Hydrogen Storage through Nanostructured Polymeric Materials

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Overview

Timeline
- Project start: July 2007
- Project end: June 2012
- % complete: 20%

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 FY07
  - $ 200 K
- Funding for FY08
  - $ 616 K

Partners
- Interactions/collaborations
  - U of Chicago
  - DOE HSCoE Members
  - NREL
  - N. Carolina U.
  - Others
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 $H_2$ Adsorbent

- Polymer surface properties such as specific surface area and porosity can be controlled at molecular level
- Polymer-hydrogen can be enhanced through incorporating different functional groups and atomically dispersed metals
- Polymers are generally stable under the temperature and humidity required for hydrogen storage application
- Polymer can be scaled-up for production with existing industrial infrastructure

Selected Literature Reports on Polymeric $H_2$ Adsorbent

**Approach**

**Argonne/U of Chicago Approach to Polymer Design**

- We will produce high surface area & narrow pore size through stereo-contorted polymer design
- We will incorporate “metallic” feature to polymer through conductive backbone
- We will improve polymer-H₂ interaction with by Introducing coordinated metal elements and various functional groups through synthetic approach
- We will explore the feasibility of “trapping” hydrogen through semi-rigid framework

*An example of ANL/UofC polymer with conductive backbone incorporated with different elements*

**Control surface property and the interaction with hydrogen through design & synthesis at the molecular level!**
Approach

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

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

Modeling & Simulation (ANL)
- H₂-polymer interaction study via ab initio, DFTB & MD methods
- Advanced X-ray characterization
Progress Summary

- Three series of porous polymers based on our design principles were successfully synthesized. Two groups showed promising surface properties (U of Chicago)

- Specific surface area and porosity of 11 polymer samples were measured, some of which showed high SSA and narrow pore distribution (Argonne)

- Upgrade of Sievert isotherm apparatus and analysis method were completed. System is now used for high pressure (up to ~75 bar) measurement (Argonne)

- Hydrogen uptake of several polymers were measured at both RT and 77K with pressure up to 75 bars. A carbon molecular sieve (CMS) material was also investigated as the reference material (Argonne)

- Theoretical modeling/simulation study was initiated (Argonne)
Progress – Design & Synthesis of Porous Conjugated Polymers

- Seven porous polymers with conjugated aromatic planes were designed and synthesized.
- Porosity was created and controlled through cross-linking of monomers with different stereo-contorted structures.
- Polymer samples have demonstrated good surface properties and high stability towards heat and moisture.

Proposed Structures of the Selected Examples

PC1

PD2
Progress – Surface Property Characterization for Conjugated Porous Polymers

N\textsubscript{2}-BET Surface Characterization

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area (m\textsuperscript{2}/g)</th>
<th>Total Pore Volume (cm\textsuperscript{3}/g)</th>
<th>Median Pore Diameter (nm)</th>
<th>Density (g/cm\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC2</td>
<td>468</td>
<td>0.265</td>
<td>0.76</td>
<td>0.66</td>
</tr>
<tr>
<td>PD2</td>
<td>762</td>
<td>0.425</td>
<td>0.64</td>
<td>0.39</td>
</tr>
<tr>
<td>PC1</td>
<td>769</td>
<td>0.427</td>
<td>0.62</td>
<td>0.66</td>
</tr>
<tr>
<td>PC2b</td>
<td>818</td>
<td>0.498</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>PQ1</td>
<td>1043</td>
<td>---</td>
<td>---</td>
<td>0.38</td>
</tr>
<tr>
<td>PM1</td>
<td>517</td>
<td>---</td>
<td>---</td>
<td>0.42</td>
</tr>
<tr>
<td>PL1</td>
<td>758</td>
<td>---</td>
<td>---</td>
<td>0.46</td>
</tr>
<tr>
<td>CMS</td>
<td>837</td>
<td>0.423</td>
<td>0.47</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Relatively high surface area and narrow pore distribution can be achieved through rational polymer design. Further improvement is still necessary.
Progress – Design & Synthesis of Polymers with Conductive & Polyimide Backbones

- Five porous polymers with conductive or polyimide backbones were designed and synthesized with the goal of enhancing hydrogen-functional group interaction.
- Polymers prepared with spiral core linked by thiophene and bi-thiophene groups demonstrated relatively high surface area and promising pore size distribution.
- The surface property of the polymers with imide group were mixed.

