New Carbon-Based Porous Materials with Increased Heats of Adsorption for Hydrogen Storage

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Overview

**Timeline**
- Start date: 9/1/2008*
- End date: 8/31/2012
- 0% complete*

**Barriers**
- Hydrogen storage
  - Gravimetric target
  - Volumetric target
  - Increased heat of adsorption

**Budget**
- Total project funding
  - DOE share: $1,295,493
  - Contractor share: $321,833
- FY08 Funding: $0
- FY09 Funding: $385,812

**Overview**
9/1/2008 is official start date. Funding not received until March 2009.
Relevance

Overall Project Objectives

• Develop new materials to meet DOE volumetric and gravimetric targets for hydrogen storage
  – Metal-organic frameworks (MOFs)
  – Polymer-organic frameworks (POFs)
  – Tight integration of synthesis, characterization, and modeling

• Increase heats of adsorption as a means to meet volumetric and gravimetric targets at ambient conditions
Objectives for Current Year

• Metal-organic frameworks
  – Measure heats of adsorption and hydrogen uptake in existing cation-containing MOFs
  – Develop a new class of cation-containing MOFs

• Polymer-organic frameworks
  – Develop new POFs with high heats of adsorption
  – Use building blocks that increase microporosity and can bind lithium ions

• Modeling
  – Determine whether catenation is beneficial
  – Develop model for cation-containing MOFs
Approach

Snurr
Computational elucidation, design and modeling

Hupp
Synthesis and characterization of MOFs

Kanatzidis
Synthesis and characterization of POFs

Nguyen
Design and synthesis of SBUs for MOF and POF assembly
Approach

Enhance $\text{H}_2$ uptake via introduction of cations

• Two approaches for introducing cations
  – Framework reduction
  – Alkoxide functionalization

• Mechanisms for increased uptake
  – Enhanced London dispersion interactions due to enhanced framework polarizability?
  – Enhanced adsorption due to increase in electric field?
  – Enhanced adsorption due to charge/quadrupole interactions?
  – Enhanced adsorption due to ion-induced displacement of catenated frameworks?
**Approach**

*Metal-organic Frameworks*

- Introduce charge via desirable cations
- Cation placement known and controllable
- Alkoxide formation should not greatly alter structure
- Alkoxide frameworks not air sensitive
Approach

Metal-organic Frameworks

Milestones for FY09

- Achieve 8 kJ/mol heat of adsorption at low coverage
- Achieve 8 kJ/mol heat of adsorption with little drop-off at higher coverages
- Achieve 10 kJ/mol heat of adsorption at low coverage

Hydroxyl-functionalized MOFs

Approach

Polymeric-organic Frameworks

- Tailorable, microporous polymers containing π-conjugated phenyl groups linked together
- Modular construction
  - Two synthesis methods
    - Schiff’s base chemistry
    - “Click” chemistry
  - Components chosen to produce loosely-packed, extended 3D networks
- Attributes of POFs that make them attractive for hydrogen storage
  - Very low density
  - Three-dimensional semi-rigid character
  - Designed microporosity through inefficient packing of polymer chains
  - Built-in functional groups for tuning H₂ interaction
  - Ability to generate systematic series of materials will provide increased understanding of gas adsorption and ultimately optimization
Approach

Polymer-organic Frameworks

Milestones for FY09

- Synthesize POFs with surface areas > 1500 m²/g
- Introduce Li ions into POFs
- Demonstrate tunability of microporosity
- Achieve 8 kJ/mol heat of adsorption at low coverage
Molecular Modeling

• Determine effect of catenation on H\textsubscript{2} adsorption in Northwestern paddlewheel MOFs using
  – grand canonical Monte Carlo (GCMC) simulations
  – existing force fields that have been validated for other MOFs
• Develop model for cation-containing MOFs
  – Determine H\textsubscript{2}/cation interactions with quantum chemical methods
    • DFT for geometries
    • MP2 with large basis set for energies → heat of adsorption
  – Fit QM results to analytic forms for GCMC
  – Use GCMC to predict effects of different cations, cation loading, pore size, etc. on hydrogen uptake
Approach

Molecular Modeling

• Milestones for FY09
  – Determine whether catenation is beneficial for hydrogen uptake in MOFs without cations
  – Develop model for cation-containing MOFs

Example: Hydrogen in IRMOF-1

Technical Accomplishments and Progress: Previous Work

One of two identical networks shown

- Synthesis of a reducible-framework material
- Struts can be reduced with lithium.
Technical Accomplishments and Progress: Previous Work

• Zn$_2$(NDC)$_2$(diPyNI) MOF is reduced upon exposure to Li$^0$ in DMF

• H$_2$ uptake is nearly doubled with 5% doping

• Heat of adsorption substantially increases

Technical Accomplishments and Progress: Previous Work

- Enhancement effects extend to other cations
- Enhancement effects extend to other MOFs
- Enhancements scale with cation-induced surface area modulation

Technical Accomplishments and Progress: Previous Work

Using modeling, established that H$_2$ uptake in MOFs fall into 3 regimes:

- At low P, uptake correlates with heat of adsorption
- At intermediate P, uptake correlates with surface area
- At high P, uptake correlates with free volume

Technical Accomplishments and Progress: Previous Work

Using modeling, quantified the trade-off between free volume and heat of adsorption for H$_2$ storage in MOFs.

Both are necessary.

△ IRMOF-1; ◇ IRMOF-9; ☆ IRMOF-10; ○ IRMOF-14; + IRMOF-16; □ Cu-BTC

Collaborations

• Argonne National Laboratory
  – Dr. Karen Mulfort: SAXS and other characterization
  – Dr. Peter Stair: Raman characterization

• Universidade Federal Ceara, Fortaleza, Brazil
  – Profs. Celio Cavalcante, Diana Azabedo, Mardonio Lucena: high pressure adsorption measurements, round-robin validation of uptake measurements

• Nature of the collaborations
  – We have existing relations with these groups, but the collaboration on hydrogen storage is just starting.
  – These groups are external to the DOE H₂ Program
Proposed Future Work

• MOFs
  – Develop non-catenated, high-area, cation-containing MOFs
  – Continue to measure H₂ uptake and heats in new materials

• POFs
  – Develop new cation-containing POFs
  – Continue to measure H₂ uptake and heats in new materials

• Modeling
  – Validate model against experimental data
  – Extend modeling to POFs

• Go/No-Go Decision at end of FY10
  – Project will continue into Phase 2 if any materials have a volumetric capacity of 45 g/L at −40°C and 100 atm; or if any materials have a gravimetric capacity of 6 wt% at −40°C and 100 atm; or if any materials display heats of adsorption above 10 kJ/mol. Note that these are capacities of the materials alone.
  – The Phase 2 transition would include down selecting materials.
Summary

• We are developing new materials to meet DOE hydrogen storage targets
  – Metal-organic frameworks (MOF)
  – Polymer-organic frameworks (POF)
• The new concept is to introduce cations into MOFs and POFs to improve the heats of adsorption, which will improve room temperature storage.
• We have already developed 2 strategies for introducing cations into MOFs.
• Integration of molecular modeling and experiment will aid in reaching our goals.