VI.D.2 A Synergistic Approach to the Development of New Classes of Hydrogen Storage Materials

Jeffrey R. Long (Primary Contact), A. Paul Alivisatos, Marvin L. Cohen, Jean M. J. Fréchet, Martin Head-Gordon, Steven G. Louie, Alex Zettl
Dept. 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 (Primary Contact), Samuel S. Mao
Lawrence Berkeley National Laboratory
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: Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811; E-mail: Carole.Read@ee.doe.gov

DOE Project Officer: Jim Alkire
Phone: (303) 275-4795; Fax: (303) 275-4795; E-mail: James.Alkire@go.doe.gov

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Objectives

This project brings together an eclectic group of scientists with experience in materials discovery and theoretical prediction of properties to work together in developing new types of hydrogen storage materials. Particular emphasis will be on exploring the possibilities for nanoporous polymers, nanoporous coordination solids, destabilized high-density hydrides, nanostructured boron nitride, and magnesium and light alloy nanocrystals to meet the 2010 DOE hydrogen storage system targets, especially specific energy, energy density, durability, and uptake and discharge kinetics.

Technical Barriers

This project addresses the following technical barriers from the 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

Storage Parameter	Units	2010 System Target	FY 2005 materials**
Specific Energy	kWh/kg (wt. % H_2)	2.0 (6 wt. %)	1.8 wt. % at 77 K, 890 torr $Cu_3[Co(CN)]_2$ (SA 730 m^2/g)
Specific Energy	kWh/kg (wt. % H_2)	2.0 (6 wt. %)	0.46 wt. % at 77 K, 880 torr $Mg_3[O_2C-C_{10}H_2-CO_2]_3$ (SA 190 m^2/g)
Specific Energy	kWh/kg (wt. % H_2)	2.0 (6 wt. %)	1.3 wt. % at 77K, 1 atm for polymers based on poly (styrene-co-divinylbenzene (SA ~1000 m^2/g)

Note: SA = surface area
**Data is based on material only, not system value

Approach

The University of California-Berkeley and Lawrence Berkeley National Laboratory have formed a collaborative, interdisciplinary group to research promising nanostructured materials for hydrogen storage. A total of 7 themes or subprojects are currently planned:

- Synthesis and characterization of nanoporous polymers (Fréchet)
- Synthesis and characterization of nanoporous coordination solids (Long)
- 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)
- Synthesis and characterization of nanostructured boron nitrides (Zettl) and development of predictive theory for application in design of new boron nitride structures for improved hydrogen storage characteristics (Cohen and Louie)
- Synthesis and characterization of Mg and metal alloy nanocrystals (Alivisatos)
- H_2 storage performance characterization (Mao)

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.

Recent work has exposed the considerable potential for hydrogen storage in porous metal-organic framework solids such as $Zn_4O(O_2C-C_{10}H_6-CO_2)_3$. The Long group will synthesize a range of related materials incorporating light main group metal ions (e.g., Be^{2+}, Mg^{2+}, B^{3+}, and Al^{3+}) and a variety of organic bridging ligands designed specifically to have a high H_2 binding affinity. The possibility of stabilizing coordinatively-unsaturated metal centers capable of reversibly forming hydrides (e.g., $L-CrH_3(H_2)-L$) within these frameworks will be explored. In addition, lower diamondoids and molecules such as $[B(CN)_4]^-$ and $[B_6(CN)_6]^{2-}$ will be employed in constructing new light-weight frameworks with a high specific surface area. To facilitate the design of these materials, Head-Gordon and coworkers will develop first-principles methods for calculating hydrogen binding energies.

Polymers are light-weight materials that can be highly porous, yet they have been virtually unexplored as hydrogen storage materials. The Fréchet group will investigate the use of supercritical CO_2 as a porogen in generating polymers with small pore sizes and a high specific surface area. In addition, they will utilize a variety of highly aromatic prepolymers in an effort to optimize the H_2 binding affinity for the surfaces of these materials. The results of binding energy calculations will also be of use here in selecting favorable aromatic structures and functional groups.

While a large effort is underway to utilize carbon nanotubes for hydrogen storage, relatively little attention has been directed toward their boron nitride analogues. The Zettl group has devised an efficient chemical vapor deposition (CVD)-like method for using nanostructured carbon as a template in the synthesis of analogous boron nitride materials. The hydrogen storage capabilities of these and related $B_xC_yN_z$ materials will be assessed and compared with the capabilities of the carbon-based analogues. The groups of Cohen and Louie will provide theoretical expertise in guiding the synthesis of new boron nitride-containing structures with enhanced hydrogen binding characteristics.

The possibility of improving the hydrogen storage properties of elemental magnesium by controlling its crystallite size and shape, or by substitution destabilization of its hydride, will be investigated. The Alivisatos group will develop techniques for synthesizing soluble Mg nanocrystals with varying sizes and shapes. The temperatures and pressures at which these convert to MgH_2, as well the reversibility of the process, will then be studied in detail. Richardson and coworkers will explore the use of trace metal dopants in destabilizing the rutile form of $Mg(M)H_2$ in favor of a fluorite form with enhanced kinetics. Improved hydrogen storage in metal alloys will also be pursued via the foregoing approaches.

FY 2005 Accomplishments

- Utilized H_2 sorption measurements at 77 K and 87 K to determine the isosteric heat of adsorption for $Zn_4O(1,4\text{-benzenedicarboxylate})_3$ as 4.7 - 5.2 kJ/mol.

- Determined the porosity and hydrogen storage properties of the dehydrated Prussian blue analogues $M_3[Co(CN)]_2$ (M = Mn, Fe, Co, Ni, Cu, Zn). With cubic frameworks featuring exposed M^{2+} coordination sites, these materials exhibit H_2 adsorption enthalpies as high as 6.9-7.4 kJ/mol for $Ni_3[Co(CN)]_2$, with a maximum observed uptake of 1.8 wt. % and 0.025 kg/L for $Cu_3[Co(CN)]_2$ at 77 K and 890 torr.

- Synthesized and characterized $Mg_3(2,6\text{-naphthalenedicarboxylate})_3$, the first magnesium-based metal-organic framework. This material exhibits relatively high H_2 adsorption enthalpies in the range 7.0-9.5 kJ/mol, but an uptake of only 0.46 wt. % at 77 K and 880 torr. Owing to a small pore dimension, it also displays selective uptake of H_2 or O_2 over N_2 or CO.

- Synthesized and characterized a series of poly(styrene-co-divinylbenzene) beads exhibiting surface areas as high as 1,000 m^2/g. Grafting of polyaniline and polypyrrole chains onto the pore surface was further demonstrated. Reversible H_2 uptake of 1.3 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.