

IV.A.4 Reversible Hydrogen Storage Materials – Structure, Chemistry, and Electronic Structure

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Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE hydrogen storage targets:

- Cost: to be determined
- Specific energy: 1.3 kWh/kg
- Delivery pressure - 50 and 150 bar for materials-based storage systems

FY 2012 Accomplishments

- Discovered that the hydrogen desorption mechanism is a two-step process, with diffusion from the bulk involving a lower barrier than the H₂ surface desorption. To calculate catalyzed H₂ surface desorption, we found that magnetic degrees of freedom must be carefully addressed to describe the crossover of magnetic states during desorption.
- The catalytic effect of Ti-substitutional dopant on H₂ desorption from bulk MgH₂(110) surfaces was determined, including (110)/(001) step edges, and for nanoparticle MgH₂, which also addresses size effects associated with ball-mill processing.
- The efficiency of ball-milling on dispersing catalytic species has been determined using three-dimensionally electron tomography.
- The three-dimensional structure of carbon nano-scaffolds was determined and shown to be composed of a layered structure with different orientations. This has implications for the fill capacity.

Fiscal Year (FY) 2012 Objectives

- Understand the processes controlling uptake and release of hydrogen from on-board solid-state systems.
- Understand the catalytic processes operating in on-board solid-state systems.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section (3.3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (D) Durability/Operability
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

Catalytically Enhanced Hydrogen Storage Systems:

This project is conducting fundamental studies of the role of catalyst species in nanoparticles as well as the role of nanostructures for confinement of the storage medium.



Introduction

The atomic and molecular processes, by which hydrogen is adsorbed and desorbed from solid-state storage systems, both in bulk and nanoparticle form, are being investigated by using a combination of first-principle calculations and advanced characterization techniques. The dispersion of catalytic species and its function in the charging and discharging cycle are of particular interest. In addition, in the case of nanoparticle systems in which the storage material is confined within a nanoscale scaffold structure, the microstructure as a function of the number of cycles is being investigated to understand how the storage capacity degrades with the number of cycles. This investigation of the fundamental processes seeks to inform the design and development of onboard solid-state storage systems

to achieve the DOE targets as well as understand system changes during cycling, which pertains to system durability.

Approach

We utilize advanced characterization tools especially state-of-the-art transmission electron microscope (TEM) including three-dimensional electron tomography to investigate the structural and compositional changes in nano-scaffold systems as well as the dispersion of catalyst species by ball milling. Scanning tunneling microscopy is used to explore the interaction of a pure metal surface with and without catalyst species for both atomic and molecular hydrogen. In parallel, we use density functional theory (DFT) calculations to determine the role of transition-metal catalysts to increase H_2 absorption and desorption kinetics in both bulk and nanoparticle MgH_2 . This also addresses size effects associated with ball-mill processing of materials. The nudged-elastic band method is used to determine the kinetic energy barriers of reaction pathways of H_2 desorption.

Results

In collaboration with Professor Eric Majzoub, University of Missouri, $LiBH_4$ -infiltrated nanoporous carbon scaffold hydrogen storage materials are being investigated as a function of hydrogen charging and discharging cycles. The nanoporous carbon scaffolds have been found to be complex with differing column size, orientations, and curvatures all within domains that can vary from their neighbors. These observations have implications related to the fill capacity of the structures and are being correlated with processing parameters. Annealing of $LiBH_4$ above $200^\circ C$ causes the formation of granular coatings composed of cubic or cuboid nanoscale growths with dimensions of ≈ 10 - 20 nm on the outer surfaces of many scaffold particles. Following annealing these nano-crystals can be found micrometers from the host scaffold, Figure 1. The size distribution of the dispersed nano-crystals implies different migration rates along the holey carbon support substrate and that larger crystals are formed by particle agglomeration. Preliminary results, including the cubic structure of the ejected material, and first-principle calculations performed by Majzoub suggest LiH is a likely candidate for the ejected material [1]. These results have implications regarding the long-term stability of such storage materials.

In our preliminary TEM analysis of $MgH_2 + 0.05 Ni$, milled for 1, 5, and 10 hours, and $MgH_2 + 0.05 NiCl_2$, milled for 1 hour, no appreciable differences were observed in the size distribution of the Mg particles, regardless of milling time or form of the catalyst. The shape of the $NiCl_2$ -doped material, however, was very angular and sharp compared to those doped with Ni only. The morphology of the Ni particles depended on milling time, changing from irregular shaped, spherical and elongated to predominately spherical.

