



# 2005 DOE Hydrogen Program Review

Fuel Cell and Hydrogen Research  
University of South Florida

Presented By: Lee Stefanakos

May 24, 2005

**Project ID # ST 10**

## ***Participants***

### **University of South Florida**

- J. Bumgarner (COT), M. Calves (COT), C. Ferekides (EE), B. Krakow (CERC), Arun Kumar (ME), Ashok Kumar (ME), L. Langebrake (COT), D. Morel (EE), G. Moore (CERC), S. Onishi (COT), M. Smith (CERC), S. Srinivasan (CERC), E. Stefanakos (EE), J. Wolan (ChE), 5 graduate students, 1 undergraduate.

### **University of Florida**

- Y. Goswami (ME), L. McElwee-White (Chemistry), B. Lear (ME), S. Ingley (ME), H. Weaver (Chem Eng), D. Deshpande (ME), S. Vijayaraghavan, (ME), Nikhil Kothurkar (ME), 6 graduate students

### **University of Central Florida**

- Clovis Linkous (FSEC), Nahid Mohajeri (FSEC), Colin Bateman (FSEC)

## ***Projects***

### ***Hydrogen Storage (ST 10)***

- Transition Metal Hydrides (USF and UF)
- Nano-structured Materials (USF)
- Hydrogen Storage Components (USF)

### ***Hydrogen Production (STP2)***

- Solar Photoelectrochemical (USF)
- Solar Photocatalytic (USF)
- Thermochemical Cycle (UF)
- Biomass Gassification (UF)
- Solid State Ionic Conductors (USF)

### ***Fuel Cells (STP2)***

- Modified Engin. Polymers (FSEC)
- PEM Fuel Cell Research (UF)
- PEM Fuel Cell Research (USF)

# Overview



## Timeline

- Oct 2004 to May 2008
- 16% Complete

## Budget

- Total project funding
  - DOE \$4.8M
  - Contractor \$1.25M
- Funding
  - FY04 \$1.9M
  - FY05 \$2.9M

## Barriers

- H<sub>2</sub> Storage
  - DOE 3.3.4.2.1 (A-D)
    - Cost, weight and volume, efficiency, durability, hydrogen capacity and reversibility, Physisorption and Chemisorption mechanisms

## Partners

- University of Hawaii, Dept of Chemistry
- Hy-Energy, Inc
- NNRC, University of South Florida
- NREL
- SWRI

# H<sub>2</sub> Storage Objectives



## Development of H<sub>2</sub> storage systems by:

### Approaches

1. Carbon doped nanocomposite materials
2. Nanoscale hydride material
3. Nanostructured film for storing hydrogen

### Targets

- 6 wt% and \$4/kWh
- Fast Absorption-desorption kinetics
- Cycle life ~1000

# Approach 1

## Carbon doped nanocomposite materials

- **Matrix Material:**

- Conducting Polymer (Polyaniline)

- Can be ionized at low temperatures and electrical potential.

