A Synergistic Approach to the Development of New Hydrogen Storage Materials, Part I

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Project ID # ST27

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Overview

Timeline
• Project start: 12/1/04
• Project end: 11/30/09
• Percent complete: 70%

Budget
• Total funding expected: $2.9M
  – $1.8M from DOE to UC Berkeley
  – $600k from DOE to LBNL
  – $500k in cost-sharing
• Funding FY07: $400k
• Funding FY08: $600k

Barriers
• Identify new materials enabling a hydrogen storage system achieving:
  – 2 kWh/kg (6 wt %)
  – 1.5 kWh/L (0.045 kg/L)
  – 4 $/kWh

Partners
• ChevronTexaco
• General Motors Corporation
• Electric Power Research Institute
Overall Program

Synthesis of porous polymers (Fréchet)
Synthesis of porous coordination solids (Long)
Calculations of $H_2$ binding energies (Head-Gordon)
Synthesis of destabilized hydrides (Richardson)
$H_2$ storage characterization instrumentation (Mao)
Metal/metal hydride nanocrystals (Alivisatos)
Synthesis of nanostructured boron nitrides (Zettl)
Theory for boron nitride materials (Cohen and Louie)

*Note that the results presented here are solely from Part I, which is funded through EERE*
H₂ Adsorption in a Hypercrosslinked Polymer

poly(chloromethylstyrene-co-divinylbenzene)

Surface area = 2,200 m²/g
Sorption capacity = 3.8 wt %

77 K
Comparison of Hypercrosslinked Polymers

- Hypercrosslinked poly(chloromethylstyrene) - co-divinylbenzene
  - Surface area = 2,200 m²/g

- Hypercrosslinked poly(chloromethylstyrene)
  - Surface area = 1,300 m²/g

- Rapid desorption with no hysteresis
- Lower enthalpy of adsorption
- Does the polymer swell with pressure?

77 K

Excess H₂ Adsorbed, wt %

Pressure, MPa
Hypercrosslinked Polyaniline

Route 1:

\[
\begin{align*}
\text{Route 1: } & \quad \text{H} \quad \text{N} \quad \text{H} \quad \text{N} \quad \text{N} \quad \text{N} \\
& \quad \begin{array}{c}
\text{R} \\
\text{R}
\end{array}
\quad \text{DMF} \\
& \quad \begin{array}{c}
\text{K}_2\text{CO}_3 \\
\text{NMP}
\end{array}
\end{align*}
\]

Route 2:

\[
\begin{align*}
\text{Route 2: } & \quad \text{H} \quad \text{N} \quad \text{H} \quad \text{N} \quad \text{N} \quad \text{N} \\
& \quad \begin{array}{c}
\text{CH}_2 \\
\text{CH}_2
\end{array}
\quad \text{NMP}
\end{align*}
\]
Effect of Crosslinking Route

- Crosslinking with methylene units gives highest surface areas
H$_2$ Uptake in Hypercrosslinked Polyaniline

- Steep rise consistent with increased heat of adsorption to 8-10 kJ/mol

77 K
Variation of N$_2$ Uptake in Zn$_4$O(BDC)$_3$ (MOF-5)

<table>
<thead>
<tr>
<th>preparation</th>
<th>N$_2$ uptake (mmol/g)</th>
<th>SA$_{BET}$ (m$^2$/g)</th>
<th>SA$_{Langmuir}$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.8</td>
<td>570</td>
<td>1010</td>
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<td>2</td>
<td>14.5</td>
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<tr>
<td>6</td>
<td>3530</td>
<td>4170</td>
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</tbody>
</table>

(2) Yan, et al. Microporous Mesoporous Mater. 2003, 58, 105
(3) Li, Eddaoudi, O'Keeffe, Yaghi Nature 1999, 402, 276
Optimized Synthesis and Activation of Zn$_4$O(BDC)$_3$

\[ \text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \quad + \quad \begin{array}{c}
\text{HO-} \\
\text{C-H} \\
\text{C-OH}
\end{array} \\
\text{0.33 g, 2.0 mmol}
\]

\[ \text{H}_2\text{BDC} \quad \xrightarrow{80 \degree C, 8 h, 50 \text{ mL DEF}} \quad \text{Zn}_4\text{O(BDC)}_3 \cdot x\text{DEF} \quad \text{0.37 g, 73%}
\]

- Heating too high or too long gives yellow-brown crystals with reduced storage capacity

**Evacuation procedure**

- Soak crystals in 10 mL DMF for 8 h (6 times)
- Soak crystals in 10 mL CH$_2$Cl$_2$ for 8 h (6 times)
- Evacuate crystals at 25 °C under dynamic vacuum until an outgas rate of <1 mtorr/min is achieved
Decomposition of $\text{Zn}_4\text{O(BDC)}_3$ in Air

$\text{Zn}_4\text{O(BDC)}_3 \rightarrow \text{Zn}_3(\text{OH})_2(\text{BDC})_2 + ?$ (nonporous)

Graph showing patterns with exposure time:
- 24 h
- 12 h
- 10 min
- <1 min

Counts vs. $2\theta$
## Variation of N\textsubscript{2} Uptake in Zn\textsubscript{4}O(BDC)\textsubscript{3}

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<tr>
<td>air-free</td>
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<td>4400</td>
</tr>
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High-Pressure $\text{H}_2$ Uptake in $\text{Zn}_4\text{O(BDC)}_3$

- At 40 bar, a record physisorbed excess capacity of 7.1 wt % is achieved.
- Total uptake is the amount of gas contained within the volume of the crystals.

