Metal-Organic Frameworks Containing Frustrated Lewis Pairs for Hydrogen Storage at Ambient Temperature

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Overview

Timeline
- Project start: Dec. 2019
- Phase I end: Dec. 2020
- Phase II end: Sept. 2022

Budget
- Total project requested: $850K
  - DOE share: $680K
  - Contractor share: $170 K
- Funding received in FY2020 (Phase I)
  - $ 300 K

Barriers
- Barriers to be addressed
  A. Hydrogen binding energies
  B. Hydrogen physisorption capacity at ambient temperature
  C. New H₂ adsorption mechanism

Partners
- Interactions/collaborations
  - University of South Florida (Lead)
  - Argonne National Laboratory (Subcontractor)
  - HyMARC
Current Technology Options for on-board H₂ Storage

- Compressed hydrogen gas (high pressure >700 bar)
- Cryogenic storage of liquid hydrogen (energy consuming)
- Chemisorption using metal hydrides and chemical hydrides (irreversible and poor kinetics of hydrogen recharging)
- Physisorption using porous materials (fast charge-recharge process but very low uptake capacity at room temperature)

To reach high storage capacity for porous materials at ambient temperature, H₂ binding energy needs to be in the range of 15 to 25 kJ/mol.
## Objective – Relevance

Table 1. Technical System Targets: Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2025</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>System Gravimetric Capacity:</strong></td>
<td>kWh/kg (kg H₂/kg system)</td>
<td>1.8 (0.055)</td>
<td>2.2 (0.065)</td>
</tr>
<tr>
<td><strong>System Volumetric Capacity:</strong></td>
<td>kWh/L (kg H₂/L system)</td>
<td>1.3 (0.040)</td>
<td>1.7 (0.050)</td>
</tr>
</tbody>
</table>

Objective - Relevance

- **Phase I** – to demonstrate and deliver one FLP@MOF with reversible total gravimetric capacity ≥ 1.5 wt % and total volumetric capacity ≥ 0.012 kg H₂/L at H₂ pressure of ≤100 bar at room temperature.

- **Overall** – to produce one or more FLP@MOF that meets or exceeds the DOE’s 2025 goal of H₂ storage gravimetric density (GD) of 5.5 wt.% and volumetric density (VD) of 0.040 kg H₂/L.

Merits of FLP@MOFs & Their Impact on Technology Barriers

1. High H₂ adsorption working capacity
2. New H₂ adsorption mechanism
3. Strong H₂ binding energy
4. High H₂ uptake capacity at ambient temperature
Approach: Encapsulating FLP into MOF (FLP@MOF) for Hydrogen Storage at Ambient Temperature
Approach – Development Strategy

- FLP@MOF Design and Synthesis (USF)
  - Develop various approaches to synthesize new FLP@MOF
  - Structure characterization of FLP@MOF
  - High throughput synthesis of FLP@MOF

- Characterization & Modeling (USF/ANL/HyMARC)
  - H₂ storage capacity & reversibility measurements
  - Advanced characterization of H₂-FLP@MOF
  - Computational modelling of H₂-FLP@MOF

- Optimization & Engineering (USF/ANL)
  - Volumetric capacity enhancement of H₂ adsorption in FLP@MOF

- New FLP@MOFs with high H₂ storage capacities
- Enhancing H₂ hydrogen binding energy to 15-25 kJ/mol
- Unveiling possibly new H₂ adsorption mechanism
- Improving volumetric H₂ adsorption capacity by preparing monolithic FLP@MOF

Collaborating with HyMARC/others and leveraging existing experimental / theoretic supports are essential to the project success!
## Approach: Phase I Milestone Status

<table>
<thead>
<tr>
<th>Milestone #</th>
<th>Milestones/Go-NoGo DP</th>
<th>Milestone Verification</th>
<th>Percent Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>M 1.1.1</td>
<td>Complete synthesize at least six meso-MOFs for the incorporation of FLP</td>
<td>MOF synthesis will be carried out at USF based on literature reported method</td>
<td>100%</td>
</tr>
<tr>
<td>M 1.1.2</td>
<td>Design and synthesize a series of FLP@MOF using step-wise anchoring approach</td>
<td>FLP@MOF synthesis will be carried out at USF</td>
<td>20%</td>
</tr>
<tr>
<td>M 2.1.1</td>
<td>Complete high-pressure hydrogen storage measurements for stepwise synthesized FLP@MOFs</td>
<td>Isotherm of H$_2$ at different pressures will be measured by USF and ANL teams</td>
<td>0%</td>
</tr>
<tr>
<td>M 2.2.1</td>
<td>Complete structural studies of the first batch of FLP@MOF</td>
<td>Conventional analytic tools will be applied to study selected FLP@MOF at USF/ANL</td>
<td>10%</td>
</tr>
<tr>
<td>GNG 1.2.3</td>
<td>At least one FLP@MOF with reversible total gravimetric capacity $\geq 1.5$ wt $%$ and total volumetric capacity $\geq 0.012$ kg H$_2$/L at H$_2$ pressure of $\leq 100$ bar at room temperature</td>
<td>To be delivered to DOE designated lab for certification after initial measurement at USF/ANL</td>
<td>0%</td>
</tr>
</tbody>
</table>

