
A Synergistic Approach to the Development of New Classes of Hydrogen Storage Materials

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Program Scope

Our program 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 is 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. This project is funded jointly by BES (Alivisatos, Cohen, Louie, Mao, and Zettl) and EERE (Fréchet, Head-Gordon, Long, and Richardson), but represents a cohesive effort with close collaborations and regular meetings involving all investigators.

Recent Progress and Future Plans

Nanocrystals (Alivisatos). To investigate the potential benefits of nanosized materials and understand their interactions with hydrogen, we are synthesizing nanoparticles with different sizes, shapes, crystallinity, and composition. Our goal is to observe shape and volume changes in each nanocrystal, and further study the size-dependent kinetics of uptake and release of hydrogen. We intend to measure hydrogen cycling with *in situ* X-ray diffraction, as well as with pressure-composition isotherms. First, we will focus on the palladium-hydrogen system, which is well-understood in bulk. This work will then be extended to palladium alloys with lighter elements incorporated and other lighter nanocrystal systems.

Differently-sized Pd nanoparticles with narrow particle size distributions have been prepared (see Figure 1) for investigating hydrogen uptake and release as a function of particle size and surface-ligand composition. Being monodisperse, these nanoparticles have a strong tendency to form periodic arrays or superlattices. The arrays usually have highest packing density and provide the optimal filling of the system. On the other hand nanoparticles adsorbing hydrogen could be a part of binary periodic superlattices. Ultimately, we plan to investigate the behavior of both single-component superlattices and binary superlattices in which at least one constituent can undergo shape transformation upon hydrogen adsorption.

Nanostructured Boron Nitride (Cohen, Louie, and Zettl). Our efforts have focused on materials composed of atoms in the first two rows of the periodic table. In particular, we have been investigating the adsorption of molecular hydrogen on various nanostructured materials to find better hydrogen storage materials using *ab initio* density functional theory within GGA. Our investigation has been performed in two ways. One is to identify new materials that may store and release hydrogen more than 6% by weight at ambient condition, and the other is to find

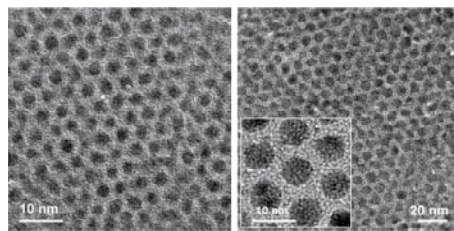


Figure 1. Transmission electron micrographs of three-dimensional superlattices formed by 3.0 nm (left) and 6.9 nm (right) Pd nanoparticles, respectively.

structural modification of known materials, such as carbon, that may increase hydrogen adsorption. We have already identified several new potential candidate materials in addition to carbon-based materials. Among those are boron nitrides and boron oxides. We also found that structural modifications, such as introducing 5-7 defects, or substitutional doping, may increase hydrogen binding energy.

We are also currently working on various polymers and their modification. Some of them show promising results. For example, when some hydrogen atoms, which have originally formed C-H bonds in polymers, are substituted by metal atoms with d electrons, such as Sc or Ti, the calculated molecular hydrogen binding energies fall into the right temperature range. Moreover, our study shows that each of these metal atoms can attract 5-6 hydrogen molecules with the right binding energy. This implies that such polymers would store hydrogen much more than 6% by weight. We are performing further calculations to check stability of polymers containing those metal atom and to verify our current results.

The experimental approach is to use the theoretical calculations to suggest the best candidate materials. We are developing synthesis and characterization techniques involving nanostructured or activated systems. For example, layered materials such as BN and $B_xC_yN_z$, are being synthesized using arc-plasma methods, CVD, and laser ablation. Often the materials undergo post-synthesis processing to increase defect concentration and effective surface area. Oxides are also being investigated in nanocrystal, layer, tube, and nanowire form. Of particular interest are systems analogous to activated carbon. Characterization is via TEM, binding energy, and surface area isotherm methods.

Nanoporous Polymers (Fréchet). Porous polymers could potentially provide an excellent support for hydrogen storage since they can be easily prepared from most often readily accessible monomers and afford very high surface area. These porous materials can be manufactured reproducibly and inexpensively on a large scale in a single reaction step from polymerization mixtures comprising suitable monomers and porogens. Although polymers represent a class of materials that may match most of the requirements set for hydrogen storage, almost no research concerning this application has been reported. Assuming just formation of a monolayer on the available surface, enhancement in the hydrogen adsorption capacity can then be achieved via an increase in surface. A simple calculation reveals that a nanoporous polymer with a surface area of 2000 m^2/g should be able to accommodate up to 5.4 wt % hydrogen. While porous polymers with surface areas of up to 800 m^2/g have already been reported, redesigning the polymerization systems can further increase this value.

