DOE Hydrogen Program

An Integrated Approach of Hydrogen Storage in Complex Hydrides of Transitional Elements

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STP_46_Karabacak

Overview

Timeline

- July 2006
- August 2009
- Percent complete 75%

Budget

- Total project funding $
  - DOE share $ 544,160
  - Contractor share $ 234,991
- Funding received in FY08 $ 183,891

Barriers

- *Barriers addressed*
  - Durability/Operability (3.3.4 D)
  - Charging/Discharging Rates (3.3.4 E)
  - Lack of understanding of Hydrogen Physisorption & chemisorption (3.3.4 P)

Partners

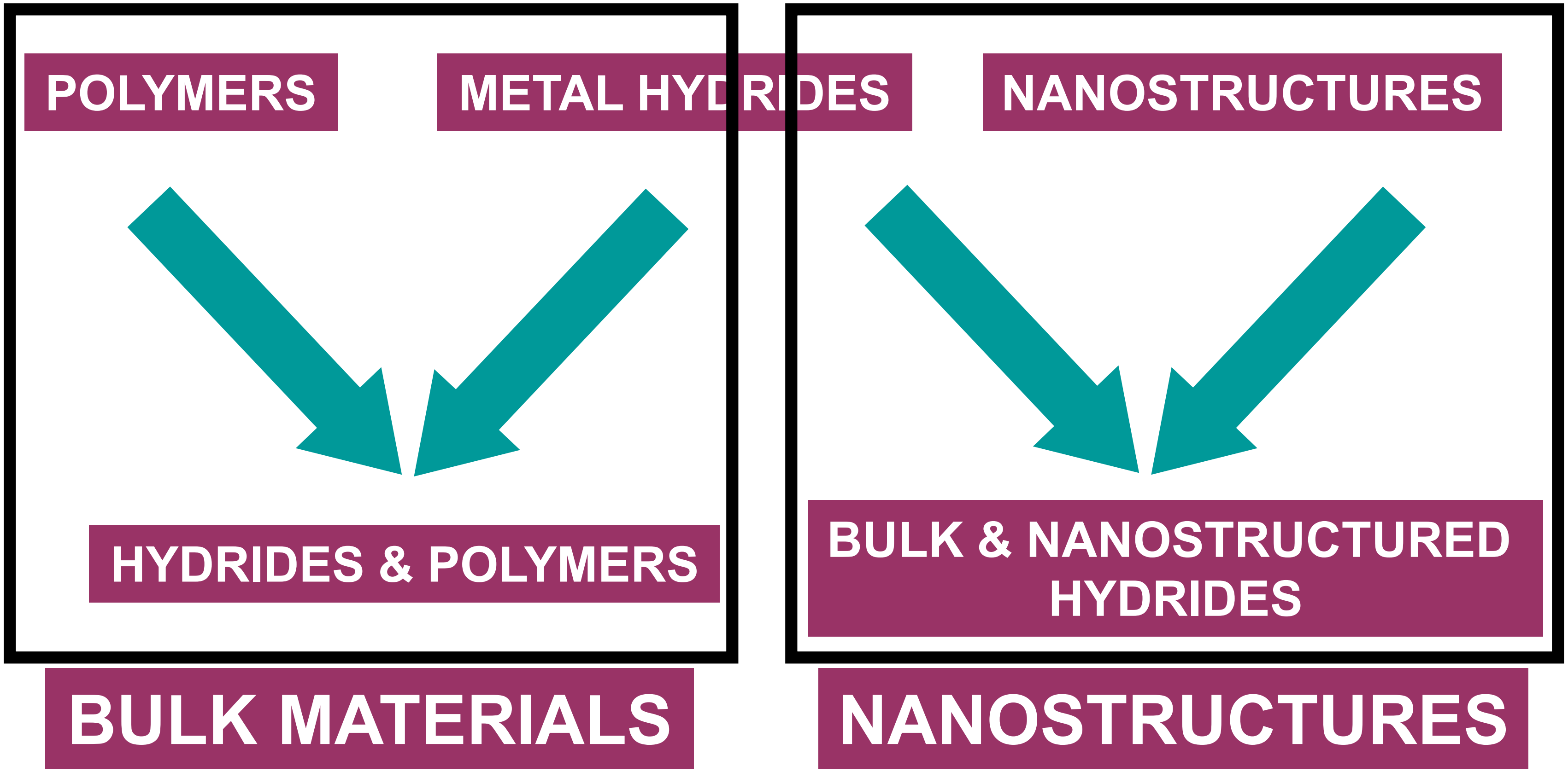
- University of Arkansas Nanotechnology Center, Little Rock
- National Institute for Isotopic & Molecular Technologies, Romania
- Los Alamos Neutron Science Center

OBJECTIVES

PARAMETER	YEAR		
	2007	2010	2015
Weight (%)	4.5	6	9
Pressure (bar)	100	100	100
Kinetics (Min.)	10	3	2.5
Temp. (° C)	-20/50	-30/50	-40/60

PROJECT TARGETS: 6 wt.% , 100 bar, 3 min , -30/50 deg C

OBJECTIVES


POLYMERS
METAL HYDRIDES
NANOSTRUCTURES
HYDRIDES & POLYMERS
BULK & NANOSTRUCTURED HYDRIDES
BULK MATERIALS
NANOSTRUCTURES

OBJECTIVES

BULK MATERIALS

- **Investigate methods for synthesizing DFT predicted metal decorated polymers[1]**
  - ***Continue testing on titanium decorated polyaniline***
  - ***Investigate feasibility of metal decoration in polyphenylacetylene.***

- **Work with a high capacity hydride complex based storage system to improve viability**
  - ***Establish reliable, scalable synthesis method for $Ca(BH_4)_2$***
  - ***Improve reversible decomposition facilitated by additives***

- **Investigate use of absorbing transition metal alloys as additives to hydride complex based storage reactions**
  - ***Characterize sorption properties of neat $LaNi_5$ alloy***
  - ***Investigate addition of activated $LaNi_5$ to other compound by mechanical mixing, chemical dispersion***

[1]Lee, H.; Choi, W. I.; Ihm, J. "Combinatorial Search for Optimal Hydrogen-Storage Nanomaterials Based on Polymers" *Phys. Rev. Let.* ***97,*** *2006. 056104*

MILESTONES

BULK MATERIALS

Month/Year	Milestone or Go/No-Go Decision
June 2008	**No-Go**: False positive confirmed in our previous preliminary absorption results with Ti-polyaniline material. A faulty valve was the cause. The problem was corrected. Subsequent testing showed conclusively no H_2 absorption for this material.
July 08	**Go**: $Ca(BH_4)_2$ selected for hydride complex work due to reports of direct formation and reversible decomposition of catalyzed material.[1,2]
September 08	**Milestone**: Work on synthesis of $Ca(BH_4)_2$ initiated due to repeated delays and difficulties with suppliers regarding this material.
Apr-08	**Milestone**: Work with Ti-Polyphenylacetlene started as a concept proofing material for the DFT predicted hydrogen absorber Ti-polyacetlene.