- **Catalysts:**

- Metal Oxides, e.g.  $\text{SnO}_2$

- Increase the catalytic reaction to ionize the hydrogen

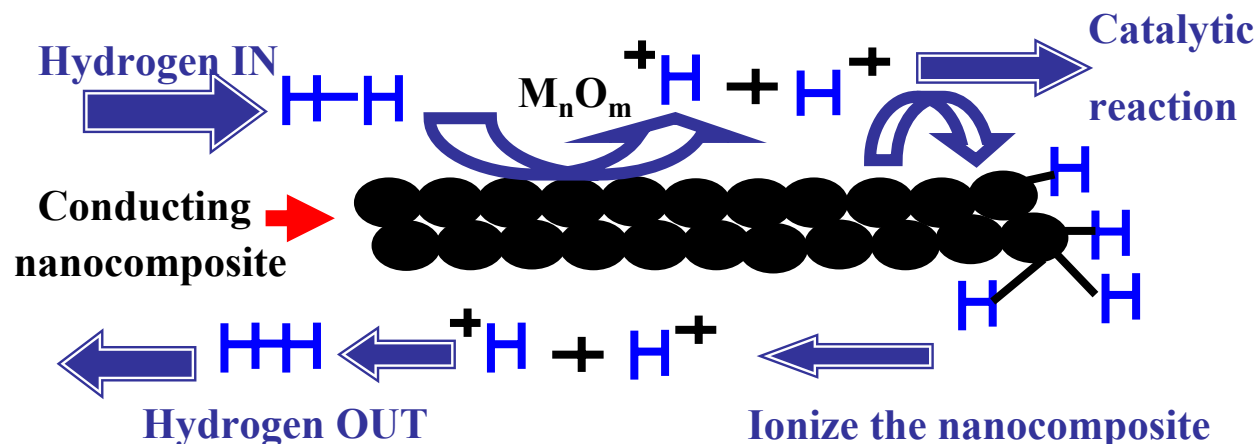
- **Dopants:**

- Carbon Nanotubes (SWCNT and MWCNT)

- Improve the porosity and interaction sites of nanocomposite material with hydrogen molecules.

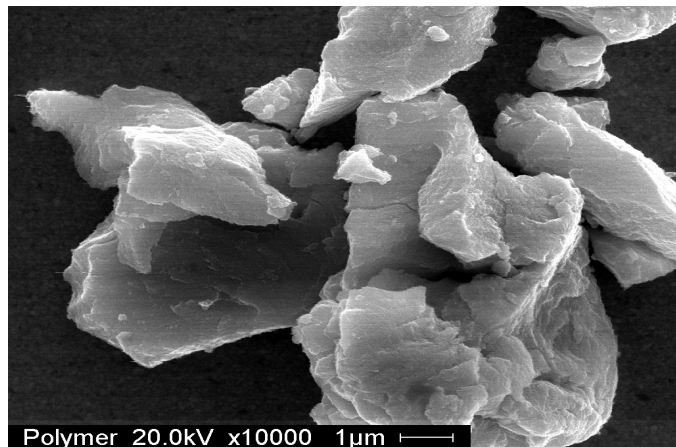
- Modified Fullerene (With  $\text{Na}^+$  and  $\text{K}^+$ )

