

IV.D.3 A Synergistic Approach to the Development of New Hydrogen Storage Materials (Part I)

Jeffrey R. Long (Primary Contact),
Jean M. J. Fréchet, Martin Head-Gordon
Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720-1460
Phone: (510) 642-0860; Fax: (510) 642-8369
E-mail: jrlong@berkeley.edu

Thomas J. Richardson, Samuel S. Mao
Lawrence Berkeley National Laboratory (LBNL)
MS 70-108B, One Cyclotron Road
Berkeley, CA 94720
Phone: (510) 486-8619; Fax: (510) 486-8619
E-mail: tjrichardson@lbl.gov

DOE Technology Development Manager:
Monterey R. Gardiner
Phone: (202) 586-1758; Fax: (202) 586-9811
E-mail: Monterey.Gardiner@ee.doe.gov

Contract Number: DE-FG36-05GO15002

Start Date: December 1, 2004
Projected End Date: 2009

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 award, with the other subprojects being funded through Basic Energy Science (BES).

Technical Barriers

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

- (B) Weight and Volume
- (C) Efficiency
- (D) Durability
- (E) Refueling Time
- (M) Hydrogen Capacity and Reversibility
- (N) 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 (**Data is based on material only, not system value)

Storage Parameter	Units	2010 System Target	FY07 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%)	1.2 w % at 77 K and 1 bar for K ₂ Zn ₃ [Fe(CN) ₆] ₂ (SA 470 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	9.8 wt% at 77 K and 70 bar for air-free Zn ₂ O(BDC) ₃ (SA 3600 m ² /g)
Energy Density	kWh/L (g H ₂ /L)	1.5 (45)	64 g H ₂ /L at 77 K and 70 bar for air-free Zn ₂ O(BDC) ₃ (SA 3600 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	3.8 wt% at 77 K and 45 bar for hypercrosslinked polystyrene (SA 1930 m ² /g)
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	1.9 wt% at 77 K and 23 bar for hypercrosslinked polyaniline (SA 630 m ² /g)

**Values given are for the materials alone, not a complete storage system.

FY 2007 Accomplishments

- The impact of coordinatively-unsaturated alkali metal ions on H₂ adsorption was studied in dehydrated variants of the compounds A₂Zn₃[Fe(CN)₆]₂·xH₂O (A = H, Li, Na, K, Rb), revealing maximum adsorption enthalpies that vary from 7.7 kJ/mol for A = Na to 9.0 kJ/mol for A = K.
- Synthesized and activated Zn₄O(BDC)₃ without exposure to air or atmospheric water, resulting in record H₂ storage characteristics: 9.8 wt% and 64 g/L at 77 K and 70 bar.
- Initiated studies on the mechanism of formation of Zn₄O(BDC)₃, revealing a rate law of rate = k[Zn(NO₃)₂]^{1.5}[BDC][H₂O]⁻¹ with an induction period.
- Successfully attached Cr(CO)₅ and Mo(CO)₅ units to the benzene rings within Zn₄O(BDC)₃.
- Utilized bulky formamide solvents to increase the pore sizes and surface areas in a series of magnesium-based metal-organic frameworks.
- Performed further characterization of hypercrosslinked polystyrene exhibiting a surface area of 1,930 m²/g. High pressure sorption measurements revealed an H₂ uptake of 3.8 wt% at 77 K and 45 bar.
- Synthesized hypercrosslinked polyaniline exhibiting reversible H₂ uptake of 1.9 wt% at 77 K and 23 bar, with enhanced H₂ adsorption enthalpies as high as 9.3 kJ/mol.
- Utilized computational methods in examining variations in H₂ binding enthalpies at exposed benzene coordinated metal sites in metal-organic frameworks of the type synthesized by the Long group. The results indicate that light transition metals such as Sc and Ti yield near-optimal binding energies, in contrast to overly strong binding at Mo and Cr.
- Developed a computation-based energy decomposition method that is fully variational (unlike existing methods), and can therefore be applied in understanding the origin of substituent effects on H₂ binding energies.