[1] Ronnebro, E.; Majzoub, E. H. "Calcium Borohydride for Hydrogen Storage: Catalysis and Reversibility" *J. of Phys. Chem.* **111**, 2007. 12045-12047

[2] Kim, H. J.; Jin, S.; Jae-Hyeok, S.; Cho, Y. W. "Reversible Hydrogen Storage in Calcium Borohydride $Ca(BH_4)_2$" *Scripta Materialia* **28**, 2008 481-483

APPROACH

BULK MATERIALS

- **Metal Decorated Polymers**
  1. Validate polymerization (IR or NMR)
  2. Attempt binding with titanium through solid state reaction (grinding, milling, pressing, heating)
  3. Test for hydrogen absorption (Sieverts)

- **$Ca(BH_4)_2$**
  1. Analyze neat compound for comparison (XRD, DSC, IR, Sieverts)
  2. Combine with additives (grinding, pressing, milling, or solvent dispersion)
  3. Thermally decompose then attempt to reform $Ca(BH_4)_2$ (Sieverts)

- **Absorbing alloys as additives**
  1. Sorption characteristics of alloy must be well characterized (Sieverts)
  2. Combination with commercial alanates and borohydrides (grinding, pressing, chemical dispersion)
  3. Test for changes in decomposition, reformation of complex – alloy mixture

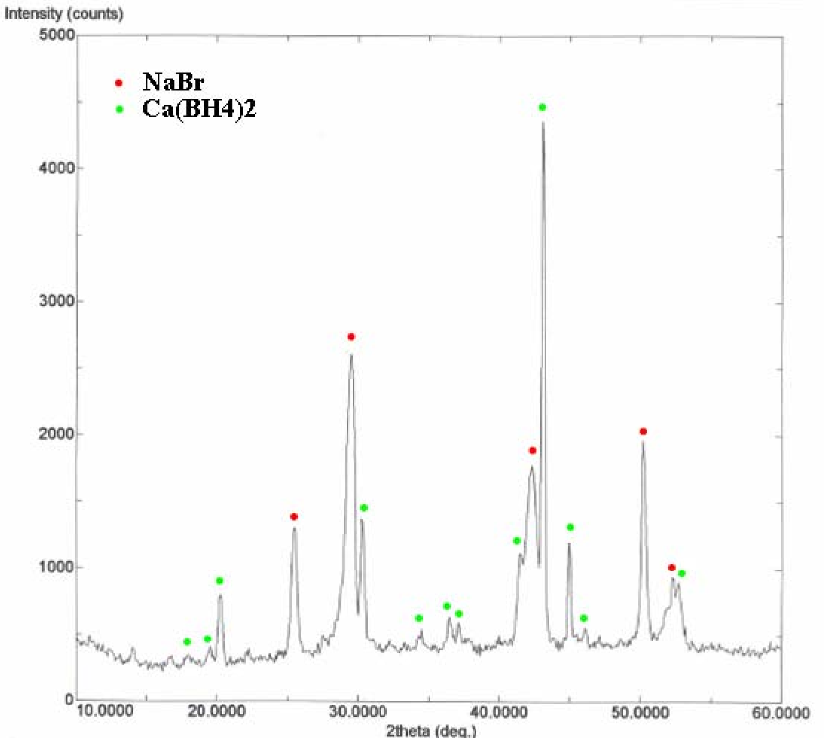
TECHNICAL ACCOMPLISHMENTS

BULK MATERIALS

$Ca(BH_4)_2$ - Solid State Ion Exchange Synthesis

$$2NaBH_4 + CaBr_2 \rightarrow Ca(BH_4)_2 + 2NaBr$$

- We successfully demonstrate that this reaction will proceed in solid state
- Materials are ground together, and pressed into a pellet in a hydraulic press
- The pellet is heated under vacuum or inert atmosphere at 220ºC for 48 hours
- Products need additional processing to isolate $Ca(BH_4)_2$



XRD of reaction products

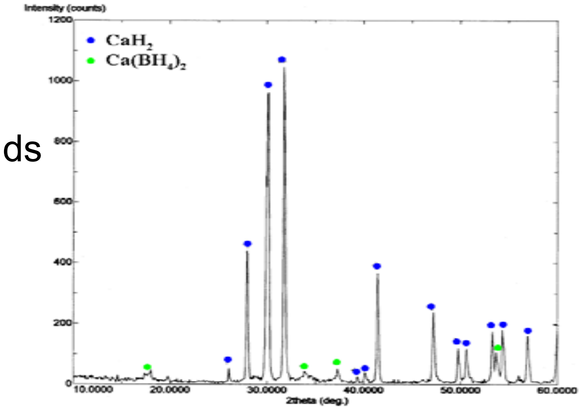
TECHNICAL ACCOMPLISHMENTS

BULK MATERIALS

$Ca(BH_4)_2$ - Other Synthesis Methods Attempted

Borane Solution / Hydride Type Reactions

$$CaH_2 + 2Et_3N \cdot BH_3 \xrightarrow{reflux} Ca(BH_4)_2 + 2Et_3N$$



- Despite numerous reaction conditions variations attempted, yields were much too low in all cases to extract $Ca(BH_4)_2$
- Reaction proceeds, but stalls out leaving mostly un-reacted CaH_2 (XRD of typical products shown)

Solvent Ion Exchange

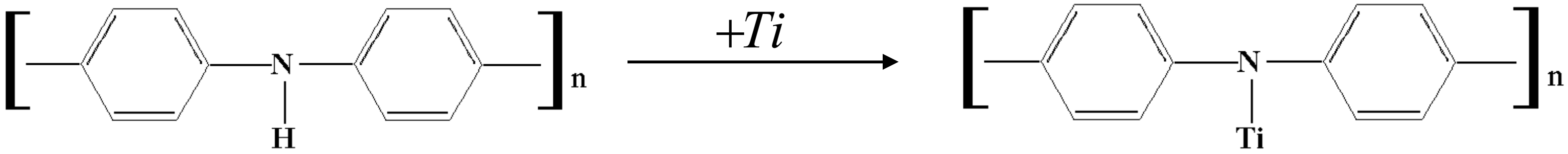
$$2XBH_4 + CaY_2 \xrightarrow{reflux} Ca(BH_4)_2 + 2XY; \quad X = Li, Na \quad Y = Cl, Br$$

- Solvents tried include: Et_2O, Pyridine, (1,4)Dioxane, THF
- Ca(BH4)2 has a high affinity for ethers in which it is soluble and reacts with some solvents (notably pyridine) under certain conditions
- Some of these reactions are convenient for obtaining Ca(BH4)2 in solution, but isolating pure solid is problematic in all cases

TECHNICAL ACCOMPLISHMENTS

BULK MATERIALS

Titanium Decorated Polyaniline



- Theoretically predicted[1] to absorb 4.1% H_2 by weight at 30 bar at 25ºC
- Synthesis attempted by grinding powdered polyaniline with titanium nanoparticles then pressing into a pellet, and regrinding
- IR spectra revealed removal of the N-H bond suggesting possible binding of Titanium
- *Zero absorption*[2] was measured for this material up to 130 bar at 25ºC both before and after high temperature hydrogen soak

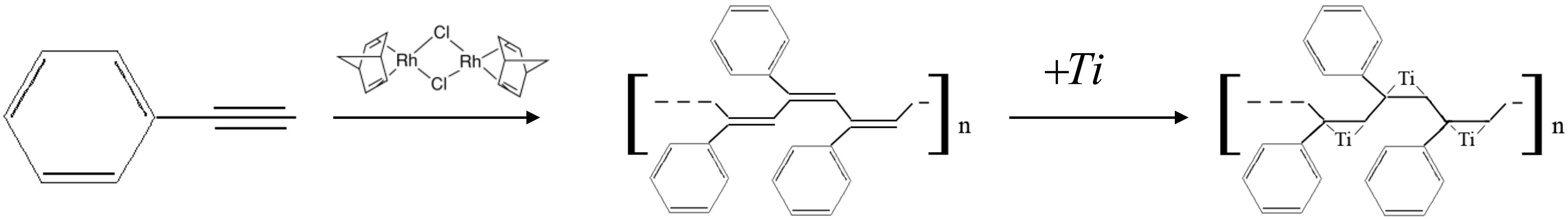
[1]Lee, H.; Choi, W. I.; Ihm, J. "Combinatorial Search for Optimal Hydrogen-Storage Nanomaterials Based on Polymers" *Phys. Rev. Let.* **97,** *2006. 056104*

[2] Our preliminary results had indicated some absorption for this material, but this was discovered to be a data artifact caused by a faulty valve.

