

## IV.A.1o Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials

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### Objectives

- Develop fundamental understanding of metal hydride reaction kinetics:
  - Kinetics limit practicality and reversibility of many promising metal hydride material systems.
    - Mg, Mg<sub>2</sub>Si, Li<sub>4</sub>Si, NaAlH<sub>4</sub>, LiBH<sub>4</sub>+MgH<sub>2</sub>, etc.
    - Initial work on Mg<sub>2</sub>Si showed that kinetic issues prevent system from achieving reversibility.
  - Catalyst additions have shown some success in improving kinetics for some systems (ie. Ti in NaAlH<sub>4</sub>), but little is known about the nature of these effects.
  - Little is known about the kinetic mechanisms present in these systems, and in order to improve the kinetics for any of these metal hydride systems a sound understanding must be developed.
- Develop understanding of metal hydride nanostructure thermodynamics:
  - Many systems suffer from inappropriate thermodynamics (equilibrium pressure).
    - Mg, Al.

- Continuum modeling suggests that reaction thermodynamics should be modified by reducing particle size to the nanometer regime.
- Develop understanding of metal hydride structures during phase change:
  - Material structure can play important role in reaction kinetics, especially during solid state phase transformations such as those in metal hydride reactions.
  - Understanding the interplay between material structure and reaction kinetics may provide insight on how to successfully engineer new materials with improved kinetics and storage properties.

### 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:

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

### Technical Targets

Our project conducts fundamental research of metal hydride storage material reaction kinetics and thermodynamics, examining the effects of material structure and particle size on each using thin films and vapor deposition techniques to probe the effects in a controlled and quantitative manner. The research addresses the following DOE 2010 hydrogen storage technical targets:

- Gravimetric Capacity: 0.06 kg H<sub>2</sub>/kg
- Min/Max Delivery Temperature: -40/85°C
- System Fill Time: 3 min
- Minimum Full Flow Rate: 0.02 (g/s)/kW

## Accomplishments

- X-ray investigations showed that deeper cycling leads to faster loss of material texture and slower discharge rates, evidence for mixed solid phase epitaxial (SPE)/non-SPE regrowth mode.
- Quartz crystal microbalance (QCM) chamber constructed and initial measurements made of Peq in Mg and Pd systems.
- Neutron reflectivity experiments show a hydrogen (deuterium) [H(D)] distribution gradient through multilayer samples as well as evidence for in-plane structure.



## Introduction

The mechanism and kinetics of the metal/metal hydride transformation in metal hydride hydrogen storage materials plays a crucial role in determining whether a material meets the DOE on-board storage targets for 2010 and 2015. A fundamental understanding of these issues provides valuable insight into the ways in which various material systems can be engineered in order to meet specific material targets. Additionally, as the ability to engineer materials on the nano-scale emerges, new routes to tailoring specific material properties become possible. Specifically, by reducing the dimensions of metal hydride storage materials you can alter properties such as the hydrogen vapor pressure and storage capacity.

We extensively investigated reduced dimension metal hydride material systems and their hydrogen charging and discharging properties. We determined kinetic behavior and transformation mechanisms for magnesium based thin film material systems using in situ hydriding and dehydriding with detailed X-ray diffraction (XRD) to examine the effects of material cycling. We also investigated the effects of reduced dimensionality on destabilized material systems such as Mg<sub>2</sub>Si. Additionally, we modeled the effects of reducing dimensions of hydrogen storage materials to the nano-scale (i.e. nanoparticles), revealing the possibility of drastically altered hydrogen storage properties in metal hydride nanoparticles, and constructed an analysis chamber to probe the differences in hydrogen storage properties (both thermodynamic and kinetic) between bulk and nanoscale systems.