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 award:

- Synthesis and characterization of nanoporous coordination solids (Long)
- Synthesis and characterization of nanoporous polymers (Fréchet)
- First-principles determination of H₂ 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 investigation of the use of metal-organic frameworks as hydrogen storage materials. During the course of our investigations into the reaction of Zn₄O(BDC)₃ (BDC²⁻ = 1,4-benzenedicarboxylate) with metal-carbonyl complexes, we discovered that it slowly decomposes upon exposure to atmospheric water. After 24 hours, Zn₄O(BDC)₃ decomposed completely to form a crystalline material of formula Zn₄O(BDC)₃(H₂O)₅ and unknown structure. Gas adsorption measurements of this decomposition product have shown it to be nonporous. Given its rapid decomposition in a humid atmosphere, we synthesized Zn₄O(BDC)₃ with minimum exposure to water. The best results were obtained when all purification and activation was performed under dry dinitrogen and using anhydrous solvents.

Samples of Zn₄O(BDC)₃ synthesized using our air-free work-up show dramatically improved gas uptake compared with material synthesized using published procedures. Nitrogen adsorption measurements of both materials performed at 77 K showed type I sorption isotherms with a Brunauer-Emmett-Teller (BET) surface area of 3,600 m²/g for the sample synthesized using our method, compared with 3,100 m²/g for the sample synthesized using published procedures. Hydrogen adsorption measurements performed at 77 K and 50 bar, showed an uptake of 7.2 excess wt%

H₂ for Zn₄O(BDC)₃ synthesized using our methods, a nearly 50% improvement over the 4.9 excess wt% H₂ observed for Zn₄O(BDC)₃ synthesized using published procedures. Using the pore volume measured via helium adsorption, the total adsorption of a container filled with Zn₄O(BDC)₃ was calculated to be 9.8 wt% H₂ and 64 g H₂/L at 77 K and 70 bar. Owing to a near ideal pore diameter, this represents the highest volumetric storage capacity yet observed for a metal-organic framework.

We have also begun research into the synthesis of metal-organic frameworks incorporating magnesium cations. Such frameworks should be considerably lighter than the more common transitional metal-based materials, leading to higher wt% H₂ uptake. For example, if cubic Mg₄O(BDC)₃ could be synthesized, the total wt% H₂ adsorbed at 77 K should increase to 12.4 wt% H₂. Our initial investigations have focused on the reaction of magnesium salts with aromatic polycarboxylic acids, such as 2,6-naphthalenedicarboxylate (NDC²⁻) and 4,4'-biphenyldicarboxylate, and 1,3,5-benzenetricarboxylate (BTC³⁻). Many magnesium-containing frameworks were synthesized using these and other ligands; however, all were completely non-porous, with coordinated solvent molecules filling the void space in the material. In order to prevent the formation of these non-porous structures, we synthesized similar frameworks using larger solvent molecules that would not be able to fit in the void space of the known structure, forcing the formation of more porous frameworks. For example, we found that changing the solvent from DMF to DEF (diethylformamide) in the synthesis of Mg₃(NDC)₃(DMF)₄ led to a different spatial arrangement of the linkers around the metal cluster. The resulting framework, Mg₃(NDC)₃(DEF)₄, has a surface area of 500 m²/g, compared with 0 m²/g for Mg₃(NDC)₃(DMF)₄. Similarly, changing the solvent from DEF to DiPrF (diisopropylformamide) in the synthesis of Mg₆(BTC)₄(DEF)₄ led to the synthesis of Mg₆(BTC)₄(DiPrF)₄, which appears to have significantly increased pore size based on the crystal structure. Work is underway to scale up the synthesis of these materials in order to obtain further gas uptake measurements and to apply this strategy of increasing solvent bulk in order to increase porosity of other frameworks.