TECHNICAL ACCOMPLISHMENTS

BULK MATERIALS

Titanium Decorated Polyphenylacetylene



- Polyacetylene is predicted[1] to absorb a large amount of H_2 by weight at 30 bar at 25ºC when titanium is adjoined to the double bond
- Because of the likely difficulty with synthesizing polyacetylene, we selected polyphenylacetylene as a substitute to test the titanium bond concept.
- Polymerization of phenylacetylene by a rhodium catalyst was verified by IR and NMR by verification of the double bond
- Titanium bonding was attempted by grinding with titanium nanoparticles, pressing, and heating at 200ºC for 48 hours, followed by grinding again
- *Zero absorption* was measured for this material up to 130 bar at 25ºC both before and after high temperature hydrogen soak

[1]Lee, H.; Choi, W. I.; Ihm, J. "Combinatorial Search for Optimal Hydrogen-Storage Nanomaterials Based on Polymers" *Phys. Rev. Let.* ***97,*** *2006. 056104*

[2] Our preliminary results had indicated some absorption for this material, but this was discovered to be a data artifact caused by a faulty valve.

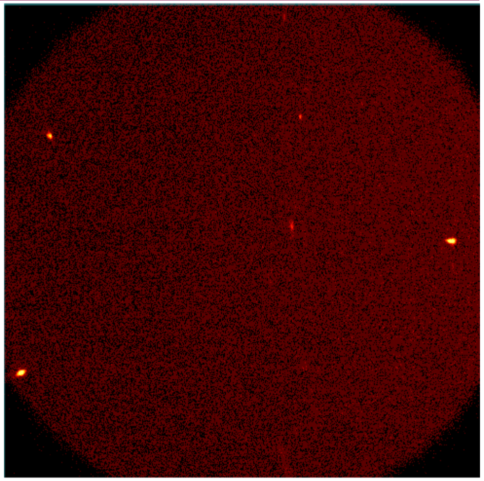
TECHNICAL ACCOMPLISHMENTS

BULK MATERIALS

$LaNi_5$ Alloy - Initial Characterization

As Alloyed (commercial)

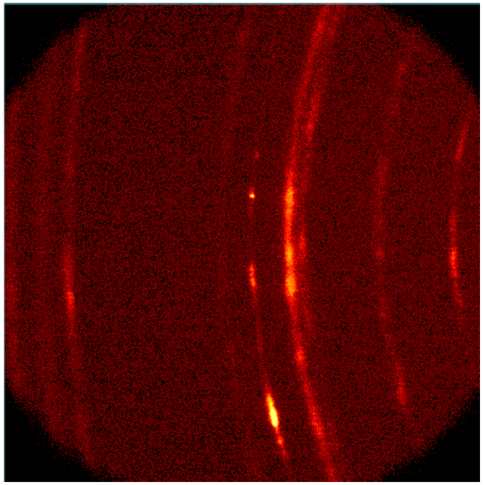
• (right) The raw XRD data from our area detector. Theta increases to the left. Note the high crystallinity.



• (left) High crystallinity is again evident from the large grains of alloy.

After Activation and First H_2 Aborption

• (right) Although the crystal structure type is not changed, the lattice dilations from absorption cause fractures and the material turns into finer particulates.



• (left) The internal stresses of lattice dilation caused by the hydrogen have pulverized the alloy into a fine powder. No mechanical processing was performed.

TECHNICAL ACCOMPLISHMENTS

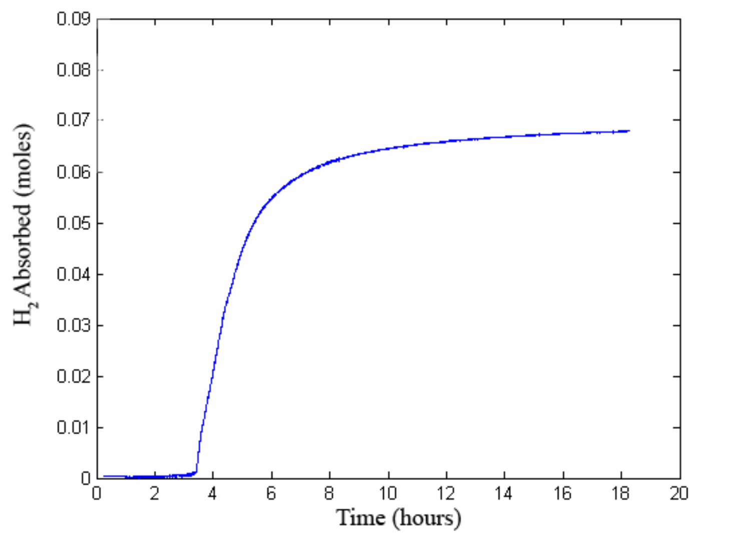
BULK MATERIALS

$LaNi_5$ Alloy - Initial Characterization

$$LaNi_5 + 3H_2 \rightarrow LaNi_5H_6$$

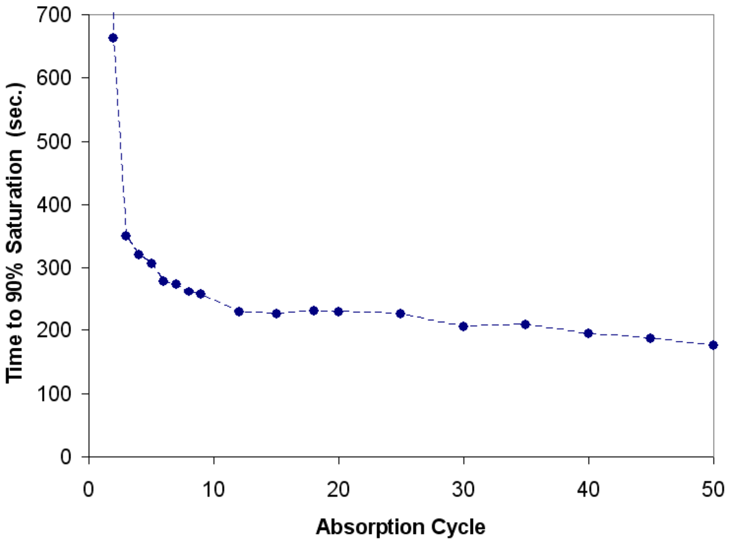
The initial absorption rate after activating the alloy is extremely sluggish, but increases rapidly as the alloy is cycled

Initial H_2 absorption



Initial absorption of $LaNi_5$ after chemical activation. The sample was held at a constant 500 psia at room temperature overnight.