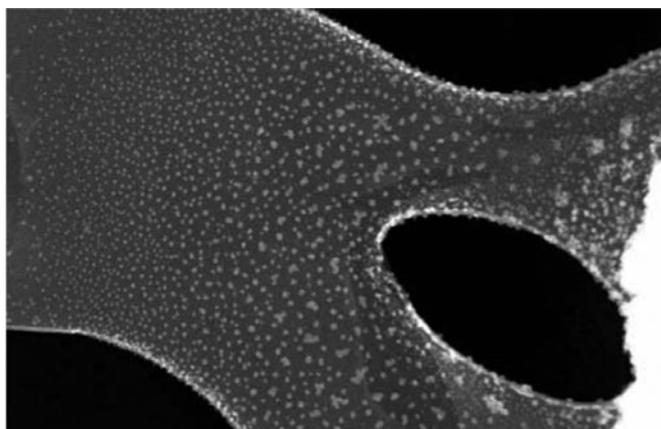


FIGURE 1. High-angle annular dark-field scanning transmission electron microscope images of a $LiBH_4$ -infiltrated carbon scaffold particle heated to $200^\circ C$, showing long-range ejection of nanocrystals from the scaffold surface along the holey carbon support grid.

The density of Ni particles also decreased with increased milling time. Energy-dispersive X-Ray spectroscopy (EDS), Figure 2, reveals that the Ni catalyst becomes increasingly delocalized and dispersed with increasing milling time. After 10 hours of milling time, few Ni particles remain, and the diffuse Ni background has increased and appears to be almost uniformly dispersed. Point spectra confirm a roughly stoichiometric ratio of Ni and Mg (0.05:1) in regions where no distinct Ni particles are observed. These observations have implications for the role of catalytic species at enhancing hydrogen charging and discharging.

Previous studies have shown that the overall desorption enthalpy of H_2 from MgH_2 nanoparticles only decreases significantly when the particle size decreases below 5 formula units. Recently, using DFT simulations of desorption enthalpies, we reported that there is no size effect for initial H_2 desorption from MgH_2 surface with(out) defects versus MgH_2 amorphous nanoparticles. All the data are shown in Figure 3. We have considered both singly- and doubly-bonded H . Figure 3 shows that a singly-bonded H is removed from an amorphous MgH_2 nanoparticle of 31 formula units with a desorption energy of 148 $kJ/(mol-H_2)$ in reference to free H_2 . Because a singly-bonded H cannot be found on $MgH_2(110)$, where only doubly-bonded H exist, a step surface was constructed. The desorption energy of singly-bonded H from this step surface is 140 $kJ/(mol-H_2)$ – within 6% of the nanoparticle result. For doubly-bonded H , we found a similar result, i.e., 240 $kJ/(mol-H_2)$. The lack of a size effect in the initial H -desorption can be understood by the fact that $Mg-H$ bond is local in nature. This result provides insight to the fundamental mechanisms of hydrogen uptake and release.

Kinetic barriers in nanoparticles, in principle, may be reduced due to the free surface and altered bonding. Nonetheless, from Figure 4, we find that the desorption enthalpies for a nanoparticle are unaffected and, for the

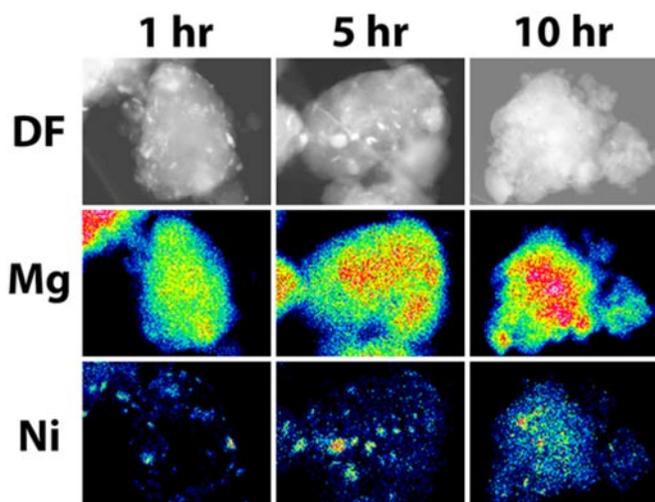


FIGURE 2. High-angle annular dark-field scanning transmission electron microscope images of $\text{MgH}_2 + 0.05 \text{ Ni}$ specimens and their corresponding EDS chemical maps of Mg and Ni. As milling time increases, the Ni becomes increasingly delocalized and dispersed throughout the Mg. At 1 hour, the Ni still resides mostly in distinct Ni nanoparticles. By 5 hours, distinct Ni nanoparticles still account for most of the nickel, but a diffuse background of Ni is visible throughout most of the Mg. By 10 hours, few nanoparticles of Ni remain, with most of the Ni dispersed.