## Approach

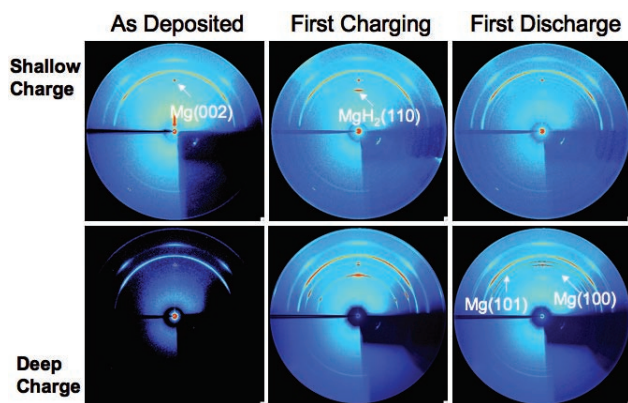
In order to determine ways to engineer material systems to meet the DOE on-board storage targets for 2010 and 2015 we use a combination of thermodynamic modeling efforts combined with nanoscale material synthesis and various characterization techniques to

gain a better understanding of the underlying kinetic mechanisms present in the metal hydride phase transformations. We make extensive use of XRD techniques, using both in-house facilities and facilities at the Stanford Synchrotron Radiation Laboratory (SSRL), to characterize the structural changes of material systems as they undergo phase changes during hydrogen absorption and desorption. We can then correlate this structural information with kinetic data about the absorption and desorption rates to relate the structure of materials to their kinetic behavior. Additionally, we employ the use of a QCM apparatus to quantify the hydrogen uptake in extremely small sample sizes, allowing us to determine reaction thermodynamics and kinetics for thin film and nanoparticle samples. Finally, the modeling efforts provide insight on where future experiments should focus and help to explain behaviors seen in experimentally synthesized samples prepared using physical vapor deposition techniques.

## Results

Over the last year, we continued utilizing our thin film deposition and analysis capabilities to investigate the fundamental kinetic mechanisms present in metal/metal hydride phase change reactions as well as the effect of particle size on both reaction kinetics and thermodynamics.

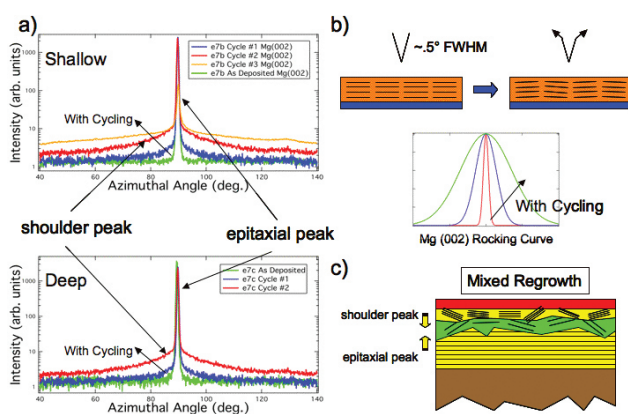
Material cycling is of great concern in the DOE long-term storage material goals. In order to successfully engineer a material to withstand repeated cycling under normal operating conditions, we need to develop a fundamental understanding of the kinetic mechanisms present during the hydrogen absorption/desorption reactions. Our previous work examining epitaxial thin films of Mg showed kinetic modification with a loss of thin film texture. As the films were cycled, the film texture degraded with a faster loss of discharge kinetics as the films were cycled deeper (further to completion during the hydrogenation reaction). In order to more closely examine the relationship between textural degradation and material reaction kinetics, we designed a new experiment utilizing the XRD facilities available at the SSRL. We compared two films, one cycled “shallow” (charged at 85 psi H<sub>2</sub> and 100°C for 2.5 hrs) and one cycled “deep” (charged at 90 psi H<sub>2</sub> and 100°C for 13 hrs), taking 2-dimensional XRD patterns after each charging and discharging cycle. The patterns for each sample in the as-deposited state, after the first charging and after the second charging are shown in Figure 1. Both films start out with sharp epitaxial Mg (002) peaks out of the sample plane. After the first charging both samples show the appearance of less textured MgH<sub>2</sub> (110) in addition to the remaining Mg (002) peak. However, in the “deep” cycled sample the MgH<sub>2</sub> that grows in displays less texture than that in the “shallow” sample. After dehydrogenating the samples



**FIGURE 1.** Two-dimensional XRD patterns for “shallow” and “deep” cycled Mg thin films showing the patterns in the as-deposited state, after the first hydrogen charging and after the first hydrogen discharging.