H_2 Absorption Time Vs cycle



Absorption rates increase with initial cycling of $LaNi_5$. Conditions for absorption cycles were 145 psia of H_2 constant and 33ºC. Dehydriding occurred at 80ºC.

FUTURE WORK

BULK MATERIALS

Calcium Borohydride Decomposition and Reformation Study

$$Ca(BH_4)_2 \xleftrightarrow{catalyst} CaB_6 + 2CaH_2 + 10H_2$$

Maximum Reversible H_2 by weight: 9.6%

Minimum Theoretical Release Temperature[1]: 94ºC

Interest: Among the few borohydride reactions that has been proven to be reversible,[2,3] this reaction has some of the most favorable thermodynamic characteristics.

Method: We wish to test additives which have yet to be applied to this material that have documented catalytic effects[4]. We also wish to elucidate the mechanism which allows the borohydride to reform from gaseous hydrogen. (Sieverts, XRD, DSC, IR)

[1] Ozolins, V.; Majzoub, E. H.; Wolverton, C. "First-Principles Prediction of Thermodynamically Reversible Hydrogen Storage Reactions in the Li-Mg-Ca-B-H System" *JACS* **131** 2009. 230-237

[2] Ronnebro, E.; Majzoub, E. H. "Calcium Borohydride for Hydrogen Storage: Catalysis and Reversibility" *J. of Phys. Chem.* **111**, 2007. 12045-12047

[3] Kim, H. J.; Jin, S.; Jae-Hyeok, S.; Cho, Y. W. "Reversible Hydrogen Storage in Calcium Borohydride $Ca(BH_4)_2$" *Scripta Materialia* **28**, 2008. 481-483

[4] Zaluska, A.; Zaluski, L. "New Catalytic Complexes for Metal Hydride Systems" *J. of Alloys and Compounds* **404**, 2005. 706-711

FUTURE WORK

BULK MATERIALS

DFT Predicted Destabilized Borohydride Reaction

$$5Ca(BH_4)_2 + 2LiBH_4 \rightarrow Li_2B_{12}H_{12} + 5CaH_2 + 13H_2$$

Maximum Reversible H_2 by weight: 6.7%

Minimum Theoretical Release Temperature[1]: 83ºC

Interest: This reaction, predicted to occur recently by Ozolins *et al.* is (to our knowledge) yet untested. The reaction temperature is slightly below that of pure $Ca(BH_4)_2$

Method: Initially the reaction will be treated as simply as possible: commercial reagents simply ground or milled together. Focus will be on validation of the reaction conditions and byproducts. (Sieverts, XRD, DSC, IR)

[1] Ozolins, V.; Majzoub, E. H.; Wolverton, C. "First-Principles Prediction of Thermodynamically Reversible Hydrogen Storage Reactions in the Li-Mg-Ca-B-H System" *JACS* **131** 2009. 230-237

FUTURE WORK

BULK MATERIALS

Absorbing Alloy Interactions with Reversible Hydride Complexes

Alloy: $LaNi_5$

Reactions: I. $NaAlH_4 \leftrightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2 \leftrightarrow NaH + Al + \frac{3}{2}H_2$

II. $Ca(BH_4)_2 \xleftrightarrow{catalyst} CaB_6 + 2CaH_2 + 10H_2$

Interest: $LaNi_5$ is selected because of the wealth of information available, its quick kinetics, and room temperature absorption of hydrogen. We have characterized it well, and can differentiate between effects caused by the alloy and competing effects.

Method: We will initiate study on I. which is a reversible, well known system. This will make it easier to see what effects the alloy has using different incorporation techniques. We will then move to higher capacity reversible systems with more unknowns such as II. (Sieverts, XRD, DSC, IR)

SUMMARY

BULK MATERIALS

- **More rigorous examination of the polymers we have prepared has shown that they do not absorb hydrogen. The reason for this is unclear, as direct evidence of titanium bonding was never demonstrated.**

- **We intended to begin decomposition / reformation studies with Ca(BH4)2 over the last 6 months. Delays with chemical suppliers made this infeasible. We initiated some work on chemical synthesis of this compound instead until the delays subside.**

- **Curious about potential interactions between alloy systems and complexes, we initiated study of the well known hydrogen absorption alloy $LaNi_5$. We have characterized the neat alloy sufficiently to proceed to combination.**

OBJECTIVES

NANOSTRUCTURES

- Investigation of **maximum hydrogen storage capacity, thermal stability, and adsorption/desorption kinetics of thin films and nanostructures of magnesium (model system), magnesium alanate, and magnesium borohydride** for hydrogen storage.

- Utilization of **glancing angle deposition (GLAD)** technique for the growth of **nanorod arrays of magnesium (Mg) as a model system, magnesium alanate ($Mg(AlH_4)_2$), and magnesium borohydride ($Mg(BH_4)_2$).**

- Utilization of a new **quartz crystal microbalance (QCM)** gas chamber system for the dynamic investigation of **maximum hydrogen storage capacity and adsorption/desorption kinetics of the nanostructures produced with nanograms measurement sensitivity.**

- Investigation of **effect of catalyst** on hydrogen adsorption/desorption properties of magnesium, magnesium alanate, and magnesium borohydride. Possible **catalyst materials that we plan to incorporate are Pt, Ti, Ni, Pd, and V.**

MILESTONES

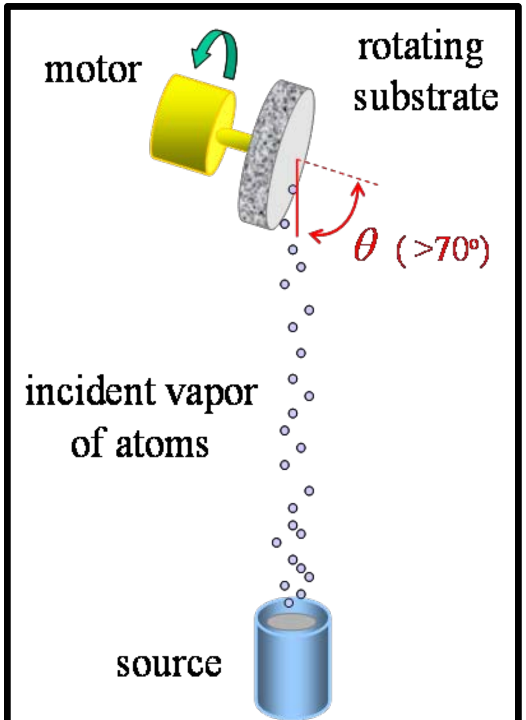
NANOSTRUCTURES

Month/Year	Milestone or Go/No-Go Decision
July-08	**Milestone:** Fabrication of nanostructures in the shapes of vertical “nanoblades” using GLAD approach. Material: Mg as model system.
Sep-08	**Milestone:** Finished the set-up and up-gradation of a QCM gas chamber with an RGA attachment for the dynamic measurement of hydrogen adsorption/desorption kinetics, thermal stability, and oxidation properties of nanostructured coatings.
Sep-08	**Milestone:** Finished further investigation of thermal stability and oxidation properties of thin films and nanostructures produced by GLAD. Material: Mg as model system.
Dec-08	**Milestone:** Using new QCM set-up, started to obtain hydrogen storage capacity and adsorption/desorption properties of thin films and nanostructures produced by GLAD. Material: Mg as model system.
May-09	**Milestone:** Will start the investigation of hydrogen adsorption/desorption properties of magnesium borohydride and alanate thin films and nanostructures produced by GLAD. Materials: $Mg(AlH_4)_2$ and $Mg(BH_4)_2$