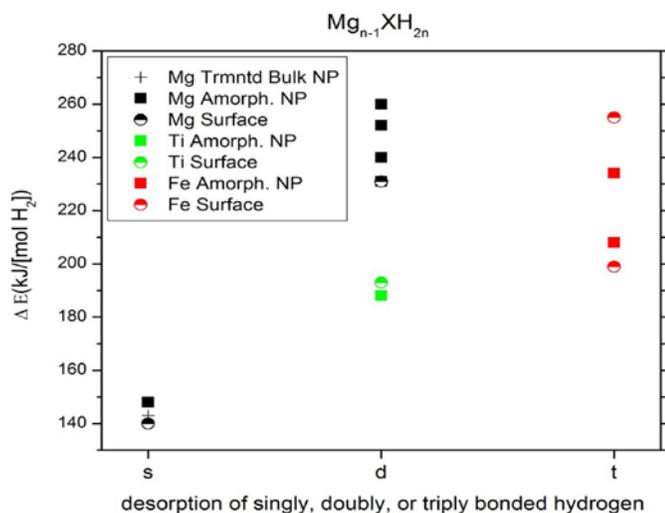


FIGURE 3. Desorption energies of singly-, doubly- and triply-bonded H from various structures. “Mg Trmtd Bulk NP” is the bulk-terminated $\text{Mg}_{31}\text{H}_{62}$ after relaxation. “Mg Surface” refers to (110)/(001) step edge and (110) surface. “Ti Surface” is the relaxed (110) surface with a single Ti substitutional dopant for Mg. “Fe Surface” is the reconstructed (110) surface with Fe substituting Ti.

desorption pathways thus far investigated, the barriers (1.85 eV) are also similar to the bulk MgH_2 (1.83 eV), see publications. Therefore, only doping can affect the enthalpies and barriers.

For doped bulk surfaces, we found that a single Ti dopant is effective in reducing the kinetic barrier by 0.41 eV.

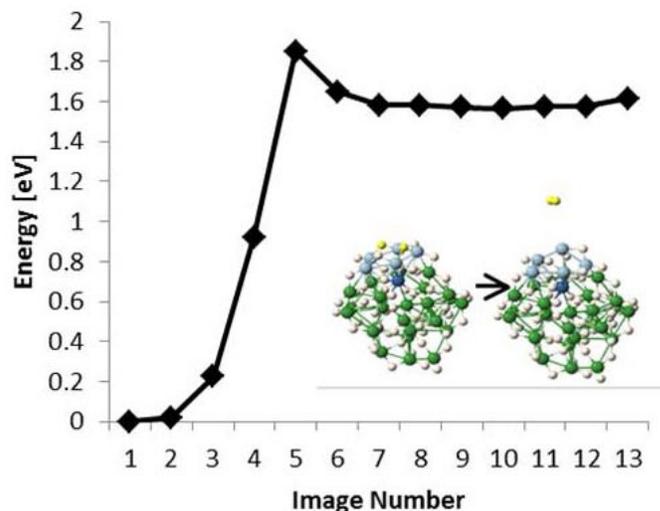


FIGURE 4. Kinetic barrier (nudged elastic band) results for H-desorption from undoped nanoparticle $\text{Mg}_{31}\text{H}_{62}$ with 1.85 eV barrier, which is similar to undoped $\text{MgH}_2(110)$ bulk surface.

