Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture

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Project Overview

Funding
- Total project funding
  - DoE share: $4.4M
- Funding for FY17: $1.4M

Project Participants
- PI: Jeffrey Long (LBNL)
- Co-PI: Jeffrey Neaton (LBNL)
- Co-PI: Maciej Haranczyk (LBNL)

Partners (unfunded under this program)
- MOF production (Mosaic Materials)
- System development (Inventys)
- Process modeling (CCSI$^2$, EPRI)

Overall Project Performance Dates
- Project start date: 6/1/2017 (funded from ?/?/2017)
- Project end date: 5/31/2021

Overall Project Objectives
Development of a transformational technology based upon a diamine-appended MOF for post-combustion CO$_2$ capture at a power plant
Metal-Organic Frameworks (MOFs)

BET surface areas up to 7100 m²/g
Density 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 we make a MOF with surfaces densely coated with amine groups?

Zn₄O(1,4-benzenedicarboxylate)₃
MOF-5

Yaghi et al. Nature 2003, 423, 705
Férey Chem. Soc. Rev. 2008, 37, 191
A MOF with a High Density of Exposed M$^{2+}$ Sites

$\text{MX}_2 \cdot 6\text{H}_2\text{O} + \text{H}_4\text{dobdc} \rightleftharpoons \text{M}_2(\text{dobdc}), \text{M-MOF-74}$

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

Dietzel, Morita, Blom, Fjellvåg Angew. Chem., Int. Ed. 2005, 44, 6354
A MOF with a High Density of Exposed M\(^{2+}\) Sites

\[ \text{MX}_2\cdot 6\text{H}_2\text{O} + \text{H}_4\text{dobdc} \rightarrow \text{M}_2(\text{dobdc}), \text{M-MOF-74} \]

(M = Mg, Mn, Fe, Co, Ni, Cu, Zn)
A MOF with a High Density of Exposed $M^{2+}$ Sites

$MX_2 \cdot 6H_2O + $ 

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

$M_2(dobdc)$, M-MOF-74  
($M = \text{Mg, Mn, Fe, Co, Ni, Cu, Zn}$)

-Activated frameworks have Langmuir surface areas of 1280-2060 m$^2$/g
-Record high density of open metal coordination sites per unit mass or volume
An Expanded Form of Mg$_2$(dobdc) (Mg-MOF-74)

Expanded channels have a diameter of 18 Å and are lined with open Mg$^{2+}$ sites

McDonald, Lee, Mason, Wiers, Hong, Long J. Am. Chem. Soc. 2012, 134, 7056
Appending Diamine Groups

- Dangling amines coat the periphery of the channel leaving space for rapid CO$_2$ diffusion

McDonald, Lee, Mason, Wiers, Hong, Long J. Am. Chem. Soc. 2012, 134, 7056
Strong, Selective CO₂ Adsorption

High affinity of alkyl amines for CO₂ results in high capacity at low pressure

Very little N₂ uptake observed, leading to high selectivity of S = 200

McDonald, Lee, Mason, Wiers, Hong, Long J. Am. Chem. Soc. 2012, 134, 7056
CO$_2$ Adsorption in the Presence of Water

- No loss of CO$_2$ capacity under wet flue gas conditions

CO$_2$ Adsorption from a Wet Simulated Flue Gas

Adsorption at 40 °C from mixture of 15% CO$_2$ in N$_2$ saturated with water

Mason, McDonald, Bae, Bachman, Sumida, Dutton, Kaye, Long, J. Am Chem. Soc. 2015, 137, 4787
Step-Shaped Isotherms via Cooperative CO$_2$ Binding

- Very little hysteresis upon desorption of CO$_2$
- Step shifts rapidly to higher pressure with increasing temperature
Classical versus Cooperative Adsorbents

amine solutions and other amine adsorbents
diamine-appended MOFs

2 wt % CO$_2$ removed, $\Delta T = 100 ^\circ$ C
15 wt % CO$_2$ removed, $\Delta T = 50 ^\circ$ C

McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odo, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long *Nature* 2015, 519, 303
Insertion and proton transfer results in metal-bound carbamate

Ammonium cation from neighboring site forms an ion pair with the carbamate

McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odo, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long Nature 2015, 519, 303
Ammonium Carbamate Chains

- Insertion of CO$_2$ into the metal-amine bond together with proton transfer
- One-dimensional ammonium carbamate chains indicate origins of cooperativity