APPROACH

NANOSTRUCTURES

Glancing Angle Deposition (GLAD)



- Large surface-to-volume ratio ,
- Control of crystal orientation,
- Lower oxidation rate,
- Porosity allows for volumetric changes

- **Quartz Crystal Microbalance (QCM) method for the investigation of hydrogen storage, thermal stability, and oxidation properties of nanostructures and thin films produced**

APPROACH

NANOSTRUCTURES

Nanostructured Materials to be Studied

Nanostructured Material	Hydrogen Storage (wt %)	Decomposition T (°C)
$Mg(AlH_4)_2$ Magnesium Alanate [1]	**9.3**	**200**
$Mg(BH_4)_2$ Magnesium Borohydride [2]	**14.9**	**320**
Mg Magnesium [3]	**7.6**	**300**

Model System ← Mg

+

Catalyst Incorporation

Pt
Ti
Ni
Pd
V

[1] Fichtner etal. Journal of Alloys and Compounds 356-357: 418-422, 2003.
[2] Zuttel *et al.* Renewable Energy 33(2): 193-196, 2007; Zuttel *et al*. Journal of Alloys and Compounds 446-447: 315-318, 2007.
[3] Sakintuna et al. Int. J. of Hydrogen Energy 32: 1121-1140, 2007; Li *et al.* J. Am.. Chem. Soc. 129: 6710-6711, 2007; Wagemans *et al.* J. Am.. Chem. Soc. 127: 16675-16680, 2005.

TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

UP-GRADIATION of a QUARTZ CRYSTAL MICRO-BALANCE (QCM) SYSTEM with RESIDUAL GAS ANALYZER (RGA) DEVELOPED IN-HOUSE

DOE funded

SPECIFICATIONS

- Operating Pressure Range: 10^{-4}– 50 bars
- Gasses available: Hydrogen, argon, oxygen
- Stable Temperature Range: room temperature – 500 ^{o}C
- Nanostructure/thin film coating surface area: ~ 1 cm^2
- Mass Sensitivity: down to 0.001 ng/cm^2
- Capable of measuring two sample at a time
- In-situ Residual Gas Analysis (RGA) analysis capability

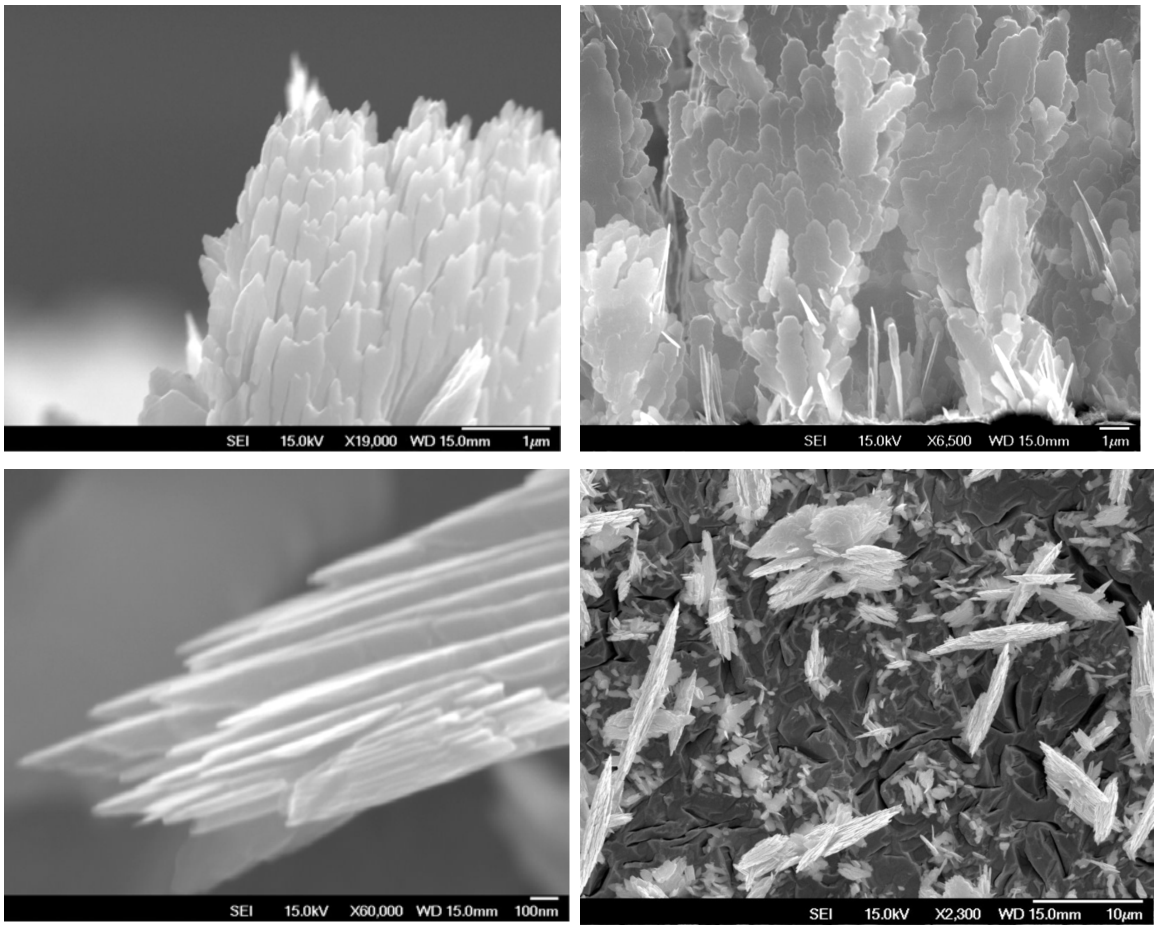
COMMERCIAL DEVICE:
Not Available
OUR COST: ~ $ 10,000

TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

Cross-Section SEM Images

Top-View SEM Images



Deposition conditions:

GLAD Thermal Evaporation

Tilt angle: 80^o

Pressure: $7.5 * 10^{-6}$ mbar

Rotation: 1 RPM

Substrate : QCM crystal

Length of nanoblade-trees: ~ 7 μm

Thickness of nanoblade-leafs: ~30nm

Mg Nanoblades by GLAD

TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

Development of Experimental Procedures for QCM Hydrogen Storage Measurements

- ***Procedure 1:*** A single QCM crystal is used for reference and storage measurements. Experimental procedure is performed first on an empty QCM crystal for baseline measurements followed by thin film or nanostructure coating on the same crystal, and then by measuring the QCM data of the coated crystal.

  Pros & Cons: 1. Temperature and pressure effects on measurements are minimized, 2. Longer sample preparation

- ***Procedure 2:*** Dual QCM crystals are used one for reference and the other coated one for storage measurements.

  Pros & Cons: 1. Quick sample preparation, 2. Bare and coated crystals might have different response to the changes in temperature and pressure, that can lead to limitations in dynamic adsorption/desorption analysis

- ***Procedure 3:*** Dual QCM crystals, which are both coated with thin film or nanostructures, are used for simultaneous measurement of H2 storage values of two samples. Comparison of crystals' initial and final frequencies at the same temperature (e.g. after heating followed by cooling) are used in order to determine storage levels in nanostructures and thin films. A multi cycle storage process can also be performed in order to calculate total H2 storage that occurs between two temperature points. For the first cycle, storage is measured by heating from room temperature to a set temperature and cooling back to RT. Then in the following cycle, crystal is heated to a higher temperature then in the first cycle and cooled back to RT again in order to calculate the H2 storage gain occurred in the second cycle.

