High-Capacity and Low-Cost Hydrogen-Storage Sorbents for Automotive Applications

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Overview

Timeline

- Project Start: June 2015
- Project Length: 3 years

Barriers

- A. Inadequate hydrogen uptake
- J. Inadequate thermal conductivity
- O. Inadequate understanding of adsorption processes

Budget

- Total Project Budget: $1,115,617
  - Total Recipient Share: $0
  - Total Federal Share: $1,115,617
- Percent Complete: 0%

Partners

- DOE: Sponsor and Funding
- Argonne National Lab
- Texas A&M University
Relevance

- Design and synthesize new materials which meet DOE gravimetric and volumetric targets while being cost-effective
- Thoroughly study the effect of open metal sites on hydrogen adsorption
- Analyze the possibility of using highly porous engineered carbons as a binder to improve packing density and thermal conductivity

<table>
<thead>
<tr>
<th>Milestone/Decision Point</th>
<th>Quarter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>12</td>
<td>Demonstrate one material with 0.075kg_{H2}/Kg_{sorbent}</td>
</tr>
<tr>
<td>M5</td>
<td>18</td>
<td>Demonstrate &gt;30% increase in packing density or 2x increase in thermal conductivity</td>
</tr>
<tr>
<td>D2</td>
<td>24</td>
<td>Demonstrate one Material with 0.10kg_{H2}/Kg_{sorbent} and 0.05 kg_{H2}/L_{sorbent}</td>
</tr>
<tr>
<td>M10</td>
<td>36</td>
<td>Demonstrate material with suitable uptake to allow for a system capacity of 0.055kg_{H2}/Kg_{system} and 0.040 kg_{H2}/L_{system}</td>
</tr>
</tbody>
</table>
# Approach

Year 1 consists of new materials discovery and characterization of proven materials.

Demonstrate at least one of the MOF/POP sorbents with gravimetric hydrogen storage capacity reaching 0.075 kg/kg\textsubscript{sorbent}.

<table>
<thead>
<tr>
<th>Tasks</th>
<th>Task Title</th>
<th>Milestone Type (Milestone or Go/No-Go Decision Point)</th>
<th>Milestone Number (Go/No-Go Decision Point Number)</th>
<th>Quarters from Start of the Project</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.1 &amp; 3.2.2.</td>
<td>Development of the first batch ligand library for MOF sorbents</td>
<td>Milestone</td>
<td>M1</td>
<td>2</td>
</tr>
<tr>
<td>3.2.5</td>
<td>Advanced characterization on H\textsubscript{2}-sorbent interaction using synchrotron X-ray based techniques</td>
<td>Milestone</td>
<td>M2</td>
<td>3</td>
</tr>
<tr>
<td>3.2.1 &amp; 3.2.2.</td>
<td>Development of 1st generation of MOF sorbents for H\textsubscript{2} storage</td>
<td>Milestone</td>
<td>M3</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Go/No-Go Decision point</td>
<td>D1</td>
<td>4</td>
</tr>
</tbody>
</table>
New Approach - H₂ Storage Beyond “Chahine Rule”

- Improve hydrogen – sorbent interaction through high valance metal center
- Improve hydrogen – sorbent interaction through unsaturated metal site
- Improve volumetric capacity and heat-transfer through ZIF-derived, metal doped carbons

Enhancing H₂ adsorption enthalpy could improve storage uptake capacity beyond the limit by simple van der Waals interaction
Preliminary Accomplishments-MOF Synthetic Pathways

• Post-Synthetic Metathesis and Oxidation (PSMO)

Through a sequential methathesis of labile metals and subsequent oxidation stable crystalline high valent MOFs have been obtained

Preliminary Accomplishments-
Stable MOFs

- PCN-426(Fe/Cr) are synthesized through the PMSO method
- The MOFs maintain their structure across a wide PH range
- This allows for the synthesis of MOFs with rare or unreported nodes with high-valent metals

Preliminary Accomplishments - MOF Synthetic Pathways

• Kinetically Tuned Dimension Augmentation (KDTA)

• Utilizing a piece by piece approach the kinetics of MOF growth can be tuned to ensure crystallinity.

• This led to 34 new Fe(III) MOFs and is highly scalable

Nat. Commun., 2015, 5, Article number: 5723
Preliminary Accomplishments - Stable MOFs

- PCN-250 is a promising example of a KDTA synthesized MOF
- Costs could be <$50/kg to manufacture
- Extremely robust

Nat. Commun., 2015, 5, Article number: 5723
Preliminary Accomplishments - Hydrogen Uptake

- **PCN-250**

<table>
<thead>
<tr>
<th>Capacity</th>
<th>Pressure / bar</th>
<th>Capacity, packing density / g/L</th>
<th>Capacity, crystal density / g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volumetric capacity*</td>
<td>97.7</td>
<td>39</td>
<td>85</td>
</tr>
<tr>
<td>Deliverable capacity*</td>
<td>5 – 97.7</td>
<td>23</td>
<td>50</td>
</tr>
</tbody>
</table>

PCN-250 exceeds the Chahine rule prediction by 50% but capacity is ~half of DOE target for packed MOF

*Courtesy of NREL*
Collaboration

• TAMU will design synthesize, and characterize new materials

• ANL will perform x-ray characterization studies, develop ZDC based binding agents and perform ALD Studies

• All deliverables will be sent to DOE for external Validation
Challenges

• While Chahine’s Rule applies to many compounds it doesn’t to others.

• Finding the determining factor other than pure surface area, such as open metal site density or pore geometry is key to overcoming current limitations

• The feasibility of scale-up and bulk physical properties must also be easily maintained from lab scale
Proposed Work-Stable MOFs with Open Metal Sites

- New MOFs with stable unsaturated nodes are under study
- Introducing a large number of open metal-sites is hypothesized to greatly increase hydrogen-framework interactions
Proposed Work—Improving Adsorption Enthalpy through Unsaturated Metal Center (UMCs) in MOF by ALD

- Various N-containing ligand will be used to prepare MOF at TAMU with open chelation site to react with metal complexes
- Metal-ligand complexes can be introduced by atomic layer deposition at ANL
- UMCs can be formed after removing complex ligand to enhance H₂-adsorbent interaction
Proposed Work- Improving Volumetric Capacity & Thermal Conductivity through Engineered Carbon

Hydrogen storage volumetric capacity intertwines closely with gravimetric capacity and sorbent density

Volumetric capacity & thermal conductivity can be improved by compounding MOFs with engineered carbon (EC)

- High surface area, soft EC can be prepared from porous precursors
- EC surface can also be functionalized for H₂ adsorption
Summary

• New materials for the adsorption of hydrogen for onboard fuel use will be studied

• The effect of open metal sites will be probed through new materials discovery and ALD metal doping

• Implementation of engineered carbon based binders will be used to increase packing efficiency and thermal conductivity

• Through collaboration new composite materials will be created to meet the DOE targets