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

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- Part of the DOE Metal Hydride Center of Excellence -

This presentation does not contain any proprietary or confidential information
Overview

• **Timeline**
  – Project Start Date: FY05
  – Project End Date: FY09
  – Percent Complete: New Project

• **Budget**
  – Total project funding (expected)
    • DOE share $778,828
    • Contractor share $199,093
  – Funding for FY05:
    • DOE share $150,000
    • Contractor share 37,500

• **Barriers Addressed**
  – Hydrogen Capacity and Reversibility
  – Weight and Volume
  – Efficiency
  – Lack of Understanding of Hydrogen Physisorption and Chemisorption

• **Targets**
  – 6% Gravimetric Capacity
  – .045 kg/L Volumetric Capacity
  – -30/80°C min/max Delivery Temp.

• **Partners**
  – DOE Metal Hydride Center of Excellence Members
  – MHCoE sub-team on thermodynamically tuned nanophase materials
    • (Caltech, JPL, HRL, U. Hawaii)
Objectives

• **Perform In-Situ Structural Studies of Hydrogen Storage Materials**
  – Utilize high brightness x-ray source at Stanford Synchrotron Radiation Laboratory
  – Construct Sieverts apparatus for *in-situ* control of hydrogen content
  – Demonstrate feasibility of *in-situ* synchrotron studies

• **Investigate Light Metal Hydride Model Material Systems**
  – Use engineered thin film model systems to investigate phase change and catalytic processes associated with hydrogen cycling

• **Develop Kinetic Model of Nanoparticle Phase Transformations**
  – Build continuum models of nanoparticle kinetics to illuminate mechanisms of hydride formation in nanoscale materials
Approach

- **In-Situ Structural Studies**
  - Real time structural analysis using high brightness synchrotron radiation
  - *In-situ* hydrogen charging of candidate materials
  - Correlate structural changes with hydrogen charging characteristics

- **Model Material System Design and Synthesis**
  - Design and grow model material systems using physical vapor deposition techniques such as sputtering
  - Use input from MHCoE partners and kinetic modeling to select candidate materials

- **Kinetic Modeling of Nanoparticle Transformations**
  - Model kinetic processes of phase transformations in nanoparticles to guide future material selection and design
  - Apply existing thermodynamic data to new model to shed light on nanoscale processes
**Model Systems: Mg/Pd Nanostructured Films**

- **Pd- and Pd/Ti-capped Mg films**
  - **Pd cap:**
    - Catalyzes H2 dissociation
    - Rapid diffusion of H atoms
    - Source for atomic hydrogen
  - **Ti cap:**
    - Suggested as another possible catalyst candidate

- **Thin film vapor phase synthesis:**
  - Atomic scale control of composition
  - Engineer interface density and catalyst geometry
  - One-dimensional diffusion geometry
  - Ideal for reaction kinetic studies

- **Samples sent to HRL team for compositional analysis**
  - Determine impurity content (especially oxygen)
Model Systems: Mg/Pd Nanostructured Films

- Films Analyzed Using X-Ray Diffraction (XRD) to Examine Structure/Composition
- Diffraction Results:
  - Mg film with strong (002) texture
    - No presence of second orientation or phase (e.g. MgO)
  - Rocking curve width 5.2°
- Demonstrates Ability to Deposit Highly Textured Mg Thin Films
  - Nanostructured model system: proof of concept
Model Systems: Mg/Pd Nanostructured Films

- **SIMS Depth Profiling Data**
  - Shows film composition as function of depth from surface
  - Deuterium (2H) signal shows hydriding behavior of Mg thin film
Model Systems: Mg/Pd Nanostructured Films

- **Mg/Pd Multilayer Films:**
  - Demonstrates atomic level control of composition and catalyst distribution through controlled sputter deposition
  - High interface density ~ 300 m²/cm³

- **Ideal structures for studies of:**
  - Catalyst effects
  - Interface effects

![Diagram of Mg/Pd multilayer on Si substrate](image)
**Model Systems: Mg/Pd Nanostructured Films**

- **Small angle x-ray scattering**
  - Peaks show strong composition modulation
  - Analysis allows calculation of bilayer periodicity
    - Samples used to determine tooling factors in sputtering chamber
- **Demonstrates Ability to Engineer Material Structures at the Nanoscale**

![Graph showing intensity vs 2θ(deg)](image-url)
Model Systems: Mg/Pd Nanostructured Films

- Tooling Factor Determination
  - Series of three multilayer samples with different bilayer periodicity
    - MgPd_Multilayer1: (60Å Mg/ 90Å Pd) nominal bilayer periodicity of 150Å
    - MgPd_Multilayer2: (90Å Mg/ 60Å Pd) nominal bilayer periodicity of 150Å
    - MgPd_Multilayer3: (60Å Mg/ 60Å Pd) nominal bilayer periodicity of 120Å
  - Measured bilayer periodicity (from low angle x-ray reflectivity scans) gives tooling factors for Mg and Pd

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\[
\begin{align*}
\delta & \text{ - reflects change in volume due to interface reaction} \\
\text{Preliminary result:} & \delta = -1.8 \text{ nm} \\
\text{Significant reaction} & \text{(to be verified in future work)}
\end{align*}
\]
Model Systems: Mg$_2$Si Nanostructured Films