- Improve hydrogen adsorption at low temperature



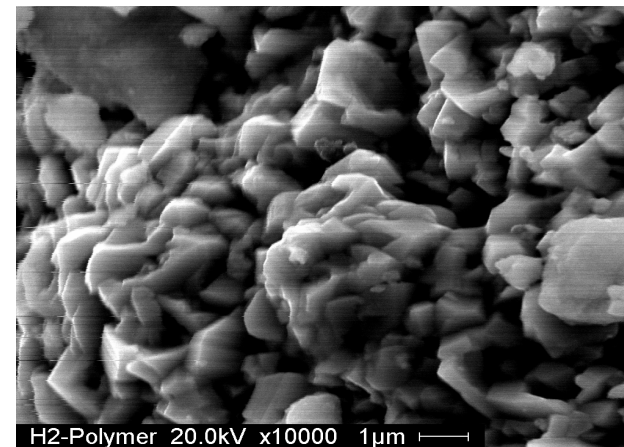
# Accomplishments/Progress

## (Approach 1) Carbon doped nanocomposite materials



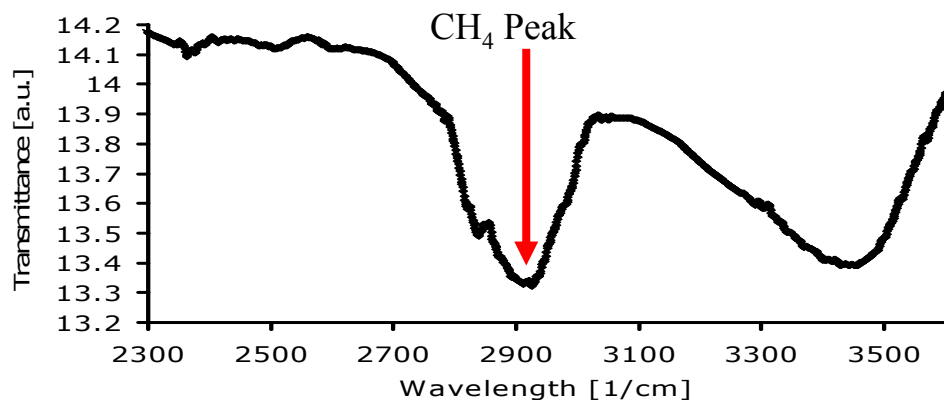
Before H<sub>2</sub> Sorption:

- Small surface area
- Crystalline structure



After H<sub>2</sub> Sorption:

- High surface area
- Bubble-like structure



**FTIR** spectrum indicating chemical bonding of hydrogen

# Accomplishments/Progress (cont'd)

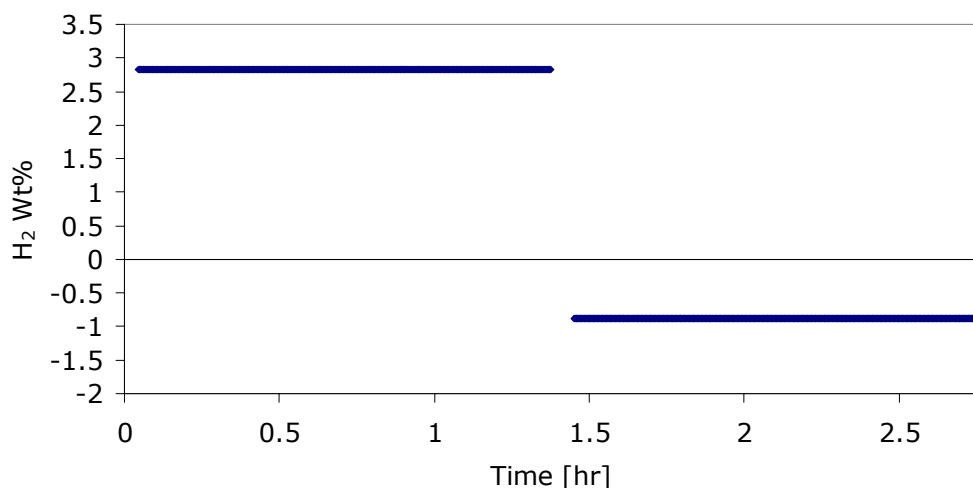
## (Approach 1) Carbon doped nanocomposite materials



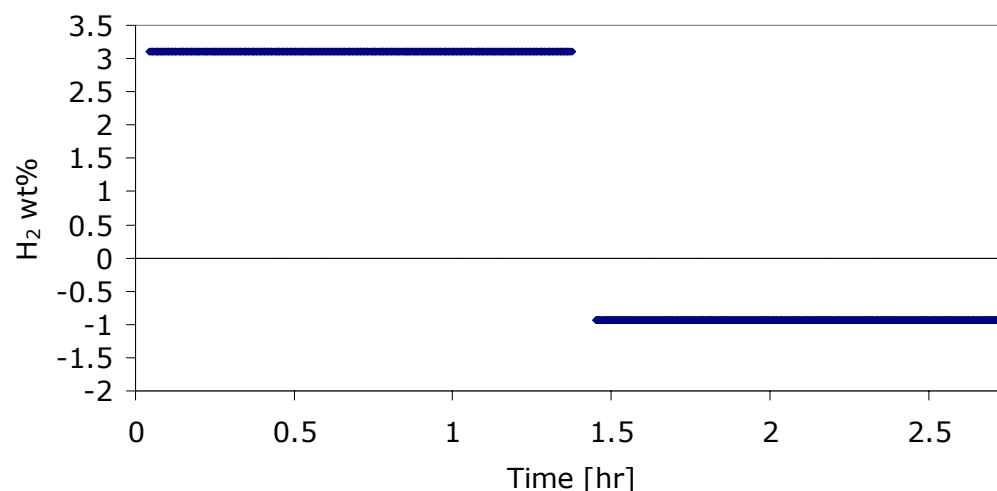
### PCT (Hydrogen Sorption) Analysis of Nanocomposite Material