some differences appear between the “shallow” and “deep” cycled films. In the “shallow” cycled film, the regrown Mg shows much of the texture of the original film, with a small amount of less textured Mg appearing. In the “deep” cycled film, however, the regrown Mg shows little of the texture of the original film, with new Mg orientations appearing in the diffraction pattern as seen in the (002) ring as well as the new (101) and (100) Mg rings. Examining the Mg (002) rocking curves for each sample, as shown in Figure 2a, we see that with each cycle some new, less textured Mg regrows as a “shoulder” peak in addition to the Mg that regrows epitaxially on the existing highly textured Mg. This is more pronounced in the “deep” cycled sample than in the “shallow” cycled sample. As the sample cycles between the hydrided and metallic state the Mg becomes more and more disordered with each cycle, with the rocking curve width increasing sequentially with each cycle as shown in Figure 2b. Together with our previous results showing evidence for solid state epitaxial regrowth in epitaxial thin film samples these results indicate that new Mg regrowth in the thin film samples occurs by a mixed regrowth mode as shown in Figure 2c where some Mg regrows epitaxially, but some regrows non-epitaxially. In conclusion, in order to maintain fast dehydrogenation kinetics efforts should be made to stabilize material microstructure through alloy additions or nanostructuring and modeling efforts should be made to explain the correlation between charging extent, charging rate, textural degradation and charging/discharging kinetics.

In addition to our studies on thin film microstructural evolution, we began implementing our new analysis chamber utilizing a QCM to monitor the hydrogen uptake quantitatively in very small (thin film and nanoparticle) samples. Our earlier continuum modeling work indicated that, as particle size decreases the thermodynamics of the hydride formation reaction may be modified, resulting in altered equilibrium

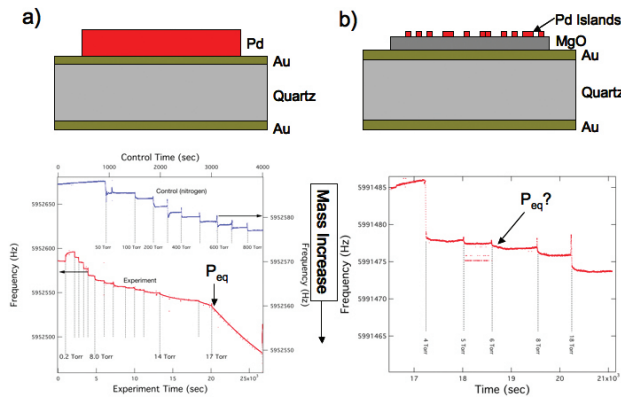


**FIGURE 2.** Textural Degradation and Kinetic Mechanisms in Epitaxial Mg Thin Films – a) Rocking curves extracted from the 2-dimensional XRD patterns for the two samples showing sharp epitaxial peaks as well as broad shoulder peaks. b) Successive peak broadening mechanism illustrated. As the film cycles it becomes more and more disordered. c) Cartoon depicting the mixed regrowth mode observed with both the SPE regrowth as well as the non-SPE regrowth.

pressure when compared to the bulk system. Our QCM analysis chamber should be able to measure hydrogen uptake in thin film samples as well as layers of isolated nanoparticles. One advantage of the QCM setup is that we can prepare the thin film and nanoparticle samples directly on the QCM crystal for analysis. For a preliminary system, we chose to investigate the Pd system because we can investigate the system without worrying that the Pd may oxidize, allowing us to transfer samples from the deposition chamber to the analysis chamber. Additionally, we can synthesize nanoscale Pd samples by several routes including solution deposition and islanded thin film growth. Pd also stores an appreciable amount of hydrogen with reasonable kinetics at lower temperatures. Some preliminary calculations by Karl Johnson [1] indicate that Pd should show a reduced equilibrium pressure as the particle size is reduced to the nanometer scale.

