Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials

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Project ID#: STP 18
04/01/08

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Overview

• Timeline
  – Project Start Date: January 2005
  – Project End Date: 2/28/2010
  – Percent Completion: ~60%

• Budget
  – Total Project Funding: $997,921
    • DOE Share: $778,828
    • Contractor Share: $199,093
  – Funding Received FY07: $150,000/$37,500
  – Funding Received FY08: $150,000/$37,500

• Barriers Addressed
  – B: Weight and Volume
  – M: Hydrogen Capacity and Reversibility

• Partners
  – HRL Laboratories: collaborations about new material systems and complex/destabilized hydride system development
  – University of Pittsburgh: collaborated to obtain interfacial energies for Mg/MgH₂ interface
  – NIST Center for Neutron Research: collaboration to investigate reacting films using neutron reflectivity
Objectives

• **Develop fundamental understanding of metal hydride reaction kinetics**
  – Kinetics limit practicality and reversibility of many promising metal hydride material systems
    • Mg, Mg$_2$Si, Li$_4$Si, NaAlH$_4$, LiBH$_4$+MgH$_2$, etc.
    • Initial work on Mg$_2$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$_4$), 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
<table>
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<tr>
<th>Date</th>
<th>Milestone or Go/No-Go Decision</th>
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| 03/2007 | **Milestone**: Model kinetic transformation processes for thin film metal hydride material systems.  
**Status**: evidence seen for moving planar interface transformation kinetics. |
| 06/2007 | **Milestone**: Begin investigation of structural correlations in other material systems.  
**Status**: New material systems being introduced into all aspects of research. Nanostructured materials being investigated. |
| 09/2007 | **Milestone**: Investigate effects of cycling on material kinetics.  
**Status**: Textural degradation seen with cycling, leads to slower discharge kinetics. |
| 09/2007 | **Milestone**: Model kinetics of nanoparticle phase transformations and begin verification of model.  
**Status**: First steps towards verification made with quartz crystal microbalance (QCM) chamber development and initial implementation. |
**Approach**

- **Thin Film Model Systems**
  - Thin film growth methods such as sputtering allow for nearly atomic level compositional control
  - Appropriate substrate choices allow for precise microstructural control
  - Initial experiments with Mg films have validated the approach as results concur with those seen for bulk Mg measurements where appropriate
    - Diffusion limited hydride growth, phase change crystallographic orientations

- **In-Situ Structural Characterization**
  - Custom designed *in-situ* hydrogen pressure chamber for use during x-ray studies with synchrotron radiation
  - Real time structural analysis to facilitate detailed kinetic mechanism determinations

- **Thin Film and Nanoparticle Uptake Monitoring**
  - Analysis chamber utilizing quartz crystal microbalance (QCM) to allow uptake measurements in thin film and nanoparticle samples

- **Transition To More Complex Material Systems**
  - After establishing techniques and approaches using simple model system, move on to two component system (Mg+Ti) and then more complex systems involving mass transport and phase segregation
Thin Film Microstructural Evolution

- **Cyclic Stability**
  - Material stability upon cycling is of great concern in the DOE long term goals
  - An understanding of the kinetic mechanisms present during material cycling is essential in order to successfully engineer a material to withstand repeated cycling under normal operating conditions

- **Previous work showed kinetic modification with loss of thin film texture**
  - Material texture degrades with cycling
  - Discharge kinetics slower with deeper cycling and less texture

- **New experiment to closely examine material texture with x-ray diffraction**
  - Compare films subjected to “shallow” and “deep” cycling
  - “Shallow” Film cycled at 85 psi and 100°C for 2.5 hrs
  - “Deep” Film cycled at 90 psi and 100°C for 13 hrs
  - Develop model for microstructural evolution with cycling
Thin Film Microstructural Evolution

As Deposited | First Charging | First Discharge

Shallow Charge

Mg(002)

MgH₂(110)

Deep Charge

Mg(101)

Mg(100)

XRD patterns from 2D image plate detectors
Thin Film Microstructural Evolution

- **Shallow**
  - With Cycling
  - shoulder peak
  - epitaxial peak

- **Deep**
  - With Cycling

**Mg (002) Rocking Curve**
- ~0.5° FWHM

**Mixed Regrowth**

Percentage of well aligned material decreases with cycling.
Thin Film Microstructural Evolution

• Data shows successive peak broadening in Mg(002) rocking curves
  – Mg(002) rocking curve becomes broader as sample is cycled between metal and hydride states
  – Less textured MgH$_2$ phase creates less textured Mg that regrows from it
  – Broadening mechanism repeats each time sample is cycled
  – Deeper cycling promotes further (faster) degradation of texture

