

IV.D.1 A Synergistic Approach to the Development of Nanostructured Materials for Hydrogen Storage (Part I)

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Objectives

Bring together an eclectic group of scientists with experience in materials discovery and theoretical prediction of properties to work on developing new types of hydrogen storage materials.

Particular emphasis is placed on exploring the possibilities of the following types of materials for meeting the 2010 DOE hydrogen storage system targets, especially specific energy, energy density, durability, and uptake and discharge kinetics:

- nanoporous polymers
- nanoporous coordination solids
- destabilized high-density hydrides
- nanostructured boron nitride
- magnesium and light alloy nanocrystals

Note that only the research on nanoporous polymers, nanoporous coordination solids, and destabilized high-density hydrides is funded through this project, with the other subprojects being funded through Basic Energy Sciences.

Technical Barriers

This project addresses the following technical barriers from the On-Board Hydrogen Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The main focus will be on meeting the following specific targets:

- By 2010, develop and verify on-board hydrogen storage materials achieving storage system targets of 2 kWh/kg (6 wt%), 1.5 kWh/L, fill time of 3 minutes for 5-kg of hydrogen, and \$4/kWh.

TABLE 1. On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2010 System Target	FY 2006 materials**
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	2.2 wt% at 77 K and 10 bar for Cu ₃ [Co(CN) ₆] ₂ (SA 730 m ₂ /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	1.6 wt% at 77 K and 1 bar for Cu ₂ [Fe(CN) ₆] ₂ (SA 730 m ₂ /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	1.6 wt% at 77 K and 1 bar for hypercrosslinked poly(styrene-co-divinylbenzene) (SA 1930 m ₂ /g)

**Data is based on material only, not system value

FY 2006 Accomplishments

- Extended characterization of H₂ adsorption within the dehydrated Prussian blue analogue Cu₃[Co(CN)₆]₂. A fully reversible storage capacity of 2.2 wt% was observed at 77 K and 10 bar. Neutron powder diffraction measurements revealed the location of the H₂ binding sites within the structure.
- Determined the hydrogen storage properties of the cyano-bridged framework solids A₂Zn₃[Fe(CN)₆]₂

($A = \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{H}_3\text{O}^+, \text{Li}(\text{H}_2\text{O})^+$). Reversible sorption capacities between 1.0 and 1.2 wt% were observed, with the enthalpy of H_2 adsorption falling in the range 7.5-9.0 kJ/mol at low surface coverage.

- Synthesized and characterized Prussian blue analogues of the type $\text{M}_2[\text{Fe}(\text{CN})_6]$ ($M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$). Uptake at 77 K and 890 torr varied from 0.0 wt% in $\text{Mn}_2[\text{Fe}(\text{CN})_6]$ to 1.6 wt% H_2 in $\text{Cu}_2[\text{Fe}(\text{CN})_6]$. A fit of the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ isotherm to the Langmuir-Freundlich equation predicts a maximum uptake of 2.3 wt% H_2 .
- Incorporated a variety of transition metal carbonyl complexes within $\text{Zn}_4\text{O}(\text{1,4-benzenedicarboxylate})_3$.
- Established high throughput methods for metal-organic framework synthesis.
- Synthesized and characterized a series of poly(styrene-co-divinylbenzene) beads exhibiting surface areas as high as 1,930 m^2/g . Grafting of polyaniline and polypyrrole chains onto the pore surface was further demonstrated. Reversible H_2 uptake of 1.6 wt% at 77 K and 1 atm was observed in one of the two materials tested thus far.
- Developed computational methods for accurately assessing H_2 binding interactions, and applied these methods in assessing binding affinities for a broad range of bare metal cations.

Introduction

Known hydrogen storage materials exhibiting promise include nanostructured carbon-based solids, chemical hydrides, and metal hydrides. Although worthy of significant further investigation, it is by no means clear that any of these systems will be able to meet the DOE performance targets for 2010. We are therefore undertaking a broad-based and coordinated effort to search for new classes of hydrogen storage materials.

