Hydrogen Storage Characterization and Optimization Research Effort

Jeffrey Long and Martin Head-Gordon
Materials Sciences Division
Lawrence Berkeley National Laboratory
June 8, 2016

Project ID #: ST133

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Timeline
- Start: October 2015
- Finish: September 2018

Budget
- Project Start Date: 10/01/2015
- FY16 DoE Funding: $795k
- DoE funding received to date: $795k
- Matching fellowship support: $197k

Barriers Addressed
- A. System Weight and Volume

Partners
- LBNL: IR, synthesis, and modeling
- NREL: synthesis and measurements
- PNNL: modeling and NMR
- NIST: neutron diffraction
- Project lead: Thomas Gennett (NREL)
Project objectives

- Develop *in situ* infrared spectroscopy as a tool for characterizing emerging H\textsubscript{2} storage materials that may allow for a driving range greater than 300 miles.
- Materials sought with the potential for meeting the DoE targets of reversible uptake:
  - 2020 targets: 5.5 % H\textsubscript{2} by mass, volumetric capacity of 40 g/L
  - “ultimate full fleet” targets: 7.5 % H\textsubscript{2} by mass, 70 g/L.
- Validate new concepts for H\textsubscript{2} storage mechanisms in adsorbents.
- Provide accurate computational modeling for H\textsubscript{2} adsorbed in porous materials.

This reporting period

- Research and development of metal-organic framework materials with high volumetric and gravimetric H\textsubscript{2} capacities (Barrier A).
Role of LBNL within the Effort

Hydrogen Storage Characterization and Optimization Research Effort

Researchers at NREL, LBNL, PNNL, and NIST are tasked with supporting the DoE Hydrogen Storage Program through validation of:
1) Properties of emerging hydrogen storage materials
2) New concepts for hydrogen storage mechanisms
3) Computational methods for predicting hydrogen storage properties

LBNL:
1) IR spectroscopy with precise H₂ dosing at $T = 10\text{-}300 \text{ K}$, $P \leq 100 \text{ bar}$
2) Mechanistic validation:
   Can exposed cations in adsorbents reach target of $\Delta H = -15 \text{ kJ/mol}$?
   Is it possible to adsorb two, three, or four H₂ per metal cation?
3) Accurate modeling of H₂ adsorbed within porous materials
Q2: Evaluate choices for various infrared spectrometer setups for in situ gas dosing. 100% complete

Q3: Order DRIFTS instrument that will be best and most functional for the desired in situ H₂-dosed experiments over a temperature range of 15-373 K and up to 100 bar hydrogen pressure at 298 K based on experience testing several similar instruments. 100% complete

Q4: Complete installation of the DRIFTS instrument and demonstrate that the DRIFTS instrument is operating with a resolution of 10 cm⁻¹ by measuring spectra for a sorbent standard and comparing with accepted published data. 0% complete
In Situ Infrared Spectroscopy

- Infrared spectroscopy with *in situ* gas dosing probes behavior of adsorbed species
- Allows investigation of adsorption in crystalline and non-crystalline materials

**In Situ Infrared Spectroscopy**

- H₂ molecules adsorbed on different sites have different infrared energy shifts
- Shift of H₂ signals correlates to changes in isosteric heats of adsorption
- Measurements at multiple temperatures yield site-specific enthalpies of adsorption

### Relevance: DoE 2020 Hydrogen Storage System Targets and FY16 Project Targets

#### DoE 2020 Storage Targets

<table>
<thead>
<tr>
<th>Property</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>gravimetric capacity</strong></td>
<td>5.5 wt % H₂</td>
</tr>
<tr>
<td><strong>volumetric capacity</strong></td>
<td>40 g H₂/L</td>
</tr>
<tr>
<td><strong>operating temperature</strong></td>
<td>-40 to 60 °C</td>
</tr>
<tr>
<td><strong>maximum pressure</strong></td>
<td>100 bar (project target)</td>
</tr>
<tr>
<td><strong>refueling rate</strong></td>
<td>1.67 kg H₂/min</td>
</tr>
<tr>
<td><strong>cycle life</strong></td>
<td>1500 cycles</td>
</tr>
<tr>
<td><strong>cost</strong></td>
<td>$333 per kg H₂</td>
</tr>
</tbody>
</table>

- MOFs can meet volumetric capacity in relevant temperature range if multiple H₂ molecules can be bound to each metal center.