• Compilation of data shows evidence for mixed regrowth modes
  – Characteristics of both solid phase epitaxial (SPE) and non-SPE modes seen in x-ray rocking curve progressions
  – Both broad shoulder and sharp epitaxial peak shapes seen
  – Mechanism depicted in cartoon on previous slide
Thin Film Microstructural Evolution

• Conclusions

  – Deeper cycling promotes faster degradation of thin film texture, leading to slower discharge rates
    • New XRD measurements provide further evidence and more insight into the nature of the degradation

  – Successively broadening rocking curves indicate gradual degradation of texture as material is cycled

  – In combination with previous observation of solid phase epitaxial (SPE) regrowth in epitaxial Mg films, new observations suggest a “mixed” regrowth mode with characteristics of both SPE and non-SPE mechanisms

  – Stabilizing material texture and microstructure should lead to improved hydrogen discharge kinetics and better stability with cycling

  – New data (yet to be processed) showing effect of cycling on charging kinetics should provide insight into mechanisms responsible for this effect

  – Efforts should be made to stabilize material microstructure through alloy additions, nanostructuring, etc. and models should be developed to explain correlation between charging extent, charging rate, textural degradation and charging/discharging kinetics
QCM Studies: Can Size Change Thermodynamics?

• Continuum modeling indicates that reaction kinetics and thermodynamics should change as particle size is reduced
  – Large effects should show up when particles reach few nanometers in size

• QCM analysis provides a method for measuring hydrogen uptake in very small sample sizes to verify predictions of models
  – Capability to measure sub-monolayer amounts of hydrogen uptake

• Nanoscale samples can be prepared directly on QCM crystal:
  – Solution deposited nanoparticles
  – Islanded thin films

*Based on preliminary calculations by Karl Johnson’s team
QCM Studies: Can Size Change Thermodynamics?

- **Palladium as a model system:**
  - Stores appreciable amount of hydrogen
  - Good kinetics
  - Preliminary calculations by Karl Johnson indicate that there should be an effect with reduced particle size
    - Equilibrium pressure should decrease

- **Thin film samples to verify technique**
  - Grow Pd film on QCM crystal as substrate
  - Compare $P_{eq}$ to reported values for bulk Pd

- **Nanoscale Pd samples to test the size dependence**
  - Solution deposited nanoparticles
  - Islanded thin films formed by a thin layer of Pd deposited onto MgO layer
QCM Studies: Can Size Change Thermodynamics?

- **Measurements made on Pd thin film**
  - 400 nm Pd sputtered onto QCM crystal
  - Exposed to 2% H₂ gas mixture (balance N₂) at room temperature (22°C)
  - Pressure adjusted until uptake observed in film

- **Uptake seen to set in at ~17 Torr H₂ partial pressure and 22°C**
  - Different from bulk value reported as ~17 Torr at 30°C, but fairly close

- **Confirmation of data needed to verify observation**
  - Repeat experiment

- **Performing experiment at different temperatures allows reconstruction of Van’t Hoff plot and extraction of thermodynamic parameters**
QCM Studies: Can Size Change Thermodynamics?

- Measurements made on islanded Pd film grown on QCM crystal
  - 50 nm MgO evaporated onto QCM crystal at room temperature
  - 1 nm (nominal) Pd evaporated onto MgO at 300°C

- Evidence seen for $P_{eq} \approx \text{6 Torr} \ \text{H}_2$ partial pressure
  - Signal small compared to much larger film of Pd

- More measurements needed to verify observation
  - Observed $P_{eq}$ difference compared to bulk and thin film matches direction predicted by calculations
    - $P_{eq}$ decreases with reduced particle size
QCM Studies: Can Size Change Thermodynamics?

- Measure Mg film $P_{eq}$ to verify technique capabilities

- Measurements made on Mg thin films with Pd capping layer
  - 400 nm Mg + 25 nm Pd sputter deposited onto QCM crystal
  - $P_{eq}$ measurements made at RT and 50°C
  - Data shown at right compared to other literature values for thin films and bulk systems

- Our data does not match reported values exactly, more work needed

- QCM allows measurements to be made at much lower temperatures than other techniques

- Data taken before temperature control system improvements
  - Our measured $P_{eq}$ values are higher than others
  - Additional measurements needed to verify initial measurements
QCM Studies: Can Size Change Thermodynamics?