Approach

The combined team of UC-Berkeley and LBNL have formed a collaborative, interdisciplinary group to research promising nanostructured materials for hydrogen storage. A total of seven themes or subprojects are currently underway; the following four are funded through this project:

- Synthesis and characterization of nanoporous coordination solids (Long).
- Synthesis and characterization of nanoporous polymers (Fréchet).
- First-principles determination of H_2 binding energies with predictive applications in design of new nanoporous hydrogen storage materials (Head-Gordon).

- Synthesis and characterization of destabilized high-density hydrides (Richardson).

Our approach will be to explore numerous possibilities for new materials, and narrow our focus as the research progresses. The synergy of many scientists in one location working toward a common goal is expected to accelerate our progress and lead to new ideas via cross-fertilization.

Results

Nanoporous Coordination Solids. Over the past year, we have continued our study of porous coordination solids with coordinatively unsaturated metal atoms for use as hydrogen storage materials. Following our work on hydrogen sorption in $\text{M}_3[\text{Co}(\text{CN})_6]_2$ ($M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) materials, we have examined the Prussian blue analogues of the type $\text{M}_2[\text{Fe}(\text{CN})_6]$ ($M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$). Unfortunately, these materials were found to be considerably less thermally stable than previously studied Prussian blue analogues. Even under gentler dehydration conditions, the N_2 storage capacities indicated significant framework collapse for $\text{Co}_2[\text{Fe}(\text{CN})_6]$ and $\text{Ni}_2[\text{Fe}(\text{CN})_6]$, and complete collapse for $\text{Mn}_2[\text{Fe}(\text{CN})_6]$. The sole exception was $\text{Cu}_2[\text{Fe}(\text{CN})_6]$, which has a BET surface area of 730 m^2/g , similar to that of other Prussian blue analogues and suggesting that its framework is largely intact. Hydrogen sorption measurements of these materials were also consistent with varying degrees of framework collapse upon dehydration. Uptake at 77 K and 890 torr varied from 0.0 wt% in $\text{Mn}_2[\text{Fe}(\text{CN})_6]$ to 1.6 wt% H_2 in $\text{Cu}_2[\text{Fe}(\text{CN})_6]$. A fit of the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ isotherm to the Langmuir-Freundlich equation predicts a maximum uptake of 2.3 wt% H_2 , slightly higher than the saturation value of 2.2 wt% observed for $\text{Cu}_3[\text{Co}(\text{CN})_6]_2$ at 10 bar and 77 K.

In order to better understand the effect of the coordinatively unsaturated metal sites on dihydrogen sorption, we synthesized and measured the sorption properties of a series of Prussian blue analogues with varying numbers of $[\text{M}(\text{CN})_6]^{n-}$ vacancies. We found that the weight percent hydrogen sorbed at saturation decreased with decreasing vacancies in the lattice. However, the enthalpy of adsorption of dihydrogen for all materials, include those with no coordinatively unsaturated metal sites, was between 6.0-7.5 kJ/mol. This suggests that the dihydrogen interaction with the coordinatively unsaturated metal sites is comparable to, or weaker than, the dihydrogen interaction with the cyanide ligands or the metal-cyanide bonds. To further elucidate the nature of sorbed H_2 in these materials, in collaboration with the Neumann and co-workers at NIST, powder neutron diffraction measurements were taken of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2$ in the presence of deuterium. These measurements showed that at a loading of

1 H₂/Cu²⁺, 25% of the hydrogen molecules were interacting with the open coordination sites on Cu²⁺, with the remainder interacting with the pore walls, demonstrating the H₂ can be adsorbed through binding to an open metal coordination site.