**The focus of Phase I is to deliver one FLP@MOF with reversible total gravimetric capacity $\geq 1.5$ wt $\%$.**
Accomplishments: Ligand Synthesis

- The following ligands have been synthesized for the construction of MOFs.
Accomplishments: Preparation of meso-MOFs.

- Meso-MOFs: MOF818, FDM-3, Tb-TATB, Zr-UIO-68, Zr-UIO-678F, PCN-333(Fe), PCN-333(Cr), UIO-68, MIL-101(Cr), MIL-101-4F and MIL-101-Br(Cr) with the structures shown below have been prepared as planned.
Accomplishments: Synthesis of Lewis acids and Lewis bases for FLP

- The following two Lewis acids have been prepared.

  - \[ \text{MesB(C}_6\text{F}_5)_2 \]
  - \[ \text{B(C}_6\text{F}_5)_3 \]

- The following two Lewis bases have been prepared.

  - DABCO
  - HMTA
Accomplishments: Step-wise anchoring of FLP on MOF through coordination interaction

- The following two sets of FLPs have been encapsulated in PCN-333(Cr) and MIL-101(Cr) using step-wise anchoring approach.

\[
\begin{align*}
&\text{DABCO} + \text{B(C}_6\text{F}_5)_3 \\
&\text{DABCO} + \text{MesB(C}_6\text{F}_5)_2 \\
&\text{PCN-333 (Cr)} \\
&\text{MIL-101 (Cr)}
\end{align*}
\]
Collaborations: Working with HyMARC

- **HyMARC – SNL**
  - High pressure analysis
  - Surface characterization tools

- **HyMARC – PNNL**
  - In situ NMR study

- **HyMARC – LLNL**
  - Modeling/simulation of H$_2$-FLP@MOF Surface XPS

- **HyMARC - NREL**
  - Measurements of Qst for H2 adsorption in FLP@MOF
  - Capacity certification

Looking forward to formulating detailed experimental plan through the discussion with HyMARC members!
The high-pressure sorption instrument at USF will need to be well calibrated to collect reliable high-pressure H₂ sorption isotherms particularly at pressure close to 100 bar.
Proposed Future Work

### Remaining Phase I Activities
- Synthesis of a series of mesoporous MOFs
- Incorporation of FLPs into the synthesized mesoporous MOFs via step-wise anchoring approach
- Optimize FLP vs MOF formulation through high throughput synthesis
- Structural characterizations of the prepared FLP@MOFs with conventional and advanced tools
- High pressure H2 storage capacity measurements

### Planned Phase II Activities
- Developing other approaches to incorporate FLPs into MOFs
- Continue high throughput synthesis/screening of FLP@MOFs and optimization of FLP@MOFs
- High pressure hydrogen storage measurements
- Advanced characterizations and mechanistic studies of H2 adsorption in FLP@MOFs
- Computational modeling/simulation support
- Process engineering of FLP@MOF

Any proposed future work is subject to change based on funding levels.
Technology Transfer Activities

- A Provisional Patent Application entitled “FRUSTRATED LEWIS PAIR-IMPREGNATED POROUS MATERIALS AND USES THEREOF” has been filed.
Eight ligands have been synthesized for the construction of MOFs.

Six meso-MOFs: MOF818, FDM-3, Tb-TATB, Zr-UIO-68, Zr-UIO-67-8F, PCN-333(Fe), PCN-333(Cr), UIO-68, MIL-101(Cr), MIL-101-4F and MIL-101-Br(Cr) with the structures shown below have been prepared.

Two Lewis acids and two Lewis bases have been prepared for FLPs.

Two sets of FLPs have been encapsulated in PCN-333(Cr) and MIL-101(Cr) using step-wise anchoring approach.
Acknowledgements

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