#### FY16 Targets

1. **Q1**: Computational chemists will initiate investigation of the most promising structures for the desired pore domain size and chemistry within porous aromatic frameworks (PAFs) or block copolymer (BCP) using first-principles electronic structure calculations with range separation and dispersion corrections. **100% complete**

2. **Q2**: Synthesize a porous aromatic frameworks material with metal-chelating sites and a Langmuir surface area of at least 1000 m²/g. **100% complete**

3. **Q3**: Synthesize and characterize a carbon based sorbent with catechol functionalized pore domains that contain unsaturated metal centers attached to the materials matrix. **95% complete**

4. **Q4 Go/No-Go**: Demonstrate the ability to bind two H₂ molecules to one metal center in a metal-organic framework, porous aromatic framework, or carbon-based material. **100% complete**

---

http://energy.gov/sites/prod/files/2015/05/f22/fcto_myrdd_storage.pdf
Approach: Metal-Organic Frameworks

- BET surface areas up to 7100 m²/g
- Densities as low as 0.13 g/cm³
- Tunable pore sizes up to 10 nm
- Channels connected in 1-, 2-, or 3-D
- Internal surface can be functionalized

Can these high-surface area materials be used for hydrogen storage at ambient temperatures?

Zn₄O(1,4-benzenedicarboxylate)₃

MOF-5

Yaghi et al. Nature 2003, 423, 705
Férey Chem. Soc. Rev. 2008, 37, 191
At 100 bar and 77 K, a record physisorbed storage density of 66 g/L is achieved.

At 298 K, framework offers little improvement over density of pure H₂ gas.

A MOF with a High Density of Exposed M$^{2+}$ Sites

$\text{MX}_2 \cdot 6\text{H}_2\text{O}$

$+$

\[ \text{H}_4\text{dobdc} \]

$\rightarrow$

$\text{M}_2(\text{dobdc}), \text{M-MOF-74}$

$\text{(M = Mg, Mn, Fe, Co, Ni, Cu, Zn)}$

- Activated frameworks have Langmuir surface areas of 1277-2060 m$^2$/g
A MOF with a High Density of Exposed M$^{2+}$ Sites

$\text{MX}_2 \cdot 6\text{H}_2\text{O}$

$+$

$\text{H}_4\text{dobdc}$

$\rightarrow$

$\text{M}_2(\text{dobdc}), \text{M-MOF-74}$

($\text{M} = \text{Mg, Mn, Fe, Co, Ni, Cu, Zn}$)

□ Desolvation leads to square pyramidal M$^{2+}$ centers with an open coordination site
Approach:
Synthesis of a Structural Isomer of $M_2$(dobdc)

Strong H$_2$ Binding in Ni$_2$(m-dobdc)

Neutron Diffraction

Ni–D$_2$ = 2.18(4) Å

Infrared Spectroscopy

$\Delta H_{\text{ads}} = -13.7 \pm 0.5$ kJ/mol
(Ni$_2$(dobdc): $-12.3 \pm 0.5$ kJ/mol)

High charge density at Ni$^{2+}$ pulls H$_2$ close and gives record MOF binding energy

H₂ desorbs from Ni₂(m-dobdc) at higher T, consistent with stronger binding.
Close D$_2$ Packing within Ni$_2$(m-dobdc)

- Greater charge density at Ni$^{2+}$ gives closer packing for secondary adsorption site

Below 100 °C, all isotherms show greater capacity than compressed H₂ at 25 °C

Ni₂(m-dobdc) has a total capacity of 24 g/L of crystal at −75 °C and 100 bar
Increased H$_2$ Density in Ni$_2$(m-dobdc) at 100 bar

Ni$_2$(m-dobdc) shows increasing boost in capacity with decreasing temperature
Collaboration with NREL used to verify $\text{H}_2$ isotherms in $\text{Ni}_2(m$-dobdc)

Data matches within error
Accomplishments: H$_2$ Volumetric Usable Capacity

Ni$_2$(m-dobdc) at –75 °C

Total H$_2$ adsorbed (g/L of crystal)