We have also studied dihydrogen sorption in A₂Zn₃[Fe(CN)₆]₂ (A = Na⁺, K⁺, Rb⁺, H₃O⁺, Li⁺(H₂O)), in which dihydrogen may interact with the monovalent cations residing in the pores of the [Zn₃[Fe(CN)₆]₂]²⁻ framework. All five materials studied have dihydrogen sorption capacities between 1.0 and 1.2 wt%, and surface areas ranging from 470 to 600 m²/g. The enthalpy of adsorption of dihydrogen ranged from 7.5-9.0 kJ/mol at low surface coverage with the trend K⁺ > H₃O⁺ ≈ Li(H₂O)⁺ > Rb⁺ > Na⁺. This trend contrasts with that observed for the gas phase interaction between dihydrogen and alkali metals, suggesting that a variety of factors influence the strength of the metal-dihydrogen interaction beyond the size and charge of the cation.

In addition to our work on metal-cyanide coordination solids, we have also investigated porous coordination solids that can bind low-valent transition metals. These relatively electron-rich metals are expected to have a strong π back-bonding interaction with dihydrogen, resulting in a stronger metal-H₂ interaction than the electron-poor cations in the metal-cyanide compounds discussed above. Towards this end, we have synthesized the compound Zn₄O(BOP)₃ (BOP = 2-prop-2-ynoxy-1,4-benzenedicarboxylate), a cubic framework with alkyne groups extending into the pores of and therefore available to coordinate metal complexes. This material reacts with Co₂(CO)₈ to form the complex Zn₄O(BOP•Co₂(CO)₆)₃, in which the ligand environment around Co is the same as that in Me₂BOP•Co₂(CO)₆.

In addition to binding metals to pendant alkyne groups, we have also investigated binding of low-valent metals to aromatic rings in porous metal-organic frameworks. We have found that Zn₄O(BDC)₃ (BDC = 1,4-benzenedicarboxylate) reacts with Cr(CO)₆ to form the complex Zn₄O[BDC•Cr(CO)₃]₃. The carbonyl stretching region of the infrared (IR) spectrum of this material is similar to that of the molecular complex BDC•Cr(CO)₃, suggesting that the ligand environment around chromium is the same in both compounds. Similar reactions of Zn₄O(BDC)₃ with Mo(CO)₆ and W(CO)₆ yield the analogous compounds Zn₄O[BDC•Mo(CO)₃]₃ and Zn₄O[BDC•W(CO)₃]₃, respectively. After heating Zn₄O(BDC•Cr(CO)₃)₃ at 250°C under a flow of N₂ or H₂ for 10 h, the IR spectrum of the resulting material shows that all carbonyl ligands have been removed. Work is underway to scale up this reaction in order to determine the structure of this material and obtain hydrogen and other gas sorption measurements.

In collaboration with the Fréchet group, we have also been working to incorporate C₆H₆•Cr(CO)₃ units into porous polymers. Thus far we have been able to synthesize porous poly-divinylbenzene with Cr(CO)₃ fragments attached to ~50% of the benzene rings. Similar to the reaction described above for Zn₄O(BDC•Cr(CO)₃)₃, heating the polymer to 225°C under a flow of N₂ or H₂ for 10 h removes all of the carbonyl ligands.

In addition to our investigations of porous solids containing low-valent transition metals, we are also working with Symyx Corporation to develop methods for rapid synthesis and screening of metal-organic frameworks for hydrogen storage. Using instrumentation developed at Symyx for running large numbers of reactions in parallel and characterizing the resulting products, we plan to synthesize large numbers of metal-organic frameworks with different metals and bridging ligands and screen them for their potential to store hydrogen. As a proof of principle, we have explored the reaction of Zn(NO₃)₂ with 1,4-benzenedicarboxylic acid with a variety of stoichiometries, solvents, co-solvents, temperatures, and reaction times. Nearly 400 reactions were run in two days and a microscope used to image each reaction vessel. In these initial experiments 184 out of 384 reactions produced large crystals, which suggests that this is an excellent method for exploring reaction conditions for the synthesis of metal-organic frameworks. Work is currently underway to set up a system for rapidly measuring the powder x-ray diffraction pattern of these materials and to identify the unknown phases by single-crystal x-ray diffraction. Future work will be directed toward developing a system for rapid measurement of the surface area of the synthesized materials, which will provide a method for the rapid identification of promising materials for hydrogen and other gas storage.