Our first hydrogen adsorption/desorption screening experiments were carried out using various porous beads exhibiting high surface areas, but differing in their internal structure and chemistry. The surface areas varied in a broad range of 300-800 m^2/g depending on the preparative method. Most of these beads were prepared by direct polymerization of divinylbenzene or via Friedel-Crafts crosslinking reaction of slightly crosslinked polystyrene. Despite the modest surface area of these sorbents, we found materials exhibiting a promising hydrogen adsorption of 1.4 wt % at 77 K and 1 bar. We are now preparing series of polymers with surface areas exceeding 1500 m^2/g using a variety of functional monomers. These experiments should reveal the effects of chemistry on hydrogen adsorption. In addition, we are testing adsorption ability after carbonization of porous polymers at high temperature in an inert atmosphere. Although a good subject for screening, beads cannot completely fill the available space. Consequently, we are simultaneously studying nanoporous monoliths, which, in contrast to beds packed with particles, do not include any interstitial voids. This better utilization of space will increase the volumetric storage capacity. Initially, porous polymer monoliths were prepared using direct polymerization in a mold with a surface area of 380 m^2/g . Although the

surface area of these polymers does not yet reach that of particulate adsorbents, the results of adsorption experiments are promising. New techniques are now being tested for preparing monoliths with significantly higher surface areas.

Nanoporous Coordination Solids (Long). Porous materials containing coordinatively unsaturated metal centers are being explored for use as hydrogen storage materials. In metal-cyanide frameworks with lattice vacancies, such as $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, as well as in anionic metal-cyanide frameworks with interstitial cations, water occupies some of the coordination sites on the metal cation. This bound water can typically be removed by heating the framework under vacuum, leaving open coordination sites on the metal that can potentially bind hydrogen. We first examined hydrogen adsorption in a series of Prussian blue analogs of the type $\text{M}_3[\text{Co}(\text{CN})_6]_2$ ($\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$). Of these, the most promising material is $\text{Cu}_3[\text{Co}(\text{CN})_6]_2$, which stores 1.7 wt% hydrogen and 0.024 kg H_2/L at 77 K and 1 atm. Hydrogen uptake measurements at lower temperatures for $\text{Cu}_3[\text{Co}(\text{CN})_6]_2$ showed a saturation capacity of 2.7 wt% H_2 . In order to better understand the effect of varying the metal ion on hydrogen uptake, the strength of the hydrogen-framework interaction was probed by measuring the enthalpy of adsorption of hydrogen, which ranged from 7.5 kJ/mol for $\text{Ni}_3[\text{Co}(\text{CN})_6]_2$ to 5.9 kJ/mol for $\text{Mn}_3[\text{Co}(\text{CN})_6]_2$, compared to 5.5 kJ/mol for $\text{Zn}_4\text{O}(\text{BDC})_3$. Powder neutron diffraction studies of $\text{Cu}_3[\text{Co}(\text{CN})_6]_2$ in the presence of hydrogen showed that at a loading of 1 $\text{H}_2/\text{Cu}^{2+}$, 25% of the hydrogen molecules were interacting with the open coordination sites on Cu^{2+} , with the remainder interacting with the pore walls.

We have also examined H_2 adsorption in $\text{A}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ compounds, wherein it may interact with the monovalent cations residing in the pores of the $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ framework. We have synthesized and measured the H_2 sorption properties of the alkali metal series ($\text{A} = \text{Li}(\text{H}_2\text{O})^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{H}_3\text{O}^+$). All five materials have similar surface areas and H_2 sorption capacities and showed enthalpies of adsorption in the range 7.5-9.0 kJ/mol at low surface coverage, with the trend $\text{K}^+ > \text{H}_3\text{O}^+ \approx \text{Li}(\text{H}_2\text{O})^+ > \text{Rb}^+ > \text{Na}^+$.

Most recently, we have been investigating porous coordination solids that can bind low-valent transition metal complexes. These relatively electron-rich metals are expected to have a strong π back-bonding interaction with dihydrogen, resulting in a stronger metal- H_2 interaction than the electron-poor cations in the metal-cyanide compounds discussed above. Towards this end, we have synthesized analogs of $\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})_3$ with bound metal-carbonyl complexes, $\text{Zn}_4\text{O}[\text{Cr}(\text{CO})_3(1,4\text{-benzenedicarboxylate})]_3$, $\text{Zn}_4\text{O}[\text{Mo}(\text{CO})_3(1,4\text{-benzenedicarboxylate})]_3$, and $\text{Zn}_4\text{O}[\text{Co}_2(\text{CO})_6(2\text{-propynyloxy-1,4-benzenedicarboxylate})]_3$. Future work will focus on finding methods to remove the carbonyl ligands from these compounds and then measuring the H_2 sorption properties of the resulting materials.