_P (bar)_

usable capacity

5 bar desorption

100 bar adsorption
H₂ Usable Capacities in g/L of Crystal

<table>
<thead>
<tr>
<th></th>
<th>Ni₂(m-dobdc)</th>
<th>Co₂(m-dobdc)</th>
<th>Ni₂(dobdc)</th>
<th>Co₂(dobdc)</th>
<th>MOF-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C, no swing</td>
<td>11.0</td>
<td>10.5</td>
<td>9.9</td>
<td>8.8</td>
<td>8.8</td>
</tr>
<tr>
<td>–75 °C, no swing</td>
<td>19.0</td>
<td>18.2</td>
<td>18.4</td>
<td>16.5</td>
<td>15.8</td>
</tr>
<tr>
<td>–40 to 25 °C</td>
<td>18.2</td>
<td>17.3</td>
<td>16.6</td>
<td>14.0</td>
<td>12.8</td>
</tr>
<tr>
<td>–75 to 25 °C</td>
<td>23.0</td>
<td>21.9</td>
<td>21.4</td>
<td>18.3</td>
<td>16.5</td>
</tr>
<tr>
<td>–75 to 100 °C</td>
<td>23.4</td>
<td>22.3</td>
<td>21.8</td>
<td>18.6</td>
<td>16.7</td>
</tr>
</tbody>
</table>

- Values represent maximum capacity possible and will be reduced depending on packing.
- Ni₂(m-dobdc) is the top-performing adsorbent for these temperatures.
- 23.0 g/L usable capacity for –75 °C to 25 °C swing represents **58% of system target**.
Seven distinct D$_2$ adsorption sites are observed at 78 bar and 77 K.

<table>
<thead>
<tr>
<th>D$_2$···D$_2$ interaction</th>
<th>distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1···2</td>
<td>2.82(3)</td>
</tr>
<tr>
<td>2···2</td>
<td>3.02(3)</td>
</tr>
<tr>
<td>3···4</td>
<td>3.09(5)</td>
</tr>
<tr>
<td>4···5</td>
<td>3.48(3)</td>
</tr>
<tr>
<td>solid H$_2^*$</td>
<td>3.20</td>
</tr>
<tr>
<td>liquid H$_2$</td>
<td>3.61</td>
</tr>
</tbody>
</table>

*van Kranendonk, Gush Phys. Lett. 1962, 1, 22
Binding Multiple H₂ Molecules per Metal Cation

Classical

1 H₂ per metal cation

Next-Generation

4 or 5 H₂ per metal cation

☐ Volumetric capacity can be substantially increased while maintaining strong binding
Isomer of Mn$_2$(dobdc) structure with sulfido groups in place of oxido

Crystal structure shows four-coordinate Mn$^{2+}$ ions with two bound DMF molecules

Sun, Miyakai, Seki, Dincă. J. Am. Chem. Soc. 2013, 135, 8185
Structure of Desolvated Mn$_2$(dsbdc)

- Desolvated structure of Mn$_2$(dsbdc) determined
- Half of the Mn$^{2+}$ ions exhibit four-coordinate, seesaw geometry

Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long, submitted
H₂ Adsorption in Mn₂(dsbdc)

- Hydrogen uptake is not steep but has about the same capacity as Mn₂(dobdc)
- Binding enthalpy remains low for entire range of loadings

Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long, submitted
First demonstration of two H$_2$ molecules binding to a metal center in a MOF

Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long, submitted
Computational Results for Mn$_2$(dsbdc)

High-Spin Mn(II)
DFT Functional: B97M-V
Basis set: 6-31g*

- Shorter Mn–H$_2$ distances than observed experimentally
- Modeling electronics of ligand is challenging for this structure type
Mn–H$_2$ Energy Decomposition Analysis

DFT Functional: B97M-V
Basis set: def2-tzvp

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frozen</td>
<td>1.0</td>
</tr>
<tr>
<td>Polarization</td>
<td>-3.9</td>
</tr>
<tr>
<td>Charge Transfer</td>
<td>-8.4</td>
</tr>
<tr>
<td>$\Delta E$ (per H$_2$)</td>
<td>-12.5</td>
</tr>
</tbody>
</table>

- Interaction of H$_2$ with Mn$^{2+}$ has double the binding enthalpy of experiment
- New calculations are being run with updated crystal structure
Interaction of Ca\textsuperscript{2+} with H\textsubscript{2} has a shorter H\textsubscript{2} M distance than in Mn\textsubscript{2}(dsbdc)

\[ \Delta E = -17.9 \text{ kJ/mol} \]
Variations on $\text{Mn}_2(\text{dsbdc})$ for Increased $\text{H}_2$ Capacity

Different metals in the four-coordinate sites may bind more $\text{H}_2$ more strongly