Initially we grew 400 nm Pd on a commercial QCM crystal by direct current magnetron sputter deposition and transferred the sample to the analysis chamber where we exposed the sample to hydrogen gas at room temperature. Pressure effects on the crystal resonant frequency were compensated for by performing calibration runs with inert gas before exposing the sample to hydrogen. As shown in Figure 3a, the sample began absorbing hydrogen as the pressure was raised above the equilibrium pressure at 17 Torr at a temperature of 22°C. This compares somewhat favorably with the reported bulk value of 11.5 Torr. We performed a similar experiment on a nanoscale Pd sample prepared by growing a layer of MgO onto the QCM crystal followed by a thin (~1 nm) layer of Pd at 300°C. This forms an islanded Pd film with very small islands of Pd on the surface of the crystal. Similar



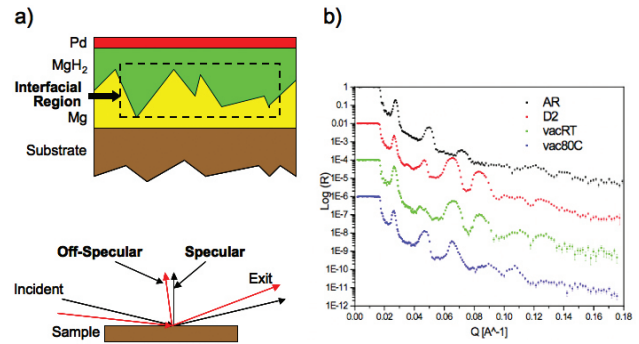


**FIGURE 3.** QCM Data and Sample Schematics for Small Pd Samples Investigated – a) Pd thin film sample with data showing equilibrium pressure attained around 17 Torr. b) Islanded Pd film sample showing possible equilibrium pressure attained around 6 Torr.

analysis to that performed on the Pd film sample showed a possible equilibrium pressure of 6 Torr as shown in Figure 3b, lower than the bulk value as predicted by Karl Johnson’s calculations. Additionally, we made measurements on a 400 nm Mg film capped with 25 nm of Pd. Our equilibrium pressure measurements do not line up directly with those values reported in the literature, but we believe much of the error was due to pressure and temperature control and measurement issues with our chamber that have since been resolved. The QCM analysis chamber will allow us to measure hydrogen uptake in very small samples at lower temperatures than those available to other techniques.

We also continued our collaboration with the team from the National Institute of Standards and Technology (NIST) to exploit the sensitivity of neutrons to hydrogen in order to further characterize the kinetics of the Mg/MgH<sub>2</sub> phase chamber in thin film systems. In our collaboration we use neutron reflectivity to track the motion of the Mg/MgH<sub>2</sub> interface and allow hydrogen depth profiling of the samples through appropriate system modeling and data analysis. In this collaboration we hope to learn how the interface motion depends on the charging and discharging conditions (temperature and hydrogen pressure), how the nature of the interface itself (roughness, sharpness, etc.) as shown in Figure 4a changes with these same conditions as well as how the nature and motion of the interface affects the phase change kinetics for hydride growth and subsequent metal regrowth.

Our initial measurements showed promising results as we observed significant changes in the reflectivity pattern of multilayer films as hydrogen incorporated into the film. Further analysis of the samples, including both specular and off-specular scans, combined with advanced modeling should enable quantitative characterization of the interfacial region in these metal



**FIGURE 4.** NIST Collaboration Schematics and Data – a) Cartoon illustrating the sample schematic and region of interest as well as the scattering geometries referenced. b) Neutron reflectivity data for a (20 nm Mg + 5 nm Pd) x 10 bilayer sample with data taken in as received (AR) state, after 17 hrs loading under ~7.5 atm D2 at 100°C (D2) (scan at room temperature under 1 atm D2), at room temperature under vacuum (vacRT), and at 80°C under vacuum (vac80C).

