous Polymers Containing Transition Metals

- To promote the orbital interaction between $\text{H}_2$ and adsorbent, transition metals were atomically dispersed into nanoporous space within the polymers.
- Fifteen samples were designed and prepared containing transition metals ($M = \text{Co, Ni, Fe, Cu, etc}$).
- Metals were incorporated either through post-doping or direct synthesis.
Progress Update – Porous Polymers Containing Transition Metals

- Post-doping: building ligation site on polymer followed by metal addition
- Direct synthesis: Incorporating metal into polymer through cross-linking of organometallic monomers

BET surface areas of selected polymers

New cross-linking chemistry of metal-containing monomers resulted in significant enhancement in surface area! Improvement of synthesis is on-going.
Progress Update – $H_2$ Uptake Isotherm & Isosteric Heat of Adsorption Measurements for Metal-containing polymer

Excess $H_2$ adsorption measurements at 77K and 87K*

Isosteric heat of adsorption as the function of hydrogen loading

*Solid symbol – adsorption: Hollow symbol – desorption

Decreasing heat of adsorption with the increase of storage capacity suggests additional $H_2$ are spread to the weaker binding sites, possibly away from metal center.
Computational modeling of strong binding of H₂ to Co in a polymer unit with atomically substituted cobalt

Binding Energy: 75 (79)

Binding energy: 46 (146)

 Binding Energy: 113 (125)

* Binding energy relative to H₂ in kJ/mol; Theory level: B3LYP/6-31G*/B3LYP/6-31G* (PW91/g4mp2large//B3LYP/6-31G*); g4mp2large is a triple-zeta basis set

** Both non-dissociative and dissociative adsorptions of H₂ on PBPY2 are favorable; Dissociation becomes less exothermic with the increase in number of H₂
Progress Update – Porous Polymers Prepared from Monomers with Non-C Element

- To generate “dipole” - “induce dipole” and electronic interactions, non-C element substitution is used to create C-X bonds (X = N, S, B, P, O, ...) within the nano-space of polymers.
- Over 20 such porous polymers with different 3-D structures were designed and prepared.

3-D structures of selected polymers with non-C element prepared at Argonne and U of Chicago
Contorted core approach enables successful substitution of N, S, etc. while maintaining high surface areas and narrow pore diameters. New approaches include B-substitution.
Progress Update – Volumetric Capacity Study

Density ~ SSA changes under compression - a case study, \( P = 50,000 \text{ lb/in}^2 \)

![Graph showing density vs. surface area before and after compression for two samples.]

**Polymer compression does not cause major changes in microporosity and SSA**

<table>
<thead>
<tr>
<th>Polymer Sample I</th>
<th>Polymer Sample II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/mL)</td>
<td>Surface Area (M²/g)</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>Surface Area (M²/g)</td>
</tr>
<tr>
<td><strong>Before</strong></td>
<td><strong>After</strong></td>
</tr>
<tr>
<td>0.208</td>
<td>0.503</td>
</tr>
<tr>
<td>1861</td>
<td>640</td>
</tr>
<tr>
<td>1.44</td>
<td>1.14</td>
</tr>
<tr>
<td>1805</td>
<td>634</td>
</tr>
</tbody>
</table>

**Correlations between gravimetric & volumetric capacities vs. adsorbent density**

**Pelletizing polymer can significantly enhance volumetric capacity!**
Collaboration

Partnership with Hydrogen Sorption Center of Excellence

- Team – 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
- Planned experiment with NIST (HSCoE member) on neutron study
- Sample exchanges with NREL and Air Products (HSCoE members) on measurement validation and benchmark material

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 & neutron studies
- Up-to-date information on new developments in sorption based materials
High pressure $^1$H NMR study on ANL-UofC polymer performed by Kleinhammes/Wu (U of North Carolina)

Sample = contorted aromatic polymer, UC-C6
SSA = 760 M$^2$/g

Free H$_2$

Adsorbed H$_2$

$E_B$ : 6.7 kJ/mol

More collaborations of H$_2$-polymer interaction studies by NMR & Neutron are underway!
Future Work