• Conclusions

– Continuum modeling suggests that nanostructured materials display altered $P_{eq}$ compared to bulk systems

– QCM analysis provides a method for measuring hydrogen uptake in very small sample sizes to verify predictions of models

– Nanoscale samples can be prepared directly on QCM crystal: solution deposited, islanded films

– Thin film Pd sample shows $P_{eq}=17$ Torr compared to 11.5 Torr in bulk systems
  • Looking into reason for difference

– Islanded thin film nanoparticle sample shows evidence for $P_{eq}$ at 6 Torr
  • More measurements needed to verify observation, but follows trend predicted by calculations and theory

– QCM measurements show promise for measuring dependence of $P_{eq}$ on particle size
Neutron Reflectivity w/ NIST

• Collaboration with NIST to exploit the sensitivity of neutrons to hydrogen in order to further characterize the kinetics of the Mg/MgH$_2$ phase change in thin film systems
  – Reflectivity measurements to track the motion of the Mg/MgH$_2$ interface
  – Hydrogen depth profiling through appropriate system modeling and data analysis

• What we hope to learn
  – How does the interface motion depend on the charging and discharging conditions (temperature and hydrogen pressure)?
  – How does the nature of the interface itself change with these same conditions (roughness, sharpness, etc.)?
  – How does the nature and motion of the interface affect the phase change kinetics for hydride growth and subsequent metal regrowth?

• Initial measurements show promising results
  – Significant change in reflectivity pattern due to incorporation of hydrogen into the film
  – Sample modeling reveals potential of technique with initial semi-quantitative results
Neutron Reflectivity w/ NIST

- **Detailed studies will enable hydrogen depth profiling of samples**
  - Verify layer-by-layer growth mechanism and refine model
  - Show the actual hydrogen content of the samples as a function of depth

- **Can also characterize the interface separating the metal and hydride phases with additional studies**
  - Off-specular scans allow detailed interface characterization
  - How rough is the interface?
  - Does the interface change character with different charging conditions?
  - How does the addition of other elements (like Ti) affect the interface character and development?
Neutron Reflectivity w/ NIST

- **Data obtained for multilayer Mg/Pd sample under various loading conditions**
  - (20 nm Mg + 5 nm Pd) x 10 sputtered onto Al₂O₃ substrate
  - Data taken in as-received (AR) state, after 17 hrs loading under ~7.5 atm D₂ at 100°C (D2) (scan at RT under 1 atm D₂), at RT under vacuum (vacRT), and at 80°C under vacuum (vac80C)

- **Models for different conditions constructed and compared to data**
  - Models indicate that layers contain more D near surface and less near substrate
  - Layers also thicker near surface than at substrate
  - Heating sample acts to redistribute the D in the layers, flattening out the gradient
  - After heating under vacuum, the sample did not return to the as-deposited state
    - D remained in the Mg and Pd layers
  - Interesting feature in off-specular scattering
    - Possible in-plane structure
Neutron Reflectivity w/ NIST

• Conclusions

– Neutron reflectivity patterns show significant changes with incorporation of D(H)

– Sample modeling and data analysis reveal D(H)-content and layer thickness gradient in multilayer sample
  • Heating sample in vacuum acts to redistribute D(H), flattening out the gradient
  • Sample does not return to as-deposited state after annealing in vacuum at 80°C
  • More experiments and modeling needed to determine implications of these observations

– With continued experiments, will gain further insight into how the interface moves and changes character with hydrogen charging and how charging conditions affect these behaviors

– Ultimately learn more about the kinetic mechanisms present in metal hydride reactions and in future use same techniques to investigate more complex systems such as Mg/Ti/Al

– Communicate findings to other groups within MHCoE and elsewhere in order to advise on suggested approaches for improving kinetics in candidate material systems
Future Work

• **Integrate QCM chamber into existing deposition chambers**
  – Develop capability to deposit thin film and nanoparticle samples onto substrate and analyze without removing from chamber
  – 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**
  – Find and exploit the limits of hydrogen uptake sensitivity for the instrument
  – Attempt to confirm theoretical predictions about the change in equilibrium pressure as particle size is reduced
  – Examine kinetics and thermodynamics for thin film and nanoparticle samples

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![Diagram of Sputter Sources](image)

QCM Chamber Integrated into Deposition System

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Future Work

• **Expand and continue collaboration with 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**
  – Finish examination of *in-situ* hydrogenation data
  – 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.
  – Examine effects of nanostructuring materials on thermodynamics and kinetics
Summary

• Relevance:
  – Reveal fundamental reaction mechanisms in metal hydride phase transformations to address kinetic limitations that plague nearly all candidate metal hydride material systems

• Approach:
  – Utilize well controlled thin film model systems and in-situ characterization to investigate kinetic mechanisms in metal hydride material systems

• Technical Accomplishments:
  – 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 hydrogen(deuterium) distribution gradient through multilayer samples as well as evidence for in-plane structure

• Collaborations and Tech. Transfer:
  – Collaboration with NIST to utilize neutron capabilities to complement x-ray work
  – Calculations from U. Pittsburgh team have given valuable insight into directions for nanoparticle storage research

• Future Work:
  – Integrate QCM chamber to existing deposition systems to allow in-situ experiments
  – Continue measurements with QCM chamber on thin film and nanoparticle samples
  – Introduce new materials into all aspects of our investigation
  – Continue with NIST neutron reflectivity experiments