Cooperative CO$_2$ Adsorption Mechanism

Position of the step should be influenced by metal-amine bond strength

McDonald, Mason, Kong, Bloch, Gygi, Dani, Crocellà, Giordano, Odoh, Drisdell, Vlaisavljevich, Dzubak, Poloni, Schnell, Planas, Kyuho, Pascal, Prendergast, Neaton, Smit, Kortright, Gagliardi, Bordiga, Reimer, Long Nature 2015, 519, 303
Manipulating the Adsorption Step Position

Substituents on diamine backbone
+CO₂
Substituents on metal-bound amine

Substituents on ammonium-forming amine
Single crystals remain intact upon grafting diamines, activating, and adsorbing CO₂

Primary amines preferentially bind to the metal center
Varying Diamine Bulk in Mg$_2$(dobpdc)

- Increased hydrocarbon bulk shifts step and also suppresses water adsorption.

Siegelman, McDonald, Gonzalez, Martell, Milner, Mason, Berger, Bhown, Long *J. Am. Chem. Soc.* 2017, 139, 10526
Variation of the Diamine Shifts the Step Position

More than 80 different diamines have now been tested in Mg$_2$(dobpdc)

Step position at 40 °C varies from ~50 ppm to >1.2 bar
Manipulating the Thermodynamics of CO$_2$ Capture

- Molecular level tunability enables manipulation of enthalpy and entropy
- Gen1 adsorbent achieves 90% capture with small temperature swing

Gen1 Material for Coal Flue Gas Capture

- Step-shaped adsorption at 40 °C and little adsorption at 100 °C
- Working capacity of 2.4 mmol/g (9.1 wt%) with a 60 °C temperature swing

Adsorption/Desorption Cycling in Gen1 Material

- TGA cycling experiments show no loss of capacity over 1000 cycles

Technical and Economic Advantages/Challenges

Advantages

- High tunability of diamine-appended framework materials
- Large working capacity due to step-shaped CO₂ adsorption
- High selectivity for CO₂ over N₂, O₂, and H₂O is possible
- Molecular level characterization is possible

Challenges

- Large scale production of the adsorbent
- Rendering the materials into a structured form
- Durability and chemical stability under real flue gas
- Reduction of regeneration cost (temperature swing)
Technical Approach and Project Scope

Synthesis of amine-appended MOFs (Gen1–Gen3)

CO₂ adsorption tests, effect of impurities, cycling performance

Collaboration with partners
- MOF production
- System development
- Process modeling

Computational prediction of suitable MOF and diamine pairs

Structure prediction

Materials synthesis & characterization

Computational analysis

Prediction of CO₂ binding energy, relative CO₂ isotherm step position, and mechanical properties

Characterization of materials for relevant parameters for a real process

Development of transformative carbon capture technologies by the cooperative insertion of CO₂ in amine-appended frameworks
Experimental Design and Work Plan

**Year 1**
- Gen1 Amine-appended MOFs synthesis
- Effect of water, $\text{SO}_x$, and $\text{NO}_x$ for Gen1 materials
- Computational prediction of suitable MOF and commercially available amine pairs

**Year 2**
- Synthesis of new amine-appended MOFs (Gen2)
- Stability and cycling performance tests
- Computational work to predict optimal amine-appended MOFs

**Year 3**
- Extensive characterization of Gen1/Gen2 materials
- Characterization of materials fabricated by industrial partners
- Expanded computational search

**Year 4**
- Gen3 materials synthesis and comprehensive characterization
- Characterization of materials tested on partners’ site

- Project management and planning
- Literature survey and synthesis and testing of any relevant materials
- Collaboration with MOF production, system development, and process modeling partners
# Project Schedule and Key Milestones (Year 1)

<table>
<thead>
<tr>
<th>Tasks</th>
<th>Milestones</th>
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</thead>
<tbody>
<tr>
<td>Synthesis of amine-appended MOFs (Gen1 materials)</td>
<td>Deliver a new material with a working capacity of &gt;2.5 mmol/g</td>
</tr>
<tr>
<td>Characterization of the effect of water, SO\textsubscript{x}, and NO\textsubscript{x} on CO\textsubscript{2} adsorption properties of Gen1 materials</td>
<td>Deliver a material that retains &gt;90% of original CO\textsubscript{2} uptake capacity after 20 cycles in the presence of water, SO\textsubscript{x}, NO\textsubscript{x}</td>
</tr>
<tr>
<td>Search optimal amine-appended MOFs within databases of reported materials</td>
<td>Propose 2 candidates whose CO\textsubscript{2} uptake capacity is greater than 3.0 mmol/g</td>
</tr>
<tr>
<td>Prediction of CO\textsubscript{2} binding energies for amine-appended MOFs</td>
<td>Propose candidates having high CO\textsubscript{2} binding energies (&gt;70 kJ/mol)</td>
</tr>
</tbody>
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## Project Schedule and Key Milestones (Year 2)