While investigating the synthesis of magnesium-containing frameworks, we noticed that the rate of formation of many frameworks varied as function of the amount of water in the reaction. In order to better understand and quantify this phenomenon, we have begun to study the kinetics of the formation of metal-organic frameworks. In our initial investigations, the reaction of Zn(NO₃)₂·6H₂O and H₂BDC in DEF was monitored by measuring the concentration of BDC²⁻ vs. time using ¹H-NMR (nuclear magnetic resonance) spectroscopy. As expected, the rate formation was found to slow significantly with increasing concentration of

water. From a concentration of 0-1 mol/L of H₂O, Zn₄O(BDC)₃ was formed and the initial rate was approximately inversely proportional to the amount of H₂O. From a concentration of 2-5 mol/L, as different framework, Zn₃(BDC)₃(H₂O)₂ was formed and the initial rate was still approximately inversely proportional to the amount of H₂O, though with a different slope. Preliminary experiments suggest that this effect is general, and can be observed for a wide variety of metal-organic frameworks. In addition, by varying the concentrations of the reactants and monitoring the rate of consumption of starting material we have determined the rate of the reaction to be:

$$\text{rate} = k[\text{Zn}(\text{NO}_3)_2]^{1.5}[\text{BDC}][\text{H}_2\text{O}]^{-1}$$

Furthermore, we found that there is a delay between the time at which the reaction is placed in a heating bath and the onset of product formation. This delay is approximately proportional to the concentration of Zn(NO₃)₂ in the reaction, and is significantly longer for reactions in DMF versus DEF. We are currently working to determine the cause of this induction period and to extend these mechanistic studies to other metal-organic frameworks.

Nanoporous Polymers. We have performed further H₂ adsorption experiments on our hypercrosslinked polystyrenes. These materials are based on a nonporous gel-type precursor, and exhibit a specific surface area of 1,930 m²/g and H₂ storage capacities of 1.55, 3.2, and 3.8 wt% at 77 K and pressures of 1.2, 20, and 45 bar, respectively. Using additional adsorption isotherms collected at 87 K and the van't Hoff equation, we have also determined the initial enthalpy of H₂ adsorption to be 6.6 kJ/mol. Based on the application of density function theory (DFT) analysis to a nitrogen adsorption isotherm, the hypercrosslinked polystyrene has a mean pore size of 1.8 nm.

We have also begun to analyze the kinetics of hydrogen storage within our polymers. We have demonstrated that a bed of 10 μm polymer beads operating at 77 K can desorb 58% of stored hydrogen within less than 0.1 seconds under isothermal conditions. This release rate, which is practically instantaneous, exceeds that required for a vehicle fuel system.

We have also identified adsorption to aromatic rings as the most likely mechanism of hydrogen adsorption onto our polymers. To test this, a series of electron donating and electron withdrawing groups were added to the aromatic rings in our porous polymer system and their effect on hydrogen adsorption analyzed. Preliminary results indicate that cryogenic adsorption to porous polymers of the type studied can be controlled via addition of electron donating and withdrawing groups to the aromatic ring. Addition of sulfonic acid and electron withdrawing nitro groups

was demonstrated to decrease hydrogen adsorption. Conversion of nitro groups to amino groups which are electron withdrawing was demonstrated to restore the capacity.

We continued to prepare and test hypercrosslinked polystyrenes for hydrogen adsorption. Our previous work included synthesis of hypercrosslinked polystyrenes with hydrogen storage capacities of up to 3.8 wt%. Building on this work, we designed new hypercrosslinked polystyrenes with even higher overall adsorption capacities. Recently, we obtained a hypercrosslinked polystyrene with a hydrogen storage capacity of 4.3 wt% at a temperature of 77 K and a pressure of 40 bar.