Conditions: Temperature = 90 °C, Pressure = 40 bar

**Hydrogen Sorption Nanocomposite**



**Hydrogen Sorption Aligned Nanocomposite**



#### Standard Nanocomposite:

- 2.8 wt% H<sub>2</sub> Adsorption
- 0.88 wt% H<sub>2</sub> Desorption

#### Aligned Nanocomposite:

- 3.1 wt% H<sub>2</sub> Adsorption
- 0.94 wt% H<sub>2</sub> Desorption

Both figures indicate rapid sorption kinetics

Full H<sub>2</sub> recovery expected with ionization of material

# Future Plans



## (Approach 1) Carbon doped nanocomposite materials

- Remainder of FY 2005:
  - Study of effect of temperature, pressure, CNT concentrations
  - Ionization of nanocomposite as a pathway to increase H<sub>2</sub> sorption to meet DOE targets
  
- FY 2006:
  - Study of effect of various conducting polymers as matrix material for improvement in hydrogen sorption and cyclic stability
  - Cyclic study of materials for cost, packing and reliability analysis of materials



# Responses to Previous year Reviewer's Comments

## (Approach 1) Carbon doped nanocomposite materials



- 1. Volumetric density for high surface area materials is important and should not be ignored in the desire to achieve high gravimetric densities.**

Yes, we are planning to analyze the volumetric density in order to understand the adsorption and desorption of hydrogen in nanocomposite materials.
- 2. USF should calculate maximum expected capacity to see whether 2010 and 2015 targets can be met. The entire system needs to be considered including the tank and the H<sub>2</sub> that must be burned to release the hydrogen from the nano-composites.**

Yes, we are in the process of calculating and optimizing methods to release the hydrogen from the nanocomposite and obtain maximum system performance
- 3. The results must include a mass balance to be credible (i.e. polymer mass loss needs to be studied and no basis for 2,000 cycle stability was clear.**

We are presently studying polymer mass loss using volumetric/gravimetric analysis and GC-MS to see what products are coming out during the adsorption and desorption of hydrogen. Moreover the 2000 cycles proposed for reversibility of the hydrogen adsorption and desorption is based on the fact that conducting polymers can undergo 2000 reversible redox cycles.
- 4. The postulated desorption mechanism needs clarification.**

The desorption mechanism is basically based on (a) the physical release of hydrogen entrapped in the porous structure when the polymer is heated, and (b) the release of hydrogen when the conducting polymer is ionized by the application of a small voltage to the composite material (due to the dissociation of bonds between conducting polymer composite material and hydrogen).

# Approach 2

## Nanoscale transition hydride materials



**Mechanochemical Synthesis  
(Reactive Gas Milling)**

**Catalytic Doping  
(Ti- butoxide,  $\text{TiCl}_3$ ,  $\text{TiF}_3$ )**

**Nanoscale Transition  
Metal Hydride ( $n\text{-Mg}_2\text{FeH}_6$ )**

### Why Nanoscale Transition Metal Hydride?

- Minimizes the H-diffusion path
- Enhances the rate of charging and discharging
- Optimizes grain size or particle size
- Improves surface and bulk sorption
- Improves cyclic life performance