<table>
<thead>
<tr>
<th>Tasks</th>
<th>Milestones</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Materials synthesis</strong></td>
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</tr>
<tr>
<td>Synthesis of new amine-appended MOFs (Gen2)</td>
<td>Deliver a new material with a working capacity of &gt;3.0 mmol/g</td>
</tr>
<tr>
<td>Characterization of the effect of water, SO$_x$, and NO$_x$ on CO$_2$ adsorption properties of new adsorbents</td>
<td>Deliver a Gen2 material that retains more than 95% of the original CO$_2$ uptake capacity after exposure to a N$_2$/CO$_2$ (= 85/15) stream containing impurities for 3 days followed by cycling tests</td>
</tr>
<tr>
<td><strong>Computation</strong></td>
<td></td>
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<tr>
<td>Search optimal amine-appended MOFs (Gen2 materials) among computationally designed materials</td>
<td>Propose 2 candidates whose CO$_2$ uptake capacity is greater than 3.5 mmol/g</td>
</tr>
<tr>
<td>Prediction of relative CO$_2$ isotherm step position</td>
<td>Based on the analyses, propose the promising candidates whose step position is lower than materials prepared in Year 1</td>
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<tr>
<td>Tasks</td>
<td>Milestones</td>
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<tr>
<td>Comprehensive characterization of all relevant parameters for a real process</td>
<td>Deliver a Gen2 material that retains more than 95% of the original CO\textsubscript{2} uptake capacity after exposure to a N\textsubscript{2}/CO\textsubscript{2} (= 85/15) stream containing impurities for a week followed by cycling tests</td>
</tr>
<tr>
<td>Characterization of materials fabricated by industrial partners</td>
<td>Design shaped materials that maintain at &gt;90% of CO\textsubscript{2} adsorption capacity</td>
</tr>
<tr>
<td>Extend the material design</td>
<td>Propose at least 1 candidate whose \textit{volumetric} CO\textsubscript{2} uptake capacity is greater than 3.5 mmol/cm\textsuperscript{3}</td>
</tr>
<tr>
<td>Prediction of mechanical strength for a real process</td>
<td>Based on the analyses, propose mechanically robust candidates (&gt;10 GPa) for practical applications</td>
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## Project Schedule and Key Milestones (Year 4)

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<th>Materials synthesis</th>
<th>Tasks</th>
<th>Milestones</th>
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<tr>
<td>Synthesis and comprehensive characterization for new (Gen3) materials predicted in Year 3</td>
<td>Deliver a Gen3 material that demonstrates &gt;3.2 mmol/g of CO₂ uptake capacity after exposure to a N₂/CO₂ (= 85/15) stream containing impurities for a week followed by cycling tests</td>
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<tr>
<td>Characterization of materials tested by partners</td>
<td>Performance of tested materials maintains at least 90% of CO₂ adsorption capacity</td>
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## Project Timeline

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<th>Year 2</th>
<th>Year 3</th>
<th>Year 4</th>
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<td>Characterization of the effect of water, SO(_x), and NO(_x) on CO(_2) adsorption properties of Gen1 materials</td>
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# Project Success Criteria