Nanoporous Polymers. Given the results obtained in the screening of commercial resins suggesting that hypercrosslinked polymers are better suited for hydrogen storage than normally crosslinked copolymers, a further study of hypercrosslinked materials was carried out. We prepared hypercrosslinked beads with a surface area significantly higher than that of the commercial polymers. The two step process we used includes first the preparation of poly(vinylbenzyl chloride) precursor beads using a typical suspension polymerization process. This is followed by a second step in which the beads are swollen in dichloroethane and a FeCl₃ catalyzed Friedel-Crafts crosslinking reaction is carried out. The specific surface area of an optimized polymer reaches values as high as 1,930 and 829 m²/g as calculated from nitrogen and hydrogen adsorption, respectively. This material adsorbs 1.55 wt% hydrogen at a pressure of 0.12 MPa. Application of the Langmuir equation reveals that only about 68% of the available surface is covered

with hydrogen at this pressure. Extrapolation indicates that coverage to 95% of the monolayer capacity would be reached at a reasonable pressure of 1.2 MPa affording a respectable hydrogen adsorption capacity of 2.2 wt% at that pressure. The nitrogen adsorption isotherm of the type 1 isotherm indicates that the polymer contains a large numbers of very small pores with a size of about 2 nm.

Upcoming hydrogen storage systems must exhibit increased capacity. In addition, the rate at which hydrogen can be stored should be fast with a current DOE goal of 1.5 kg H₂/min in 2010. Despite the high diffusion rate of the small hydrogen molecule, small pore size and long distance through kilograms of material are likely to limit this fueling rate. In contrast to hypercrosslinked gel polymers mentioned above featuring large numbers of nanopores, their macroporous counterparts enable fast mass transport through the much larger pores. However, typical macroporous polymers exhibit surface areas that only reach a few hundreds of m²/g. We demonstrated the preparation of hypercrosslinked polymers from a polymer precursor containing high percentage of divinylbenzene. Despite the general perception that these highly crosslinked polymer do not swell to a significant extent, we prepared beads with a dual pore size distribution including the original macropores and newly formed small pores. We prepared 40% crosslinked porous poly(vinylbenzyl chloride-co-divinylbenzene) beads using toluene as a porogen. These beads exhibit a specific surface area of 310 and 176 m²/g determined using nitrogen and hydrogen, respectively. Due to its relatively low surface area, the hydrogen storage capacity of the macroporous precursor is only 0.4 wt%. After applying the same hypercrosslinking process as used previously, we formed a nanoporous polymer with an almost four-fold higher surface area (measured as of 1,300 and 639 m²/g using nitrogen and hydrogen, respectively). This hypercrosslinked macroporous polymer affords a still respectable capacity of 1.2 wt% for hydrogen at 0.12 MPa. The smaller surface area limits the useful hydrogen storage capacity of the polymer, as calculated using the Langmuir equation, to 1.7 wt% H₂. The nitrogen adsorption isotherm of this porous polymer is different from that of the hypercrosslinked gel and can be classified as type 4, which indicates a material with relatively large pores. The calculated incremental surface area distribution suggests that a significant fraction of the pore surface area still originates from pores with a size of 2 nm. However, this fraction is notably smaller than that observed for hypercrosslinked gel beads. In contrast, a significant proportion of the surface area in the macroporous/nanoporous hybrid polymer originates from pores larger than 5 nm.

Computational Studies of H₂ Binding. We performed a systematic computational survey of the range of hydrogen binding affinities possible without

complete dissociation of the hydrogen molecule. We explored connections between the strength of binding and chemical features of the binding site. Molecular hydrogen interacts with a substrate through at least three chemically distinct mechanisms. Long-range dispersion interactions, or London forces, are always operative, but are the weakest interactions. Electrostatic interactions, including coupling of permanent moments (coupling of a charge to the quadrupole moment of hydrogen) as well as induction effects (induced dipole on hydrogen due to an unscreened ion) are stronger. Finally, hydrogen can participate in donor-acceptor interactions with orbitals of the bonding site to develop strong specific interactions with the substrate. In practice, all three classes of interactions are operative at once, and in a sense the job of materials design for hydrogen storage is to fine-tune the extent of these interactions to yield hydrogen binding affinities that lie in an acceptable target range (for instance approximately 15-30 kJ/mol). Our work found that exposed metal sites with significant unscreened charge are particularly promising candidates. This was published recently as a feature article, including cover art (Figure 1, top).