We are also analyzing the fundamentals of interaction between hydrogen and our hypercrosslinked polymers. Earlier, we identified adsorption to aromatic rings as the most likely mechanism of low-pressure hydrogen adsorption. We now try to separate the effect of pore size from that of hydrogen-polymer affinity in our samples. Therefore, we synthesized a large quantity of nonporous poly(divinylbenzene) and measured the enthalpy of adsorption of hydrogen. We are using this data to calculate the Lennard-Jones coefficient associated with adsorption to aromatic rings.

We have also synthesized a series of materials possessing new chemistries with a goal to achieve higher enthalpies of adsorption. The best current material we prepared exhibit initial enthalpies of adsorption in the range 7-9 kJ/mol. We are exploring different polymeric precursors and reaction conditions to design highly porous materials with even higher enthalpies of adsorption.

Recent publications have demonstrated substantial hydrogen storage ability of porous materials at room temperature based on a phenomenon called spillover. In this process, H₂ dissociates on a metal catalyst and can be transported and stored as H atoms on an adjacent surface. As a preliminary step to applying spillover to our materials, we have successfully repeated some of the spillover results of Yang et al. using a carbon support.

Our search for nanoporous materials with enhanced properties enabling hydrogen storage at temperatures higher than 77 K has focused on new chemistries. For example, we have developed a method for the preparation of entirely new type of nanoporous materials, hypercrosslinked polyanilines, with permanent porous structure and specific surface areas reaching so far up to 630 m²/g. The hypercrosslinking reaction was carried out with commercial polyanilines and formaldehyde or diiodoalkanes using both conventional and microwave assisted processes. Polyaniline swollen in an organic solvent was hypercrosslinked to form a rigid, mesh-like polymer with permanent porosity and a high surface area. The resulting materials have been characterized using infrared spectroscopy and elemental

analysis. Physical properties were determined by means of scanning electron microscopy (SEM) and nitrogen adsorption experiments. We demonstrated that short crosslinks such as those created using formaldehyde and diiodomethane produce materials with the highest surface areas. Surface area also increases with the concentration of polyaniline in solution used during synthesis. The hydrogen storage properties of all materials have been tested. A capacity of 1.9 wt% at 77 K and 23 bar was found for the best sorbent. Further optimization of reaction conditions is expected to lead to materials with much higher surface area and therefore enhanced hydrogen storage capacity. More importantly, hypercrosslinked polyanilines exhibit remarkably high affinity for hydrogen, which results in enthalpies of adsorption as high as 9.3 kJ/mol, a sharp contrast with hypercrosslinked polystyrenes we demonstrated previously, and metal-organic frameworks for which enthalpies of adsorption typically in a range of 4-7 kJ/mol.

Computational Studies of H₂ Binding. We have worked on three computational aspects of the hydrogen storage problem during the past year, that range from development of the new computational tools needed to understand the origin of trends in binding to applied work that aims to predict the precise nature of binding to a given site.

1. We have explored the electronic structure of the highly electron deficient compound, ammonia triborane, which has also been proposed as a storage material. Remarkably, we have found that the nature of the chemical bonding in this material is very different from what has been claimed in previous papers; in fact it is the smallest molecule to exhibit an intrinsic ring orbital where two electrons are shared amongst three boron atoms.
2. We have examined specific binding sites that can be potentially designed into metal-organic frameworks of the type synthesized in the Long group, which are 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] where the metal is either Sc, Ti, V, Cr, Mo, and a variety of electron-withdrawing and electron-donating substituents may be attached to the aromatic linker. The calculations show that a range of quite strong interaction strengths are possible, decreasing as the metal is made lighter, and with fine-tuning being accomplished via linker substitutions. The results suggest that light transition metals (Sc, Ti) yield near-optimal binding energies, in contrast to overly strong binding to Mo and Cr.
3. Motivated by the problem of tuning binding energies, we have also been developing an energy decomposition method that has desirable formal characteristics (it is fully variational, unlike existing

methods), and can be applied to understand the origin of substituent effects on hydrogen binding energies. We have used this tool to understand the linker substituent effects discussed above, as well as a range of other problems including alkane binding to active sites. Our energy decomposition may find broad use in the future as an aid to rational materials design, as binding energies can be interpreted in terms of physical quantities such as the interaction of permanent moments, polarization and charge transfer, and enhancements or diminishments in these effects can be sought to improve the hydrogen storage characteristics of a target binding site.