Proposed Structures of Selected Polymers

PE3

PG1
Progress – Surface Property Characterization for Polymers Crosslinked with Conductive & Polyimide Backbones

**N$_2$-BET Surface Characterization**

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area (m$^2$/g)</th>
<th>Total Pore Volume (cm$^3$/g)</th>
<th>Median Pore Diameter (nm)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE3</td>
<td>971</td>
<td>0.575</td>
<td>0.62</td>
<td>0.30</td>
</tr>
<tr>
<td>PP1</td>
<td>393</td>
<td>--</td>
<td>--</td>
<td>0.19</td>
</tr>
<tr>
<td>PK2</td>
<td>2.1</td>
<td>--</td>
<td>--</td>
<td>0.55</td>
</tr>
<tr>
<td>PG1</td>
<td>206</td>
<td>--</td>
<td>--</td>
<td>0.42</td>
</tr>
<tr>
<td>CMS</td>
<td>837</td>
<td>0.423</td>
<td>0.47</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The synthesis condition has strong influence on the polymer structures during the condensation reaction.
Progress – $H_2$ Uptake Capacity Measurement at Liquid Nitrogen Temperature

Hydrogen uptake over the polymer surface at 77 K generally follows Langmuir isotherm
Progress – $H_2$ Uptake Capacity Measurement at Liquid Nitrogen Temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gr. Uptake (Absolute)* (kg $H_2$/kg adsorbent+$H_2_{ads}$)</th>
<th>Vol. Uptake (Absolute) (kg $H_2$/L adsorbent)</th>
<th>Gr. Uptake (Excess) (kg $H_2$/kg adsorbent+$H_2_{ads}$)</th>
<th>Vol. Uptake (Excess) (kg $H_2$/L adsorbent)</th>
<th>BET SSA (M$^2$/g)</th>
<th>Modified Chahine Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQ1</td>
<td>2.1%</td>
<td>0.0080</td>
<td>1.4%</td>
<td>0.0053</td>
<td>1043</td>
<td>1.00</td>
</tr>
<tr>
<td>PC1</td>
<td>1.7%</td>
<td>0.011</td>
<td>1.2%</td>
<td>0.0079</td>
<td>769</td>
<td>1.11</td>
</tr>
<tr>
<td>PD2</td>
<td>1.2%</td>
<td>0.0047</td>
<td>0.5%</td>
<td>0.0020</td>
<td>762</td>
<td>0.77</td>
</tr>
<tr>
<td>PE3</td>
<td>2.1%</td>
<td>0.0063</td>
<td>1.2%</td>
<td>0.0036</td>
<td>971</td>
<td>1.06</td>
</tr>
</tbody>
</table>

* Values in the table represent the measurement taken at a hydrogen pressure of ~ 7 bar

- Absolute capacities are generally proportional to surface area at 77 K.
- Excess capacities diminish when the storage pressure exceeds 20 bar; significant improvement in adsorption uptake is necessary.
Progress – $H_2$ Uptake Capacity Measurement at Ambient Temperature

In contrast to CMS, $H_2$ uptakes of polymers deviate from linear increase as the function of pressure, suggesting a different $H_2$/adsorbent interaction.
Progress – $H_2$ Uptake Capacity Measurement at Ambient Temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Mass Tested (gram)</th>
<th>$H_2$ Gravimetric Uptake @ ~70 Bar (kg $H_2$/kg adsorbent+$H_2$ads)</th>
<th>$H_2$ Volumetric Uptake @ ~70 Bar (kg $H_2$/kg adsorbent+$H_2$ads)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQ1</td>
<td>0.360</td>
<td>0.43%</td>
<td>0.0016</td>
</tr>
<tr>
<td>PC1</td>
<td>0.220</td>
<td>0.55%</td>
<td>0.0036</td>
</tr>
<tr>
<td>PD2</td>
<td>0.192</td>
<td>0.66%</td>
<td>0.0026</td>
</tr>
<tr>
<td>PE3</td>
<td>0.239</td>
<td>0.45%</td>
<td>0.0014</td>
</tr>
<tr>
<td>CMS</td>
<td>0.430</td>
<td>0.54%</td>
<td>0.0049</td>
</tr>
</tbody>
</table>