$\text{Mn}_2(\text{dsbdc})$  
$\text{MnM}(\text{dsbdc})$  
$\text{M} = \text{Ca, Mg, Co, Ni, Zn}$
Ca$_2$(dsbdc) Synthesis Attempts

- Most promising phase, first two peaks are close to Mn$_2$(dsbdc)
- Lower angle peaks suggest a larger unit cell, as expected for larger Ca$^{2+}$
Mixed-Metal $\text{Mn}_{2-x}\text{Ca}_{x}(\text{dsbdc})$ Synthesis

$\text{MnCl}_2 + \text{Ca(acac)}_2 + \text{H}_4(\text{dsbdc})$ in DMF/MeOH

- Peaks match well with Mn$_2$(dsbdc), work underway to find Ca location
- 9.2% Ca replacement of Mn according to ICP analysis
Volumetric capacity can be substantially increased while maintaining strong binding.
Calculated Adsorption for H$_2$ at Catecholate-Mg$^{2+}$

Catecholate-Mg$^{2+}$
Strong binding for first two H$_2$ molecules

$$\Delta E_{\text{ads}} = \begin{align*}
-26.3 \text{ kJ/mol} & \quad -24.4 \text{ kJ/mol} & \quad -9.4 \text{ kJ/mol}
\end{align*}$$

Catecholate-Ca$^{2+}$
Strong binding for all four H$_2$ molecules

$$\Delta E_{\text{ads}} = \begin{align*}
-18.5 \text{ kJ/mol} & \quad -17.1 \text{ kJ/mol} & \quad -17.4 \text{ kJ/mol} & \quad -17.0 \text{ kJ/mol}
\end{align*}$$

Theory: def2-qzvp/B97M-V
Depletion upon MOF synthesis can expose catechols for metal insertion

Catecholate-bound M^{2+} cations can then bind multiple H_{2} molecules
Addition of water results in clean deprotection with no loss of crystallinity

Metalation of fully deprotected framework is in progress
Successful synthesis of ligand and deprotected MOF exhibiting UiO-67 structure

Successful metalation with Mg(C₄H₉)₂ with ~50% incorporation by ICP
Successful synthesis of ligand and deprotected MOF exhibiting UIO-68 structure

Metalation attempts are underway, two metals per ligand are possible
## Predicted Capacities Upon Insertion of Ca\textsuperscript{2+}

<table>
<thead>
<tr>
<th></th>
<th>Volumetric (g/L of crystal)</th>
<th>Gravimetric (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-68-catechol</td>
<td>39</td>
<td>6.6</td>
</tr>
<tr>
<td>UiO-67-biphenol</td>
<td>42</td>
<td>4.6</td>
</tr>
<tr>
<td>UiO-68-bis(biphenol)</td>
<td>48</td>
<td>7.2</td>
</tr>
</tbody>
</table>

- Predicted capacities based on 4 H\textsubscript{2}/Ca\textsuperscript{2+} and H\textsubscript{2} packing in pores of Ni\textsubscript{2}(m-dobdc)
- Proof of principle for H\textsubscript{2} on metal centers and in pores
Responses to Previous Year Reviewers’ Comments

This is the first year of this project, so there are no previous comments.
Collaborations

Project team:

- Lawrence Berkeley National Laboratory/UC Berkeley:
  Jeffrey Long: Synthesis and basic characterization of MOFs
  Martin Head-Gordon: Calculation and prediction of H₂ binding energies

- National Renewable Energy Laboratory:
  Thomas Gennett (Lead): Characterization

- Pacific Northwest National Laboratory:
  Thomas Autrey: Calculations and NMR spectroscopy

- National Institute of Standards and Technology:
  Craig Brown: Neutron diffraction and neutron spectroscopy

Additional collaborations:

- Variable-temperature infrared spectroscopy with in situ H₂ dosing
  – Stephen FitzGerald (Oberlin College)
Remaining Challenges and Barriers

- Desolvation of catecholate-bound metal cations remains a challenge
- Synthesis of the Mn$_2$(dsbdc) analogs with Ca and Ni must be finalized
- Materials with a higher density of open metal cation sites must be identified to meet volumetric and gravimetric capacity targets
Proposed Future Work

- Test many different metalation and desolvation conditions for the catechol-containing frameworks
- Narrow down synthetic conditions for Mn$_2$(dsbdc) analogs
- Metalate the high surface area porous polymers with metal-chelating sites
- Further research into new materials containing metal centers with open metal coordination sites is underway
- Install *in situ* infrared spectrometer and begin testing materials
- Continue to explore metal-H$_2$ interactions in real systems that have been realized experimentally
Technology Transfer Activities

- The $M_2(m\text{-dobdc})$ patent application was previously submitted.

