Hydrogen Storage in Metal-Organic Frameworks

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# Overview

## Timeline
- Project start date: 01/01/12
- Project end date: 12/31/14
- Percent complete: 5%

## Budget
- Total project funding $2.625M
  - DOE share: $2.1M
  - Contractor share: $0.525M
- Funding received in FY11: $0
- Planned Funding for FY12: $0.5M

## Barriers
- Identify new metal-organic frameworks enabling a hydrogen storage system achieving:
  - 1.8 kWh/kg (5.5 wt %)
  - 1.3 kWh/L (0.040 kg/L)
  - -40/60 °C operating temperature

## Partners
- National Institute of Standards and Technology
- General Motors
- Project lead-Jeffrey Long, LBNL
The H$_2$ Powered Car – Current Technologies

About 4-5 kg of H$_2$ required for a 300 mi range

Compressed Hydrogen Gas (most common)
  Significant energy spent in compression process

Liquid Hydrogen
  Large energy input for liquefaction
  Heavy and expensive cooling unit required

Chemical and Metal Hydrides
  High temperatures required for desorption, slow kinetics

Adsorbed on Metal-Organic Frameworks
Optimal Binding Enthalpy for $\text{H}_2$

**Chemisorption**
Strong binding in chemical bonds
High desorption temperature, $\Delta H$

$\text{Ideal } \Delta H_{ads} \text{ for storage at RT}$

**Physiosorption**
Readily reversible storage
$\text{H}_2$ liberated too easily at RT

**Metal-hydrides**
Ammonia, ammonia-borane
Amine complexes

**Metal-organic frameworks**
Carbons
Zeolites

**Hybrid system**
High surface area
Stronger binding of $\text{H}_2$

Ideal Pore Size for H$_2$ Storage

- Shorter-range influence of pore walls at higher temperatures
- Design of a room temperature sorbent requires careful consideration of both chemical and structural properties

Strategies for Improving H\textsubscript{2} Storage Performance

**Lightweight Materials**
- Lightweight metal ions (Be\textsuperscript{2+}, Mg\textsuperscript{2+}, Al\textsuperscript{3+})
- Improve gravimetric capacity
- New structure types (particularly with main group elements)

**Unsaturated Coordination Sites**
- Charge-dense, polarizing binding sites
- M-H\textsubscript{2} interactions at the right enthalpy for reversible storage at 298 K
- Close approach to metal center increases packing density of H\textsubscript{2}
Synthesis of a Be-based Metal-Organic Framework

Be$^{2+}_{(aq)}$ + 1,3,5-benzenetribenzoic acid (H$_3$BTB) → Be$_{12}$(OH)$_{12}$(1,3,5-benzenetribenzoate)$_4$

Tetragonal, $P-4c2$
SA$_{BET}$ = 4030 m$^2$/g

H₂ Storage Properties of Be-BTB

- High surface area coupled with low isosteric heat of adsorption (Q_st) facilitates excellent cryogenic storage properties

- Multiple pore apertures of ca. 6-7 Å leads to record gravimetric uptake in a metal-organic framework at 298 K

Synthesis of Fe-BTT – Exposed Fe$^{2+}$ Cation Sites

$$\text{FeCl}_2 + \text{1,3,5-benzenetristetrazolate} \xrightarrow{\text{DMF/DMSO}} 110 \, ^\circ\text{C}, 48 \, \text{h} \quad \text{Fe}_3[(\text{Fe}_4\text{Cl})_3(\text{BTT})_8]_2$$

Cubic, $Pm-3m$

$a = 18.82 \, \text{Å}$

D$_2$ Loading Experiments within Fe-BTT

- At higher loadings, up to 10 binding sites identified within unit cell
H₂ Storage Properties of Fe-BTT

- Enthalpy of adsorption consistent with the high charge density on Fe²⁺ metal center

Collaborations

Martin Head-Gordon, UC Berkeley/LBNL(Academic)
- Calculations of H₂ Binding Energies
  Theoretical calculations will be utilized to aid in the prediction of key new metal-organic frameworks that may meet DOE H₂ storage targets.

Craig M. Brown, NIST (National Lab)
- Characterization of Framework-H₂ Interactions
  Neutron methods will give insight into the adsorption of H₂ in newly synthesized porous frameworks.

Anne Dailly, GM (Industry)
- High Pressure H₂ Adsorption Measurements
  The most promising H₂ storage materials will be further investigated in collaboration with GM by measuring high-pressure (up to 350 bar) adsorption at relevant temperatures.
Opposing Surface Area as a Characterization Tool

- Metal-organic frameworks feature a rich diversity in the shape and connectivity of their pores, giving a distribution of opposing wall distances.
- Need an algorithm that surveys these distances using the crystal structure.
Geometric Calculation of Opposing Wall Distances

- Probe is inserted on the pore surface, and moved away in a direction normal to the surface until it collides with the opposing wall.
- This is repeated until the entire pore surface has been traversed by the algorithm to create a distribution of opposing wall distances.
Rapid Screening of Structure Types for H₂ Storage

- Algorithm could be deployed for rapid examination of a vast database of existing and theoretical structure types.
- Structure types exhibiting narrow distributions at 7 Å and 10 Å can then be experimentally tested for H₂ storage performance.
Strategies for Increasing $\text{H}_2$ Binding Enthalpy and Capacity

- Incorporation of high-valent metal cations
- Increase M-$\text{H}_2$ binding enthalpy
- Allows for high metal:ligand ratio

- Multiple metal binding sites for post-synthetic insertion of metal cations
- Potential charge balance offered by $-\text{OH}$ containing ligands may lead to increased $\text{H}_2$ uptake
Neutron methods at NIST encompass a range of seven orders in time- and appropriate storage length-scales.

Inelastic neutron scattering spectra of hydrogen adsorbed at the first (lower curve) and second sites in Cu-BTC. Assignments of rotations (R) and translations (T) are made through DFT calculations.
First-Principles Calculations of Hydrogen Binding Enthalpies and High Pressure Hydrogen Adsorption Experiments.

- Calculated optimized geometry for hydrogen binding in Mn$_3$[(Mn$_4$Cl)$_3$(BTT)$_8$]$_2$.
- Theoretical calculations will be utilized to predict optimal H$_2$ storage materials.
- A custom-made Sieverts apparatus will be used to measure H$_2$ adsorption at various temperatures up to 350 bar in promising metal-organic frameworks.
Summary

- A synergistic approach to the development of new metal-organic frameworks for hydrogen storage has recently (January 2012) been started.

- The combination of synthesis (Long), theoretical calculations (Head-Gordon), characterization (Brown), and H$_2$ adsorption measurements (Dailly) will aide in the efficient design and preparation of next-generation storage materials.