- No clear correlation between $H_2$ uptake and surface area is observed
- Major improvements in capacities are necessary to reach the targets
Progress – Investigation of Polymers from Literature

- Three polymer samples were prepared according to literature reports
- High yield was achieved through our modified synthesis process
- Surface characterization and hydrogen storage capacity measurement are underway


* Potential active sites for alkylation. Activity changes after one of the sites within the aromatic group reacts
**Progress – Computational Modeling of Hydrogen Storage in Polymers**

**Calculated Structures & \( \text{H}_2 \) Binding for PE3**

- Structures are optimized at B3LYP and MP2/631G(d) levels
- Hydrogen interaction energies are calculated at MP2/6311+G(2df,p) level

**H\(_2\) Binding inside of 3D Polymer Structure**

- 3D cross-linked structure optimized with DFT-PW91
- Add \( \text{H}_2 \)
- \( \text{Ab initio} \) MD at high H content

- Local \( \text{H}_2 \) binding energies over open surface of functional group are low
- Simulation on \( \text{H}_2 \) distribution, polymer deformation, etc., in 3D space is planned
Milestones

- Complete 1st phase experimental optimization study on TBHTP system 09/07 √
- Complete the initial design and synthesis of one new polymeric system 09/07 √
- Provide one or more polymer samples to a DOE laboratory outside of Argonne for hydrogen storage capacity measurement 01/08 √
- Complete the synthesis of one or more porous polymers reported in the open literature as benchmark materials for the current study 05/08 √
- Complete the surface property characterization and hydrogen storage capacity measurement of the benchmark materials to compare with Argonne/U of Chicago polymers 06/08 →
- Complete first PDF experiments trial on polymer/hydrogen interaction at the Advanced Photon Source 07/08 →
- Initiate theoretical simulation of the interactions between hydrogen and model polymer systems 08/08 →
- 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 08/08 →
Future Work

FY08
- Complete storage measurement and surface property characterization for all the new porous conjugated polymers prepared by U of C team. Derive a preliminary understanding of the molecular structure-capacity relationship.
- Complete the storage capacity and structural characterization of the polymers prepared according to the literature report.
- Continue to improve the measurement accuracy of Sievert apparatus for study at higher pressure region (up to 100 bar).
- Initiate preliminary X-ray PDF experiment to probe polymer structure and its interaction with hydrogen under elevated pressure.

FY09
- Continue polymer design and synthesis by preparing two additional systems of a) polymers with different main group elements and b) polymers with metal doping.
- Optimize synthesis conditions of the best systems to further enhance the surface property and storage capacity.
- Continue computational modeling of hydrogen-polymer interaction and the conformation change at the elevated pressure.
- Collaborate with other members of HSCoE in adsorption mechanistic studies (e.g. NMR, neutron, etc.)
Summary

Relevance: Developing the nanostructured porous polymers as new H₂ storage media aimed at meeting DOE performance targets for transportation applications.

Approach: Rational design and synthesis at molecular level supported by surface property/storage capacity measurement, computational modeling and advanced characterization.

Accomplishments:
- Three series of polymeric adsorbents designed and prepared with high surface area and narrow pore distribution.
- H₂ uptakes up to 75 bar studied at both 77K and RT; interesting adsorption behavior observed.

Collaboration: Core team of Argonne and U of Chicago collaborating with HSCoE members.

Future Work:
- Continuous polymer exploration and optimization.
- Improving capacity measurement & mechanistic study at high H₂ pressure.
- Understanding possible conformation change through theory and advanced characterization.