- Mosaic Materials, Inc. has developed an inexpensive, scalable synthesis of $Ni_2(m\text{-dobdc})$ and is looking to commercialize this material.
Ni$_2$(m-dobdc) shows the best volumetric usable capacities of any porous solid for H$_2$ storage up to 100 bar at ambient temperatures.

Mn$_2$(dsbdc) is the first ever example of multiple H$_2$ molecules binding to a single metal center in a MOF!

Synthesis of analogs of Mn$_2$(dsbdc) with higher binding enthalpies and more H$_2$ per metal are underway.

MOFs containing ligands with metal chelating sites have been synthesized and metalation is underway.
Summary

<table>
<thead>
<tr>
<th>Milestone</th>
<th>% complete</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Q1:</strong> Computational chemists will initiate investigation of the most</td>
<td>100%</td>
</tr>
<tr>
<td>promising structures for the desired pore domain size and chemistry</td>
<td></td>
</tr>
<tr>
<td>within porous aromatic frameworks (PAFs) or block copolymer, (BCP)</td>
<td></td>
</tr>
<tr>
<td>using first-principles electronic structure calculations with range</td>
<td></td>
</tr>
<tr>
<td>separation and dispersion corrections.</td>
<td></td>
</tr>
<tr>
<td><strong>Q2:</strong> Synthesize a porous aromatic frameworks material with metal-</td>
<td>100%</td>
</tr>
<tr>
<td>chelating sites and a Langmuir surface area of at least 1000 m$^2$/g.</td>
<td></td>
</tr>
<tr>
<td><strong>Q3:</strong> Synthesize and characterize a carbon based sorbent with</td>
<td>95%</td>
</tr>
<tr>
<td>catechol functionalized pore domains that contain unsaturated metal</td>
<td></td>
</tr>
<tr>
<td>centers attached to the materials matrix.</td>
<td></td>
</tr>
<tr>
<td><strong>Q4 Go/No-Go:</strong> Demonstrate the ability to bind two H$_2$ molecules to</td>
<td>100%</td>
</tr>
<tr>
<td>one metal center in a metal-organic framework, porous aromatic</td>
<td></td>
</tr>
<tr>
<td>framework, or carbon-based material.</td>
<td></td>
</tr>
</tbody>
</table>
## Summary

<table>
<thead>
<tr>
<th>Milestone</th>
<th>% complete</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Q2:</strong> Evaluate choices for various infrared spectrometer setups for <em>in situ</em> gas dosing.</td>
<td>100%</td>
</tr>
<tr>
<td><strong>Q3:</strong> Order DRIFTS instrument that will be best and most functional for the desired <em>in situ</em> H\textsubscript{2}-dosed experiments over a temperature range of 15-373 K and up to 100 bar hydrogen pressure at 298 K based on experience testing several similar instruments.</td>
<td>100%</td>
</tr>
<tr>
<td><strong>Q4:</strong> Complete installation of the DRIFTS instrument and demonstrate that the DRIFTS instrument is operating with a resolution of 10 cm\textsuperscript{–1} by measuring spectra for a sorbent standard and comparing with accepted published data.</td>
<td>0%</td>
</tr>
</tbody>
</table>
Technical Back-Up Slides
Accomplishments:
77 K H$_2$ Isotherms in Ni$_2$(m-dobdc)

NREL measurements:

- Data at 77 K shows Ni$_2$(m-dobdc) reaches 38 g/L, very close to system target
- NREL-measured isotherms at other temperatures verified LBNL data

*Single crystal density used for volumetric capacity determination
Mn$_2$(dsbdc) Desolvation and Purity

$\square$ Infrared spectrum indicates successful removal of all DMF in Mn$_2$(dsbdc)

Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long, submitted
High-Surface Area Porous Polymers for Metalation

- Meets milestone of porous polymer with surface area > 1000 m²/g
- Metalation and activation of polymers is underway

**PAF-1**  
1. HCHO / HCl / AcOH / H₃PO₄  
   90 ºC / 3 d  
2. P(OEt)₃ / 130 ºC / 3 d  
3. HCl / Reflux

Surface area: 1200 m²/g  
Functional group density: 3.7 mmol/g

Surface area: 835 m²/g  
Functional group density: 3.2 mmol/g