  Pros & Cons: 1. Quick sample preparation and ability to measure two samples at a time, 2. Only storage values can be measured at this time; kinetic adsorption/measurements needs some theoretical temperature effect corrections, which are currently under investigation

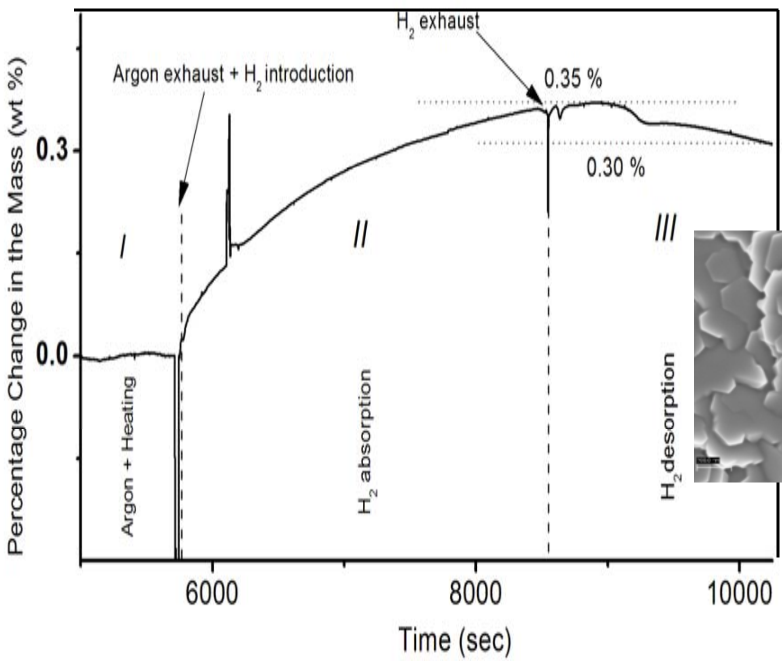
TECHNICAL ACCOMPLISHMENTS

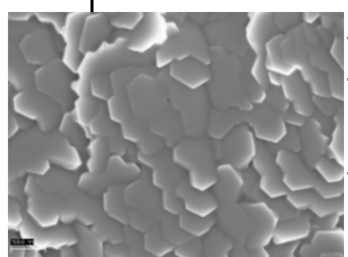
NANOSTRUCTURES

QCM Hydrogen Storage Measurements

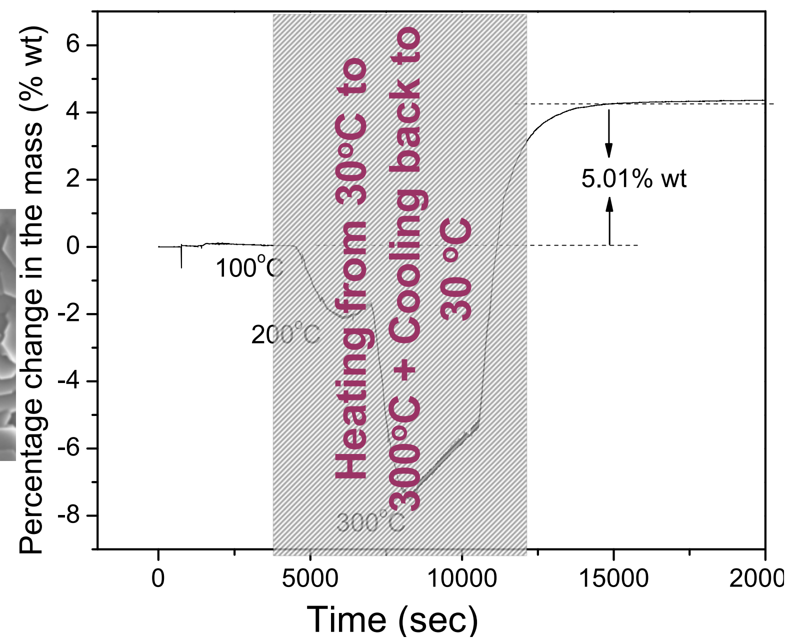
Mg Thin Film at 30 bar H_2

Procedure 1





Procedure 2



Low Temperature Mg Thin film Storage @ 30°C -100 °C → 0.35 wt %

Mg Thin Film Storage @ 30°C-300 °C → 5.01 wt %,

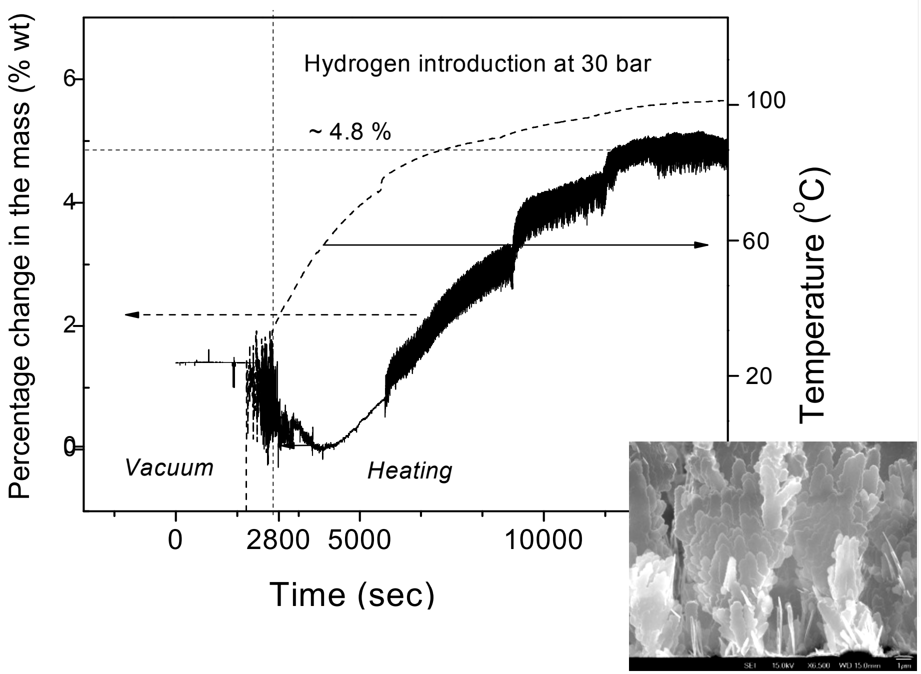
TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