Predictive Theory for H_2 Binding in Nanoporous Materials (Head-Gordon). In close support of the foregoing experimental efforts, we have completed a computational study of model complexes between H_2 and derivatized benzene dicarboxylate linkers in metal-organic frameworks, as well as simple charged ligands such as CN^- , CO , NO^+ , Cp^- , F^- , and SO_4^{2-} , free lightweight metal ions such as Li^+ , Na^+ , Mg^{2+} , Al^{3+} , and the corresponding ions complexed with simple ligands. The purpose of this study was to systematically explore H_2 binding affinities across the full scale of interaction strengths from just a few kJ/mol to hundreds of kJ/mol that may be accessible in novel hydrogen storage materials. Such a survey and associated physical insight can potentially provide ideas and perhaps principles to assist in the design of next generation synthetic targets.

There is a close link between the interaction strength and the mode of binding, and so we have placed emphasis on characterizing the physical and chemical interactions responsible for the binding affinities. These interactions range from long-range dispersion forces, which are

weakest, through to stronger electrostatic and induction effects that include the coupling of the H₂ quadrupole moment to localized charges (as associated with metal centers or charged ligands) and the induction of a dipole moment on H₂ by such charges. These interactions are each in turn smaller again than the donor-acceptor interactions between orbitals of H₂ and orbitals of the hydrogen storage material itself. However H₂ has a very deep filled level and a very high corresponding antibonding level and is therefore reluctant to participate in strong donor acceptor interactions, relative to more standard ligands.

A first message of our study is that given some level of donor-acceptor participation, or exceptionally strong electrostatic/inductive interactions, one can achieve H₂ binding affinities in the target regime of 15-40 kJ/mol considered optimal for hydrogen storage. Lightweight positively charged metal centers without d electrons are quite capable of yielding such binding affinities, as indeed are corresponding negatively charged centers such as F⁻. A second message is that because all interactions (orbital, electrostatic, dispersion) are present at once, the opportunity exists to significantly tune the binding affinity by control over the coordinating environment. Indeed we find the presence of ligands exerts a substantial perturbation on the binding affinity. Ongoing efforts are now focused upon applying these ideas in delivering specific improvements upon the new metal-organic and polymer systems described above.

Destabilized High-Density Hydrides (Richardson). In our previous work on thin film metal hydrides, we studied hydride formation in Mg-alloy films by absorption of H₂ from the gas phase and by means of electrochemical reactions. At ambient temperature, complete conversion of metallic films to the corresponding hydrides is achieved in minutes or even seconds. By varying alloy compositions and ratios, we optimized the amount of hydrogen absorbed by the films. In this program, we are now working with bulk materials. In particular, we are developing metal hydride alloy systems based on magnesium and lithium in which the thermodynamic barrier for desorption of hydrogen is reduced by alloy stabilization of the metal phase. Candidate alloys and mixtures are being prepared in powder and bulk form using standard metallurgical techniques. The phase purity is then assessed by X-ray diffraction, and storage properties are measured using the gravimetric analyzer described above. Phase analysis is carried out at different points in the hydrogen absorption-desorption cycle to determine the mechanism and sequence of reactions. Our goal is to optimize compositions through systematic variation of stoichiometries. The formulations discovered here may then be utilized in the preparation of nanocrystalline samples by the Alivisatos group, in order to study the size- and shape-dependence of their hydrogen storage properties.

Publications

1. "Hydrogen Storage in the Dehydrated Prussian Blue Analogues M₃[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 H₂ Binding and Selective Gas Adsorption within the Microporous Coordination Solid Mg₃(O₂C-C₁₀H₆-CO₂)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. "The Role of Vacancies in the Hydrogen Storage Properties of Prussian Blue Analogues" Kaye, S. S.; Long, J. R., submitted for publication.
5. "Neutron Diffraction and Neutron Vibrational Spectroscopy Studies of Hydrogen Adsorption in the Prussian Blue Analogue Cu₃[Co(CN)₆]₂" Hartman, M. R.; Peterson, V. K.; Liu, Y.; Kaye, S. S.; Long, J. R., submitted for publication.