hydride thin film samples. Our recent data, as seen in Figure 4b, shows neutron reflectivity patterns for a sample consisting of 10 bilayers of 20 nm Mg and 5 nm Pd. Data was then taken in the as-received (AR) state, after 17 hrs loading under ~7.5 atm D2 at 100°C (D2) (scan at room temperature under 1 atm D2), at room temperature under vacuum (vacRT), and at 80°C under vacuum (vac80C). As shown in the figure, the reflectivity pattern undergoes drastic changes with the introduction of hydrogen. We constructed models to compare to the measured data. The models indicate that the samples contain more H(D) near the sample surface and less near the substrate. The layers in the film swelled with the introduction of H(D), also more near the surface and less near the substrate. Heating the sample acts to redistribute the H(D) throughout the sample, reducing the gradients. After heating the sample in vacuum, it did not return to the as-deposited state and much of the H(D) remained in the sample. Also, we observed an interesting feature in the off-specular scattering indicating the possibility of an in-plane structure in the sample. This feature warrants further investigation. With continued investigations these experiments should reveal fundamental information about the nature of the interface between metals and their hydrides which relates very closely with the kinetic pathways taken as the hydride forms and dissociates.

## Conclusions and Future Directions

### Conclusions

- X-ray investigations showed that deeper cycling leads to faster loss of material texture and slower discharge rates, evidence for mixed SPE/non-SPE regrowth mode.

- QCM chamber constructed and initial measurements made of  $P_{eq}$  in Mg and Pd systems.
- Neutron reflectivity experiments show a H(D) distribution gradient through multilayer samples as well as evidence for in-plane structure.

#### Future Directions

- Integrate QCM chamber into existing deposition chambers:
  - Enables studies of Mg and other light metal hydride nanoparticles that may otherwise oxidize upon removal from chamber.
- Continue data collection and analysis with QCM chamber:
  - Attempt to confirm theoretical predictions about the change in equilibrium pressure as particle size is reduced.
- Expand and continue collaboration with the NIST team using neutron reflectivity:
  - Investigate new single layer sample to examine  $MgH_2$  growth kinetics.
  - Use new in situ sample chamber to better control exposure to  $D_2$  during analysis.
  - Develop new models to describe hydrogen incorporation kinetics.
  - Investigate off-specular scattering to examine the nature of the metal/hydride interface and the possibility of in-plane structure.
- Finalize thin film microstructural evolution work:
  - Explain observations and develop model to describe hydride growth in the thin films.
- New materials:
  - Introduce new materials into all aspects of our work; NIST collaboration, QCM analysis.
  - Mg/Al/Ti alloys, borohydrides possibly, nanoparticles, etc.

#### Special Recognitions & Awards/Patents Issued

1. Winner of the Graduate Student Poster competition at the 34<sup>th</sup> Annual SSRL Users' Meeting in Menlo Park, CA.

#### FY 2008 Publications/Presentations

1. "Quantitative Analysis of the Effects of Cycling and Alloy Additions on Material Microstructure and Reaction Kinetics in Thin Film Mg/MgH<sub>2</sub> Systems", MRS Fall 2007 Meeting, Boston, MA.
2. "Quantitative Quartz Crystal Microbalance Studies of Equilibrium Pressures in Thin Film and Nanoparticle Metal Hydrides", MRS Spring 2008 Meeting, San Francisco, CA.
3. "The Effect of Cycling on Microstructure and Reaction Kinetics in Mg/MgH<sub>2</sub> Thin Films", Stanford Synchrotron Radiation Laboratory 34<sup>th</sup> Annual Users' Meeting, Menlo Park, CA.
4. "The Effect of Cycling on Microstructure and Reaction Kinetics in Mg/MgH<sub>2</sub> Thin Films", Stanford Nanocharacterization Laboratory Open House, Stanford, CA.
5. "Inorganic Routes To Nanoparticle Synthesis", Invited Presentation, MRS Fall 2007 Meeting, Boston, MA.
6. "Nanostructured Materials for Hydrogen Storage", Invited Presentation, MS&T'07, September 2007, Detroit, MI.
7. "Neutron Scattering Studies of Hydrogen Storage Thin Film Model Systems", Lujan Center Workshop, Humphrey's Half Moon Bay, September 06-07 2007.
8. "Nanostructured Materials for Hydrogen Storage", Combined Materials Science and Engineering Physics Departmental Colloquium, Colorado School of Mines, March 2008.

#### References

1. Karl Johnson, private communication.