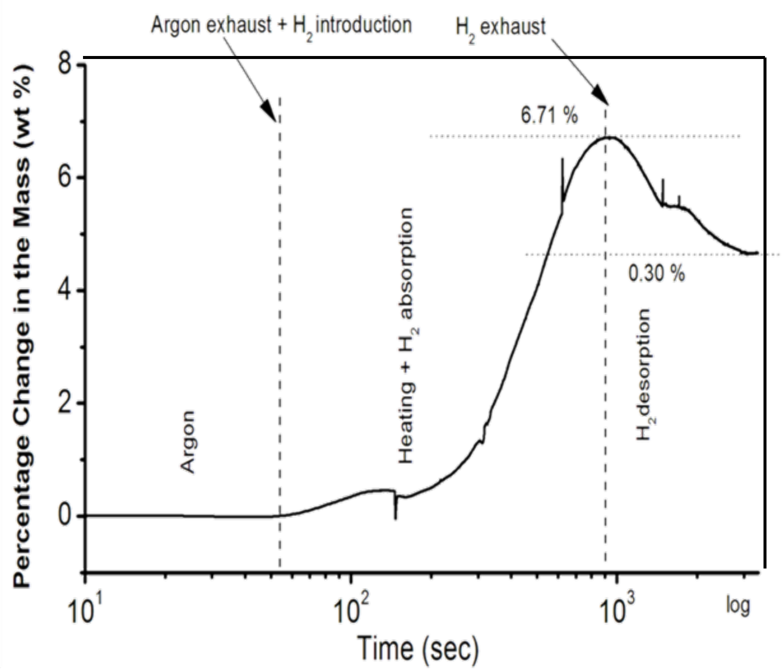
QCM Hydrogen Storage Measurements

Mg Nanoblades at 30 bar H_2

Procedure 2



Procedure 1



Low Temperature Mg Nanoblade Storage @ 30°C-100 °C → 4.8 wt %

Low Temperature Mg Nanoblade Storage @ 30°C -150 °C → 6.71 wt %

TECHNICAL ACCOMPLISHMENTS

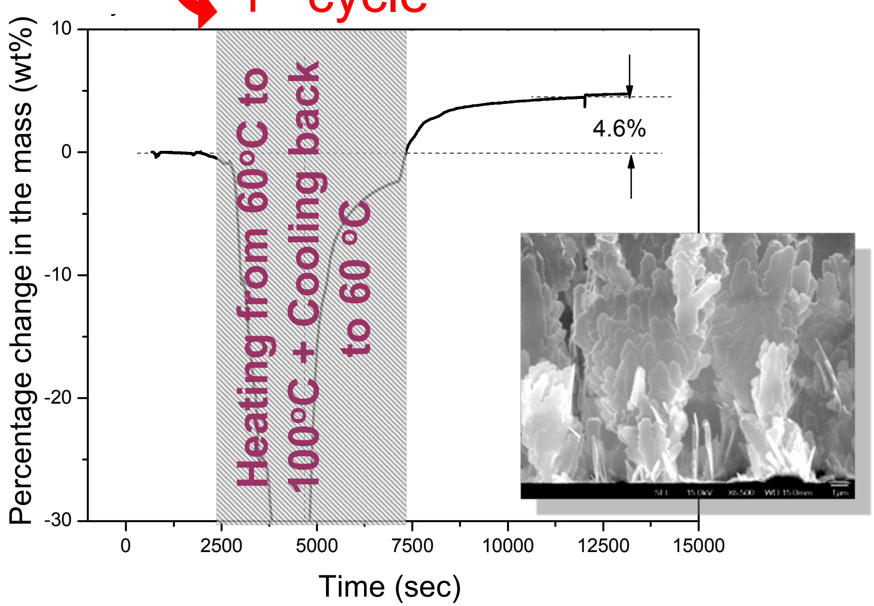
NANOSTRUCTURES

QCM Hydrogen Storage Measurements

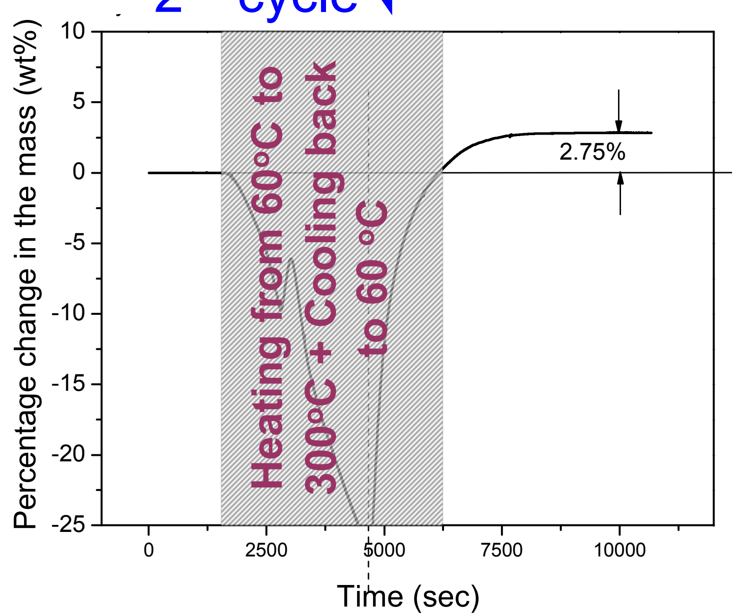
Mg Nanoblades at 30 bar H_2, Procedure 3

60°C → 100 °C → 60°C → 300 °C → 60 °C

1st cycle



2nd cycle



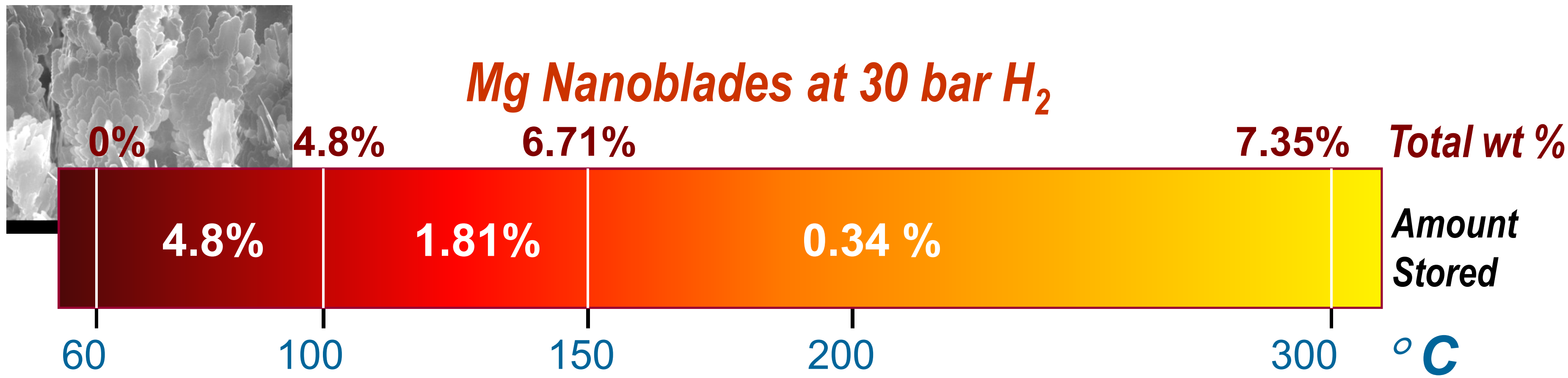
Low Temperature Mg Nanoblade Storage @ 60°C -100 °C → 4.60 wt %