Our second topic is the study of specific binding sites that can be potentially designed into metal-organic frameworks of the type synthesized in the Long group. Based on our survey calculations, we expect that coordinatively-unsaturated metal sites with charges that are not fully screened are ideal. From discussions with the Long group we have chosen to examine transition metal complexes where the metal is coordinated to an aromatic ring of the type used as the organic spacers in metal-organic frameworks. These complexes are of the form [M(CO)_nAr] (Figure 1, bottom) where the metal is either Cr or Mo (lighter elements will also be investigated later). The calculations are performed using state-of-the-art electronic structure methods, and show that a range of quite strong interaction strengths are possible, which, in general decrease as the extent of coordinative unsaturation decreases. The work is aimed at exploring the effect of the metal, the aromatic work substituents, and the accompanying ligands on the binding strength. The outcome will be suggestions for binding sites that can be employed in framework and polymer design, which can also potentially be compared against the performance of newly-synthesized materials. Collaborations will continue with the Long and Fréchet groups to explore other promising binding site designs.

Destabilized Metal Hydrides. A stainless steel vacuum system and associated reaction vessels for preparation and low-pressure treatment of metal alloy samples was assembled from commercially available components. The utility of our controlled atmosphere microbalance to reliably measure hydrogen storage behavior in magnesium alloys was tested using a magnesium-nickel alloy whose composition is Mg_{2.4}Ni. This sample did not fully react with hydrogen within the

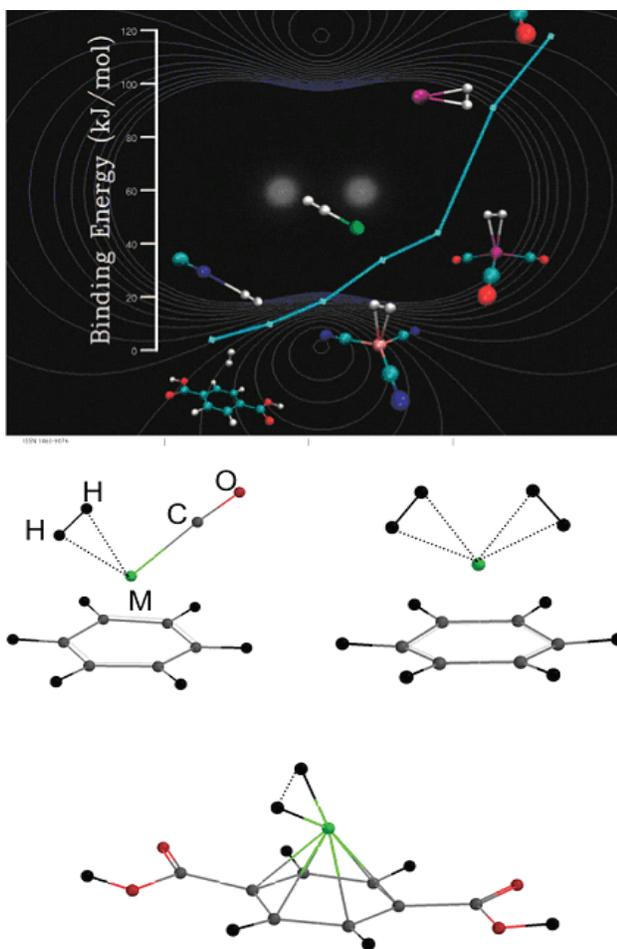


FIGURE 1. Hydrogen Binding Journal Article Artwork (top) Metal-Organic Frameworks of the form $M(CO)_nAr$ (bottom)

temperature and pressure limits of the balance, but the gross features of the measured isotherms were consistent with its known properties. Two other samples were tested, but neither showed any weight gain in hydrogen up to 500°C. Substantial buoyancy corrections had to be applied, but the repeatability was poor.