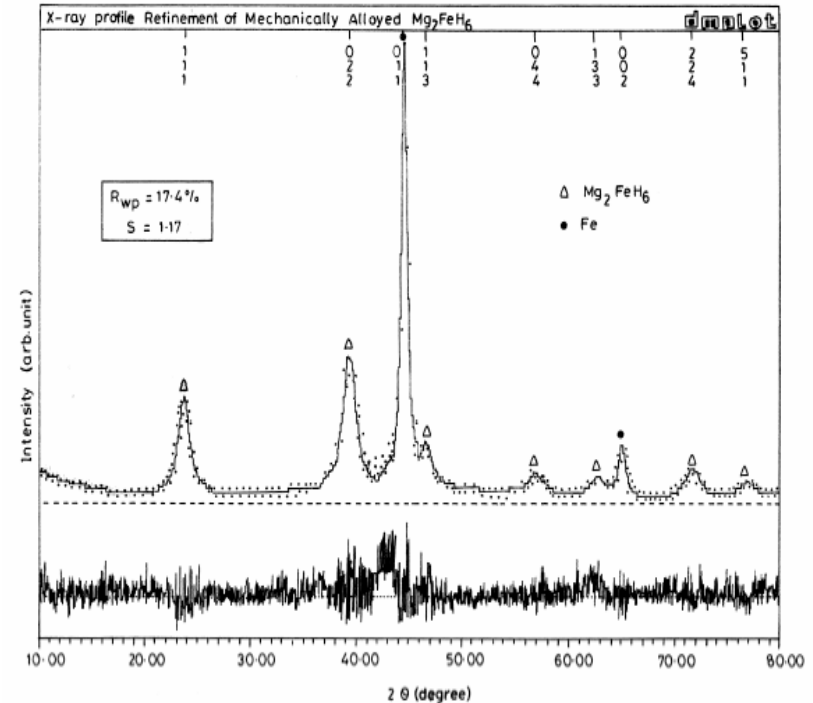
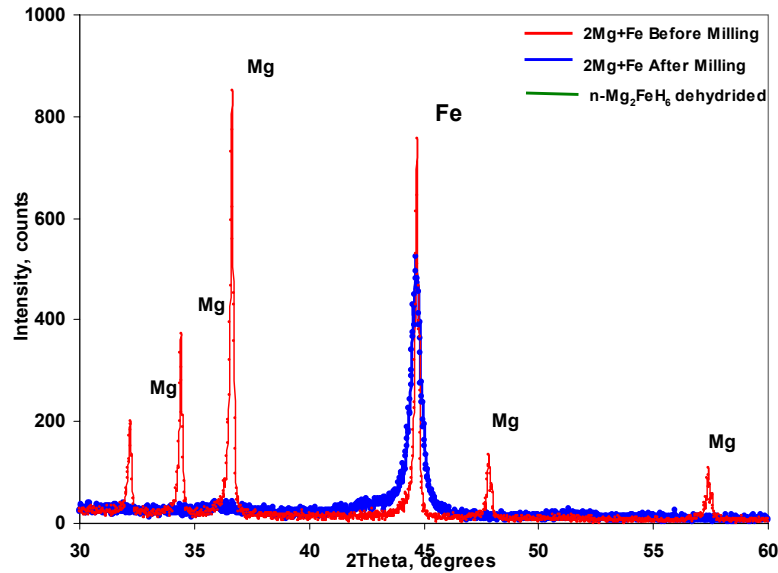
**Structural / Microstructural/Thermal/PCI  
Characterization (XRD, TEM, SEM, EDS,  
DSC, TGA, PCT)**