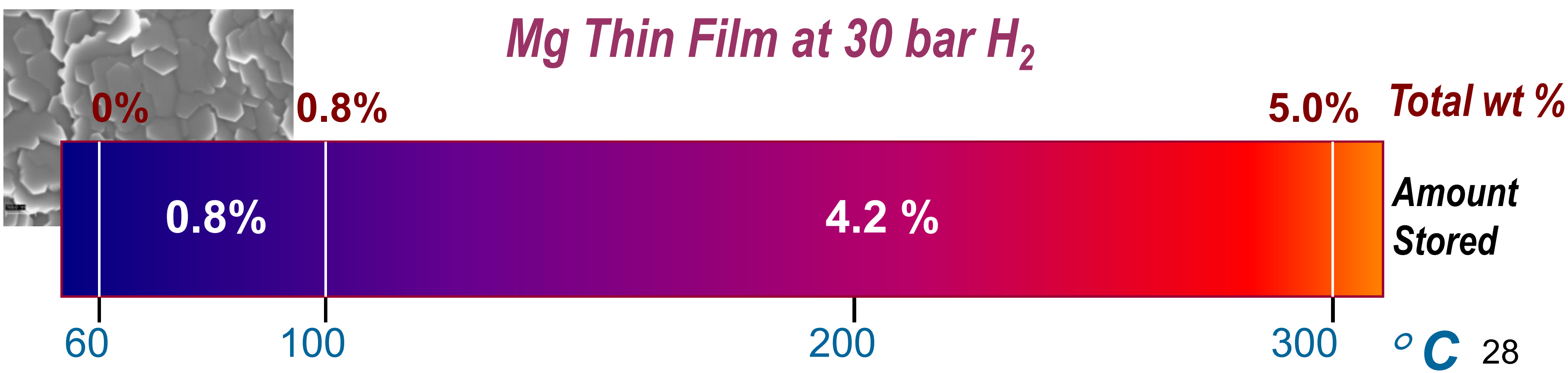
Total Mg Nanoblade Storage @ 60°C-300 °C → 7.35 wt % *(=4.6 wt% 1st cycle +2.75 wt % 2nd cycle)*

TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

Hydrogen Storage in Mg Thin Film and Nanoblades at different Temperature Intervals

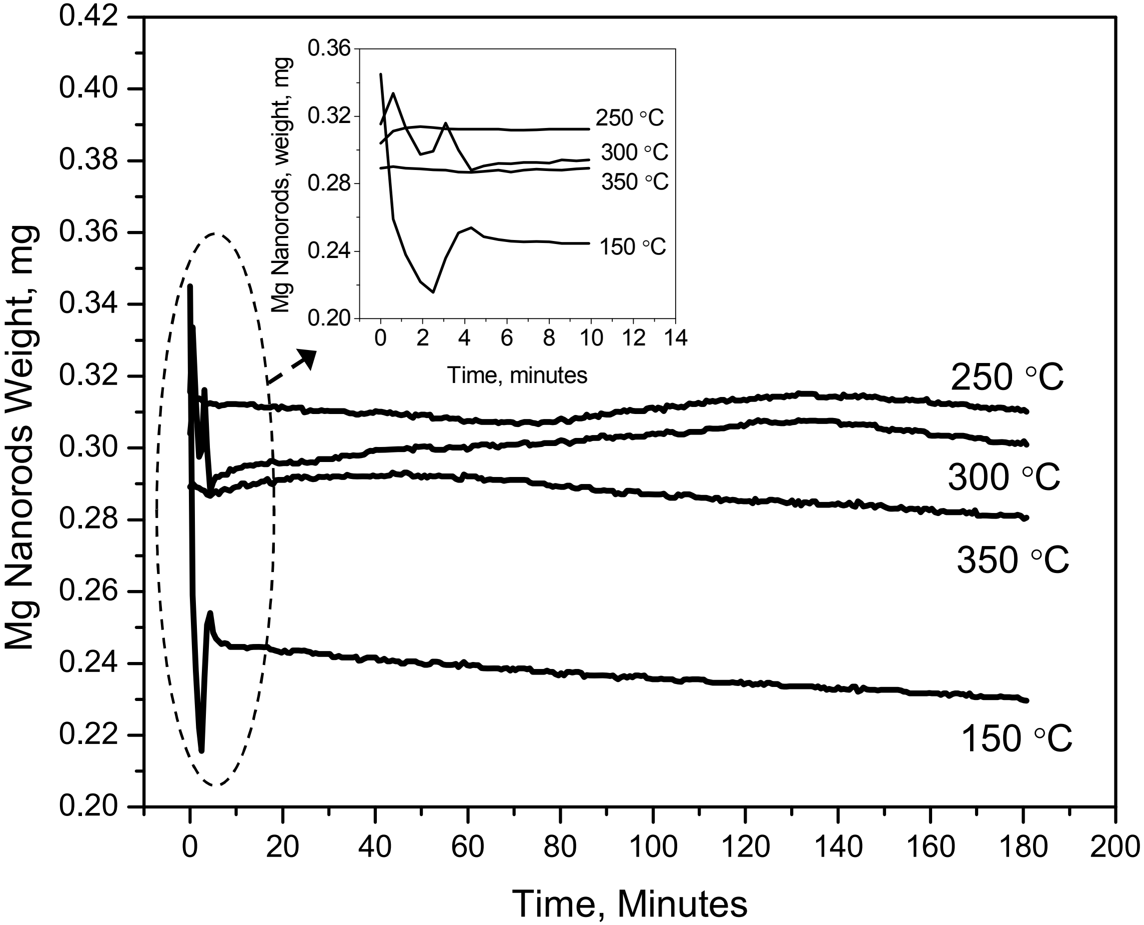


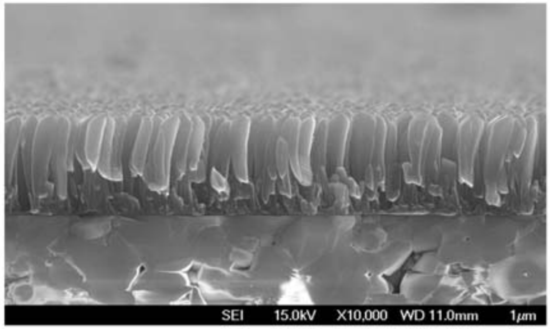


TECHNICAL ACCOMPLISHMENTS

NANOSTRUCTURES

Thermal Stability and Oxidation of Mg Nanorods under Atmospheric Conditions: Isothermal TGA results





A cross-section image of Mg nanorods sputter deposited on an alumina substrate

Reduced oxidation and enhanced evaporation in Mg nanorods at temperatures T<150 °C; enhanced oxidation at T>150 °C needs to be accounted for during low pressure hydrogen adsorption/desorption studies

SUMMARY

NANOSTRUCTURES

- **Glancing angle deposition (GLAD) technique was utilized for the growth of nanostructured arrays in the shapes of vertical nanoblades and nanorods.**
- **Mg nanostructures as model material system: Hydrogen storage capacity, adsorption/desorption kinetics, thermal stability, and oxidation properties have been studied.**
- **Significant increase in low temperature H_2 storage values (e.g. ~4.8 wt% @ 100 ^{o}C) has been observed for Mg nanostructures compared to Mg thin films (e.g. ~0.8 wt% @ 100 ^{o}C) .**
- **A new quartz crystal microbalance (QCM) system was developed and upgraded for the kinetic investigation of hydrogen storage capacity and adsorption/desorption kinetics properties of nanostructured and thin film coatings.**
- **Has started investigating magnesium borohydride and alanate for GLAD nanofabrication and hydrogen storage studies.**

FUTURE WORK

NANOSTRUCTURES

Study of hydrogen storage capacity & kinetics

- **Thin films and nanostructures of magnesium alanate and borohydride,**
- **Effect of catalysis,**
- **Effect of nanostructure size, shape & separation,**
- **Nanoblades and nanorod arrays of Mg as a model system.**