High-Pressure H₂ Uptake in Zn₄O(BDC)₃

- Knowledge of total uptake permits calculation of the volumetric storage density
- At 100 bar, a record physisorbed storage density of 66 g/L is achieved

Kinetics and Cycling for H$_2$ Uptake in Zn$_4$O(BDC)$_3$

- Results are upon exposure to a manifold of H$_2$ gas at 45 bar and 298 K
- No detectable loss in capacity or kinetics after 24 adsorption-desorption cycles

Room-Temperature H₂ Uptake in Zn₄O(BDC)₃

- At 298 K, framework offers little improvement over density of pure H₂ gas
- Due to very weak interaction of H₂ with the framework ($\Delta H_{ads} \approx 5$ kJ/mol)

Coating the Surfaces with Cr(CO)$_3$ Units

- Infrared spectrum matches that observed for molecular analogue
- Elemental analysis and NMR spectroscopy indicate attachment to all rings

Matrix Isolation Chemistry in a Framework

- Infrared spectra match those observed for molecular analogues
- Compound 3 is much more stable than analogue generated in frozen Xe
Strong H₂ Binding at Cr⁰ Centers

- Infrared spectra match those observed for molecular analogues
- Cr⁰-H₂ complex in compound 2 is stable indefinitely at room temperature!
Range of H₂ Binding Interactions

dispersion < electrostatics < charge-transfer

Lochan, Head-Gordon Phys. Chem. Chem. Phys. 2006, 8, 1357
Understanding H$_2$ Binding

A New Analysis Method

Decompose interaction energies rigorously into:

- Geometric distortion
- Frozen density interaction
- Induction
- Forward- and back-donation
- Small higher-order charge transfer

• Khaliullin, Cobar, Lochan, Bell, Head-Gordon J. Phys. Chem. A 2007, 111, 8753
Relative Effect of Substituent

Metal chosen as Cr$^0$

![Graph showing energy levels and contributions of electrostatics, back-donation, and forward donation for different substituents.](image)
Effect of Substituent (R)

- Electron-donating groups enhance binding, while electron-withdrawing groups reduce binding
  - Tunability is 7% of binding
  - Energies are for three bound H$_2$ molecules

- Correlates with back-donation, electrostatics

- Quantitative information; qualitative insight
  - BDC$^{2-}$ substituents can fine-tune binding
  - Coarse-tuning must come from different metals
Effect of Metal Substitution

- Heavier isoelectronic elements:
  \((C_6H_6)Cr(H_2)_3\) binding per \(H_2\) of 68 kJ/mol
  \((C_6H_6)Mo(H_2)_3\) binding per \(H_2\) of 84 kJ/mol

- Lighter transition elements:
  \((C_6H_6)Cr(H_2)_3\) binding per \(H_2\) of 68 kJ/mol
  \((C_6H_6)Ti(H_2)_4\) binding per \(H_2\) of 32 kJ/mol

- Shows coarse tuning is possible
  Still need to examine synergy of these effects
Destabilization of Metal Hydrides

- Attempts at alloying of Mg in order to reduce $\Delta H$
- Success in partial substitution to form $\text{Mg}_{1-x}A_x$ ($A = \text{Mn, Fe, Ni}$)
- Some increases in plateau pressures, but poor kinetics
- Attempts to substitute Na and Li for Mg are underway
Attempts to Generate MgH$_{2-x}$F$_x$ Solid Solutions

Preliminary results, not yet reproduced:

- MgH$_2$ + 10 mol% MgF$_2$ ball-milled
- 1$^{\text{st}}$ desorption at 663 K: 6.1 wt% (based on MgH$_2$ component)
- 1$^{\text{st}}$ absorption at 573 K: 7.4 wt%
- 2$^{\text{nd}}$ desorption at 663 K: 7.2 wt%

Does fluoride catalyze H$_2$ uptake and release via solid solution formation?
Destabilization of Complex Hydrides?

- Attempts at partial substitutions to adjust thermodynamics and kinetics
- Substitutions at both Mg and transition metal sites, as above
- Study effects of substituting F for H (e.g., CaH$_{2-x}$F$_x$ known for all $x$)
- Small fluoride additions reported to enhance reactivity of Mg$_2$Ni