Destabilized Metal Hydrides. Funds for FY 2007 were not received until June 2007. Efforts to reliably measure hydrogen storage behavior in new magnesium alloys such as $Mg_{2.4}Ni$ have resumed.

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 2007 Publications

1. “High Surface Area Nanoporous Polymers for Reversible Hydrogen Storage” Germain, J.; Hradil, J.; Fréchet, J. M. J.; Svec, F. *Chem. Mater.* 2006, 18, 4430-4435.
2. “The Role of Vacancies in the Hydrogen Storage Properties of Prussian Blue Analogues” Kaye, S. S.; Long, J. R. *Catal. Today* 2007, 120, 311-316.
3. “Unravelling the Origin of Intermolecular Interactions Using Absolutely Localized Molecular Orbitals” Khaliullin, R. Z.; Cobar, E. A.; Lochan, R. C.; Bell, A.T.; Head-Gordon, M. *J. Phys. Chem. A* 2007, in press.
4. “Localized Orbital Theory and Ammonia Triborane” Subotnik, J. E.; Sodt, A.; Head-Gordon, M. *Phys. Chem. Chem. Phys.*, submitted for publication.
5. “Hydrogen Adsorption in Dehydrated Variants of the Cyano-Bridged Framework Compounds $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ (A = H, Li, Na, K, Rb)” Kaye, S. S.; Long, J. R. *Chem. Commun.*, submitted for publication.

FY 2007 Presentations

- 1–21. “Hydrogen Storage in Microporous Coordination Solids with Exposed Metal Sites” Long, J. R.: Joint Sandia-LBNL Symposium on Hydrogen Storage Materials, Berkeley, CA, July 21, 2006; The 232nd Meeting of the American Chemical Society, San Francisco, CA, September 12, 2006; University of Washington, October 3, 2006; Michigan State University, October 9, 2006; University of Wisconsin, October 11, 2006; San Diego State University, October 13, 2006; University of California, Santa Barbara, October 23, 2006; Fall 2006 Meeting of the Materials Research Society, Boston, MA, November 29, 2006; University of Oregon Materials Science Institute Retreat, December 13, 2006; Sandia National Laboratories, February 5, 2007; University of Arizona, February 22, 2007; University of Notre Dame, March 29, 2007; California Institute of Technology, April 18, 2007; National Institute of Standards and Technology, Gaithersburg, MD, May 17, 2007; Nanjing University, May 31, 2007; Jilin University, June 4, 2007; Nankai University, June 6, 2007; Sydney University, June 18, 2007; Monash University, June 19, 2007; Bragg Institute, Australian Nuclear Science and Technology Organisation, June 20, 2007; Japan-USA Joint Symposium on Coordination Space, Evanston, IL, June 25, 2007.
22. “Hydrogen storage in porous solids with coordinatively-unsaturated metal centers” Kaye, S. S., International Symposium on Materials Issues in Hydrogen Production and Storage, Santa Barbara, CA, August, 2006.
23. “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, 2006.
24. “Nanoporous Polymers for Hydrogen Storage” Svec, F., International Congress of Nanotechnology, San Francisco, CA, October, 2006.
25. “Hydrogen Storage in Microporous Coordination Solids with Unsaturated Metal Centers” Kaye, S. S., Gordon Research Conference on Renewable Energy: Solar Fuels, Santa Barbara, CA, January, 2007.
26. “Hydrogen Storage via Physisorption” Long, J. R., Neutrons for the Hydrogen Economy National Community Focus Day, Australian Nuclear Science and Technology Organisation, June 21, 2007.