Preparation of magnesium alloys containing titanium and manganese was carried out by heating powder mixtures to 500°C in sealed stainless steel containers lined with molybdenum foil to prevent interaction with the vessel walls. Some de-mixing of the components during the reactions occurred despite efforts to ensure adequate mixing of the precursor powders and containment of the reaction mixture. It will be necessary either to ball mill the powders or use a reaction vessel that can withstand higher temperatures. Preparation of other alloys is in progress.

Conclusions and Future Directions

Synthetic approaches have now been developed for incorporating high concentrations of metal carbonyl units within nanoporous coordination solids and polymers. Methods for displacing CO are now under investigation, and will be followed by H_2 storage measurements for these unique materials. In addition, electronic structure calculations are underway to assess the best combinations of metal center and ligand substituents to adjust the H_2 binding energy.

FY 2006 Publications

1. "Hydrogen Storage in the Dehydrated Prussian Blue Analogues $M_3[Co(CN)_6]_2$ ($M = Mn, Fe, Co, Ni, Cu, Zn$)" Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* 2005, 127, 6506-6507.
2. "Strong H_2 Binding and Selective Gas Adsorption within the Microporous Coordination Solid $Mg_3(O_2C-C_{10}H_6-CO_2)_3$ " Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* 2005, 127, 9376-9377.
3. "Computational Studies of Molecular Hydrogen Binding Affinities: The Role of Dispersion Forces, Electrostatics, and Orbital Interactions" Lochan, R. C.; Head-Gordon, M. *Chem. Phys. Phys. Chem.* 2006, 8, 1357-1370.
4. "Neutron Diffraction and Neutron Vibrational Spectroscopy Studies of Hydrogen Adsorption in the Prussian Blue Analogue $Cu_3[Co(CN)_6]_2$ " Hartman, M. R.; Peterson, V. K.; Liu, Y.; Kaye, S. S.; Long, J. R. *Chem. Mater.* 2006, 18, ASAP.
5. "The Role of Vacancies in the Hydrogen Storage Properties of Prussian Blue Analogues" Kaye, S. S.; Long, J. R. *Catal. Today* 2006, in press.
6. "High Surface Area Nanoporous Polymers for Reversible Hydrogen Storage" Germain, J.; Hradil, J.; Fréchet, J. M. J.; Svec, F. *Chem. Mater.*, submitted for publication.

FY 2006 Presentations

1. "Hydrogen Storage in Microporous Coordination Solids with Exposed Metal Sites" Long, J. R., Korea Conference on Innovative Science & Technology, Gyeongju, Korea, December 5, 2005.
2. "Hydrogen Storage in Microporous Coordination Solids with Exposed Metal Sites" Long, J. R., Pacificchem 2005, Honolulu, HI, December 18, 2005.
3. "Hydrogen Storage in Microporous Coordination Solids with Exposed Metal Sites" Long, J. R., Symyx Technologies, Santa Clara, CA, February 21, 2006.
4. "A Synergistic Approach to the Development of New Hydrogen Storage Materials" Long, J. R., DOE Hydrogen Program Review, Arlington, VA, May 19, 2006.
5. "Hydrogen Storage in Microporous Coordination Solids with Exposed Metal Sites" Long, J. R., University of Karlsruhe, Germany, June 9, 2006.

6. "Hydrogen Storage in Microporous Coordination Solids with Exposed Metal Sites" Long, J. R., Université Louis Pasteur, Strasbourg, France, June 26, 2006.
7. "High Surface Area Nanoporous Polymers for Reversible Hydrogen Storage" Svec, F., International Symposium on Materials Issues in Hydrogen Production and Storage, Santa Barbara, CA, August 22, 2006.
8. "Hydrogen Storage in Microporous Coordination Solids with Exposed Metal Sites" Long, J. R., The 232nd Meeting of the American Chemical Society, San Francisco, CA, September 12, 2006.