We revealed a mechanism involving concerted motion of H_2 surface desorption and H bulk diffusion to reduce the barrier. We also found that magnetic degrees of freedom must be carefully addressed to describe the crossover of magnetic states during catalyzed H_2 surface desorption, from early to late stage (see 2012 publications for details). The overall kinetic barrier is 1.42 eV. In contrast, without such crossover of magnetic moment, the barrier is 1.46 eV for the same initial state with a magnetic moment of $0 \mu_B$ (Ti having H coordination 8) and 1.84 eV for a degenerated state with a magnetic moment of $2 \mu_B$ (Ti having H coordination 6). Thus, we have shown the catalytic effect of a single Ti substitution on kinetic barrier reduction is due to the concerted motion of surface H_2 desorption and bulk H diffusion. We will next study the effect of other transition-metal dopants either embedded or supported on surfaces of MgH_2 as well as dopant nanoparticles and other metal hydrides on the adsorption/desorption processes.

Conclusions and Future Directions

- Found that a single Ti dopant in MgH_2 is effective in reducing the kinetic barrier by 0.41 eV and revealed a mechanism involving concerted motion of H_2 surface desorption and H bulk diffusion to reduce the barrier.
- Found no size effect for initial H_2 desorption from MgH_2 surface with(out) defects versus MgH_2 amorphous nanoparticles.
- Found that storage material may be ejected from nano-scaffold structures during the discharge cycle.
- Demonstrated the microstructural and compositional changes associated with ball milling.

- Despite there being no size effect for the binding of H, the appearance of singly and weakly bonded H will be studied further because it is relevant to nanoparticle systems and high-indexed surfaces produced under ball-milling experiments.
- Nano-particle doping studies similar to the bulk cases will be completed. For comparison, other defects such as vacancies (prominent in ball-milled materials) will be introduced and their impact determined.
- The structural and compositional changes in ball-milled MgH_2 with Ni will be completed.
- The structure of nano-scaffold systems as a function of charging/discharging cycles will be completed.

FY 2012 Publications/Presentations

1. J.M. Reich, Lin-Lin Wang, and Duane D. Johnson, “Surface and particle-size effects on hydrogen desorption from catalyst-doped MgH_2 ,” (2012), submitted – responding to reviews.
2. Lin-Lin Wang and D.D. Johnson, “Hydrogen Desorption from Ti-doped $\text{MgH}_2(110)$ Surfaces: Catalytic effect on reaction pathways and kinetic barriers,” *J. Phys. Chem. C* 116, 7874–7878 (2012).

Presentations

1. Duane D. Johnson and Lin-Lin Wang, “Defect-Mediated Properties in Bulk and Nanoparticle Metallic Alloys: Quantitative Prediction of Phase Stability, Mechanical Properties and Kinetics,” (invited) SYMPOSIUM: Phase Stability, Diffusion, Kinetics and their Applications, Materials Science & Technology Meeting 16–20 October 2011, Columbus, Ohio.

2. Duane D. Johnson and Lin-Lin Wang, “Defect and Chemically Mediated Catalytic Behavior,” (invited) Data-rich Approaches in Catalysis Science, Spring ACS 2012 National Meeting, San Diego, CA, 25–29 March 2012.
3. Lin-Lin Wang, Duane D. Johnson, Teck L. Tan, Configurational Thermodynamics of Alloyed Nanoparticles, American Physics Society March 2012 Meeting, Boston, MA.
4. Duane D. Johnson, “Data Discovery versus Data Mining,” (invited) in USC-DOE conference on “Materials Genome: Simulations, Synthesis, Characterization and Manufacturing”, Los Angeles, 4–6 April, 2012.
5. Duane D. Johnson, “Materials Design, Synthesis, and Characterization: coupling theory and experiment with data discovery,” (invited) Argonne National Laboratory, 21 May 2012.
6. Duane D. Johnson, “Reaction Pathways for Solid-State Transformations: a proper nudged-elastic band,” (invited) symposium in honor of Warren Pickett’s 65th Birthday, UC Davis, 24 June 2012.
7. S. House, I.M. Robertson and D. Graham, “Applications of Electron Microscopy to Complex Metal Hydrides,” M&M 2011.
8. Ian M. Robertson, Josh Kacher, Grace Liu, Stephen House, “In-situ TEM studies of the response of a Material to an External Stimulus” MS&T 2011, Narayan Symposium. Invited.

References

1. Majzoub, E.H., X.F. Liu, D. Peaslee, and C.Z. Jost, *Controlling the Decomposition Pathway of LiBH_4 via Confinement in Highly Ordered Nanoporous Carbon*. *J Phys Chem C*, 2010. 114(33): p. 14036-14041.