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<td><strong>Year 1</strong></td>
<td>Prepare an adsorbent with &gt;90% CO\textsubscript{2} capture from N\textsubscript{2}/CO\textsubscript{2} (= 85/15) gas mixtures and a working capacity of &gt;2.5 mmol/g under temperature swing conditions.</td>
</tr>
<tr>
<td><strong>Year 2</strong></td>
<td>Prepare an adsorbent with &gt;90% CO\textsubscript{2} capture from N\textsubscript{2}/CO\textsubscript{2} (= 85/15) gas mixtures, a working capacity of &gt;3 mmol/g with a smaller temperature swing than MEA (80 °C), and a regeneration energy less than 2.5 MJ/kg CO\textsubscript{2}.</td>
</tr>
<tr>
<td><strong>Year 3</strong></td>
<td>Prepare an adsorbent that retains the same properties as that from Year 2 after extended high-temperature cycling in the presence of water and other flue gas contaminants (water, SO\textsubscript{x}, NO\textsubscript{x} = ~2%, 800 ppm, and 500 ppm). Synthetic cost (based on rough cost analysis) is less than $75/kg.</td>
</tr>
<tr>
<td><strong>Year 4</strong></td>
<td>Prepare an adsorbent with &gt;90% CO\textsubscript{2} capture from flue gas, a working capacity of &gt;3.2 mmol/g, and a regeneration energy less than 2.2 MJ/kg CO\textsubscript{2} after extended high-temperature exposure/cycling. Synthetic cost (based on rough cost analysis) is less than $50/kg.</td>
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### High Impact Technical Risks and Mitigation Strategies

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<th>Description of Risk</th>
<th>Mitigation Strategies</th>
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<tr>
<td>Computationally proposed materials are difficult to synthesize.</td>
<td>Computational screening will predict multiple promising materials. If one of the proposed adsorbents is difficult to prepare, we will synthesize another promising material.</td>
</tr>
<tr>
<td>Challenges are encountered with gram-scale synthesis of a sorbent.</td>
<td>The Long group has extensive expertise with preparing MOFs at the gram scale. We will focus on scalability as a parameter when evaluating new adsorbents.</td>
</tr>
<tr>
<td>Sorbents with a specific process (fixed bed or Veloxo Therm) fail to show significant reductions in energy penalty and capital cost.</td>
<td>Computational investigation will be performed to evaluate if the palletization of materials under high-pressure affects the CO₂ adsorption properties. In addition, we plan to elucidate the reasons for this from the close collaboration with system modeling partners.</td>
</tr>
<tr>
<td>Calibration of sorbent performance and process limitations can impact the performance of this FWP success criteria.</td>
<td>Accurate data collection mitigates the inaccuracy/ indefinite of the modeling data. We will carry out analysis of new materials to minimize the uncertainty (e.g. use of large quantity of material, repeat analysis to confirm the reproducibility).</td>
</tr>
<tr>
<td>Sorbent performance and scalability impact the technology system economics.</td>
<td>Any issues related to the process design will be solved in close collaboration with the partners. We will also work with MOF synthesis partners to figure out how promising sorbents will be synthesized economically.</td>
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Progress and Current Status of Project: Facilities and Other Resources

**Materials synthesis**
- Fume hoods, benches and standard equipment for wet chemistry
- Gas/vapor adsorption analyzers (e.g. N\textsubscript{2}, Ar, CO\textsubscript{2}, water)
- Thermogravimetric analyzers (TGA) coupled with a mass spectrometer
- Laboratory built breakthrough setups
- Powder X-ray diffractometer (PXRD)
- FT-IR and UV-vis spectrometers
- Grove boxes, ovens, microscopes
- SEM, NMR (solution, solid-state), EA (CHN, ICP) are available at UC Berkeley Chemistry Department
- Access to ALS for single crystal XRD analysis

**Computation**
- Powerful GPU-equipped Linux workstations
- Mid-range computing clusters with multicore 2.5 GHz Ivy Bridge and 2.3 GHz Haswell nodes
- Access to DOE’s the National Energy Resource Scientific Computing Center (NERSC) Cray XC30/XC40 “Cascade” system
Plans for Future Testing and Development

Prediction of MOF–diamine pairs
- Search optimal amine-appended MOFs within databases
- Propose 2 candidates whose CO$_2$ uptake capacity is greater than 3.0 mmol/g

Prediction of CO$_2$ binding energies
- Optimize structures and estimate CO$_2$ binding energies for Gen1 materials
- Calculate water, SO$_x$, and NO$_x$ binding energies

Synthesis of diamine-appended MOFs (Gen1 materials)
- Synthesis and characterization of Gen1 materials
- Test CO$_2$ adsorption behaviors of Gen1 materials
- Characterization of the effect of water, SO$_x$, and NO$_x$ on CO$_2$ adsorption properties on Gen1 materials

Collaboration with partners
- Discussion of technology information needs for MOF production, system development, and process modeling
- Collection and analysis of materials characterization data
- Incorporation of relevant data into design catalogue