**FY09**
- Improve H$_2$-adsorbent interaction through pore size control and rational design
- Explore new synthesis methods for metal-containing polymers and to investigate the structure-heat of adsorption correlations
- Refine modeling on H$_2$-adsorbent interaction, provide guidance to the polymer design
- Investigate the kinetics and transient properties of hydrogen adsorption over polymers

**FY10**
- Explore new non-C element substituted polymers for higher adsorption energies and storage capacity
- Continue to collaborate with HSCoE in structural & mechanistic studies (e.g. NMR, neutron, etc.)
- Explore new polymer activation methods to enhance surface property and storage capacity
Summary

Relevance: Developing the nanostructured porous polymers as H₂ storage media to meet DOE performance targets for transportation applications

Approach: Rational design and synthesis at the molecular level supported by computational modeling and advanced characterization

Accomplishments:
- Over 50 polymers from three different categories were prepared since last AMR with high surface areas (up to 1800 m²/g) and narrow pore sizes (6Å to 10Å) achieved.
- H₂ uptakes up to 5.1% at 77K and 0.5% at RT were achieved, representing significant improvement over last AMR report.
- Combined ΔH_{ads} measurement & computational modeling improved understanding on adsorption mechanism.

Collaboration: Argonne (prime) and U of Chicago (sub) partnering with HSCoE, information dissemination & experimental collaboration

Future Work:
- Continue new polymer exploration and optimization
- Explore the “hidden capacity” through activation approach
- Improve the understanding of H₂-polymer interaction via theory & advanced characterization
## Summary Table

**H₂ storage capacities for selected ANL – U of Chicago polymers**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gr. Uptake (77K, 40 bars) (kg H₂/kg adsorbent+H₂ads)</th>
<th>Vol. Uptake a (77K, 40 bars) (kg H₂/L adsorbent)</th>
<th>Gr. Uptake (RT, 70 bars) (kg H₂/kg adsorbent+H₂ads)</th>
<th>Vol. Uptake a (RT, 70 bars) (kg H₂/L adsorbent)</th>
<th>BET SSA (M²/g)</th>
<th>Type of polymer b</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANL-C1</td>
<td>4.0%</td>
<td>0.010</td>
<td>0.21%</td>
<td>0.0005</td>
<td>1233</td>
<td>C</td>
</tr>
<tr>
<td>ANL-C2</td>
<td>4.4%</td>
<td>0.009</td>
<td>0.35%</td>
<td>0.0007</td>
<td>1593</td>
<td>C</td>
</tr>
<tr>
<td>ANL-C5</td>
<td>5.1%</td>
<td>0.011</td>
<td>0.52%</td>
<td>0.0012</td>
<td>1863</td>
<td>C</td>
</tr>
<tr>
<td>UC-C10</td>
<td>2.8%</td>
<td>0.010</td>
<td>0.18%</td>
<td>0.0006</td>
<td>1043</td>
<td>C</td>
</tr>
<tr>
<td>UC-X4</td>
<td>3.2%</td>
<td>0.0085</td>
<td>0.45%</td>
<td>0.0012</td>
<td>971</td>
<td>X</td>
</tr>
<tr>
<td>UC-M12</td>
<td>3.6%</td>
<td>0.0051</td>
<td>0.40%</td>
<td>0.0006</td>
<td>1060</td>
<td>M</td>
</tr>
</tbody>
</table>

a. Volumetric capacity is calculated based on the actual density of loose polymer powders, which ranges from 0.15 to 0.5. These capacities can be increased by x2 to x5 through compression.

b. C = polymers contains only aromatics, X = polymers with non-C element substitutions, M = polymers incorporated with transition metals
Additional Slides
Supplemental Info – An example of our effort in controlling pore size through new synthetic approach

Experimental pore sizes (NLDFT) calculated from N2-BET measurement

Pore diameters can be varied by using different synthetic precursors and techniques
Supplemental Info – Benchmark study on H₂ storage capacity of a Cu-MOF

H₂ uptake of Cu-BTC measured with our Sievert apparatus showed the same capacity and P-dependent saturation as the published results.