- Mg$_2$Si film deposited by codeposition of Mg and Si
- Determine whether sample can be charged with hydrogen
  - Collaborative effort with HRL team
- Nanostructured Model System Using Novel Material and Synthesis Technique

![Diagram showing the phase diagram of Mg-Si with labels for Mg$_2$Si film, Si substrate, and 15 nm Pd Cap]
**Model Systems: Mg$_2$Si Nanostructured Films**

- **Diffraction Data Before Hydrogen Charging In RTA Furnace**
  - Mg$_2$Si (200) and Pd (111) peaks overlap nearly exactly
    - Mg$_2$Si (220): 40.156°
    - Pd (111): 40.149°
  - Sharpness and intensity of peak indicates formation of the Mg$_2$Si phase

Evidence for formation of Mg$_2$Si phase

Oscillations give thickness - used to monitor H-induced volume changes
Model Systems: Future Work

Nanoscale Material Synthesis Methods For Future Work
- Physical vapor deposition of thin films
- Thin film growth on mesoporous silica substrates
- Nanoparticle generation from condensing vapor
- Mechanical milling

Controlled formation of nanostructures and nanometer-scale chemical features
- Investigate effect of nanometer scale chemistry and structure in hydrogen-storage systems (e.g. Mg-catalyst)

Mesoporous silica substrate formed from decomposition of block-copolymer/TEOS solution

Au nanoparticle array formed by deposition onto mesoporous substrate
In-Situ Structural Studies: Progress

- Received Sieverts apparatus
  - Controlled hydrogen charging
  - Determine hydrogen storage capacity of model systems

- Plumbing and hydrogen safety safeguard installation ongoing
  - County approved piping
  - Flammable gas cabinet for compressed hydrogen storage
**In-Situ Structural Studies: Capabilities**

**Synchrotron Radiation Facilities at SSRL**

- **Characteristics**
  - High flux
  - Controlled environment
    - Temperature: RT to 1500°C
    - Control of atmosphere (e.g., H₂ pressure)

- **Parallel x-ray detection**
  - Linear (existing) Area (planned)
  - Rapid collection of diffraction data
  - 1-10 second acquisition time

- **Has Potential to Study**
  - Reaction kinetics
  - Hydrogen-induced phase transitions
  - Study these as a function of
    - Storage media size and morphology
    - Temperature and environment
**In-Situ Structural Studies: Future Goals**

**Future Work**
- Install hydrogen charging apparatus on SSRL beamline
- Perform real time structural studies while material charges
- Analyze data to correlate hydriding behavior with:
  - Reaction kinetics
  - Structural changes
**Kinetic Modeling:** Nanoscale Phase Transitions

**MgH$_2$**

Hydrogen

Mg

Smaller particles charge and discharge faster

$\tau \sim \frac{L^2}{D}$

Reaction slows with time

$z_1 \sim \sqrt{Dt}$
• Due to interface and surface effects, thermodynamic properties (melting points, structure, phase formation) of nanoparticles are distinctly different from that of bulk materials
• Thermodynamics of nanoparticles are largely unknown.

Example: Extended solid solubility

Cost of interface drives up free energy of two-phase system for nanoparticles

fcc Au-Fe extended solid solution nanoparticle (Li, Sinclair, Dai)
**Kinetic Modeling:** Extended Solid Solubility of H in Mg Nanoparticles

Interface cost drives up the energy of two-phase configuration

Two phase nanoparticle

Energy of two-phase system above that of supersaturated solution!

Kinetic Modeling: Extended Solubility in Mg$_2$Si Nanoparticles

- Predicted solubility for nanoparticle is 1000 x that for bulk
- Dramatic consequences for reaction pathways involving phase changes in nanoparticles (e.g., thermodynamically tuned systems such as MgSi)
**Kinetic Modeling: Nanoparticle Nucleation**

Nucleation of second phase has interface energy cost

Transformation occurs as interface sweeps through particle

For $r < 3r^*$ nucleation is easier than in bulk!

Easier nucleation $\quad \rightarrow \quad$ Lower driving forces needed for driving phase transitions

**Nanoparticles have:**
- Dramatically different thermodynamics and phase stability
- Faster reaction kinetics
- Easier nucleation
## Upcoming Work and Milestones

Figure 2. Project schedule for technical effort by Stanford University (Go/No-Go shown by solid circles)

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<tr>
<th>TASK AND MILESTONE</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
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<td><strong>2. Model Systems</strong></td>
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<td>Design of model system architecture</td>
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<td>Growth of thin film and multilayer systems</td>
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<td>Structural studies in Mg/catalyst multilayers</td>
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<td><strong>3. Kinetic Modeling of Nanoparticle Phase Transformations</strong></td>
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<td>Experimental guidance and material design</td>
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<td><strong>Deliverables</strong></td>
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<td>Oral and written reports</td>
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<td>Contribute to test samples to independent characterization lab</td>
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<td>One-kg nanostructured sample to Sandia for prototype testing</td>
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