**Lattice Substitution  
( $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{K}^+$ )**

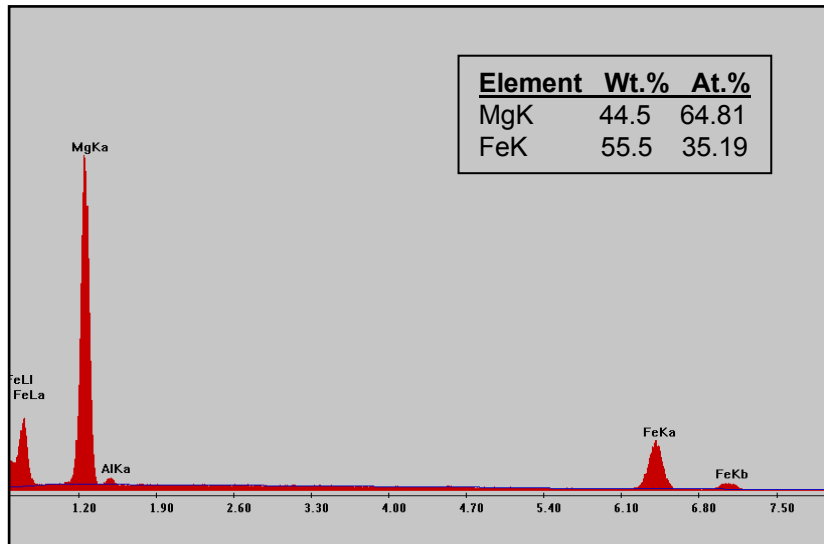
# Accomplishments/Progress

(Approach 2) Nanoscale hydride materials

## PXD and SEM/EDS of n-Mg<sub>2</sub>FeH<sub>6</sub>



Decreasing crystallinity with milling duration



- Appearance of n-Mg<sub>2</sub>FeH<sub>6</sub> phase after hydrogenation
- n-Mg<sub>2</sub>FeH<sub>6</sub> (a=0.644686 nm) ; phase proportion 63%

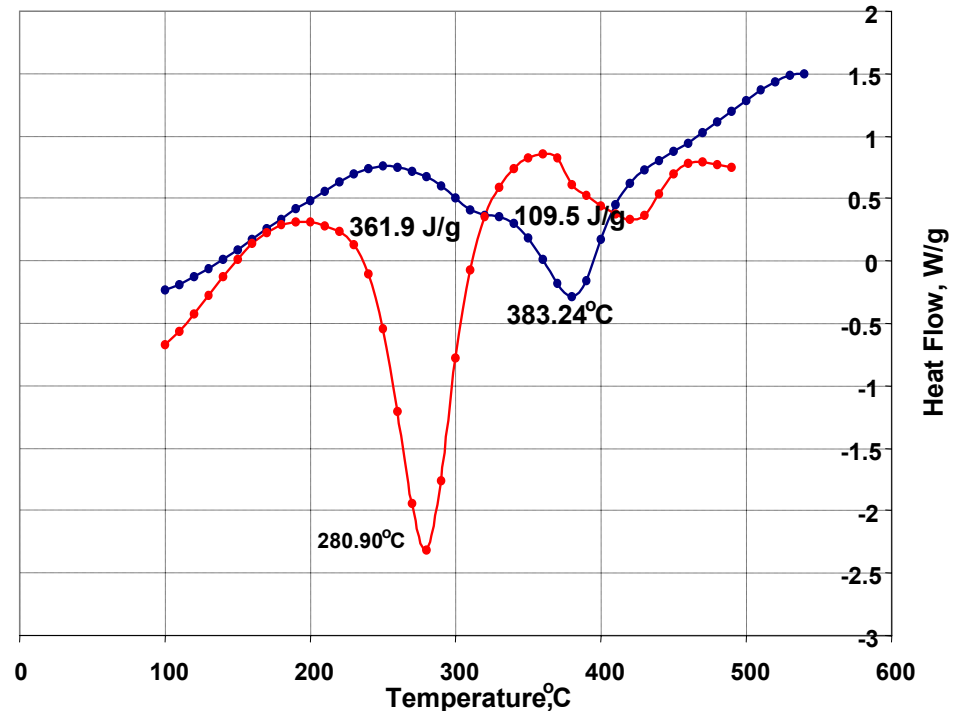
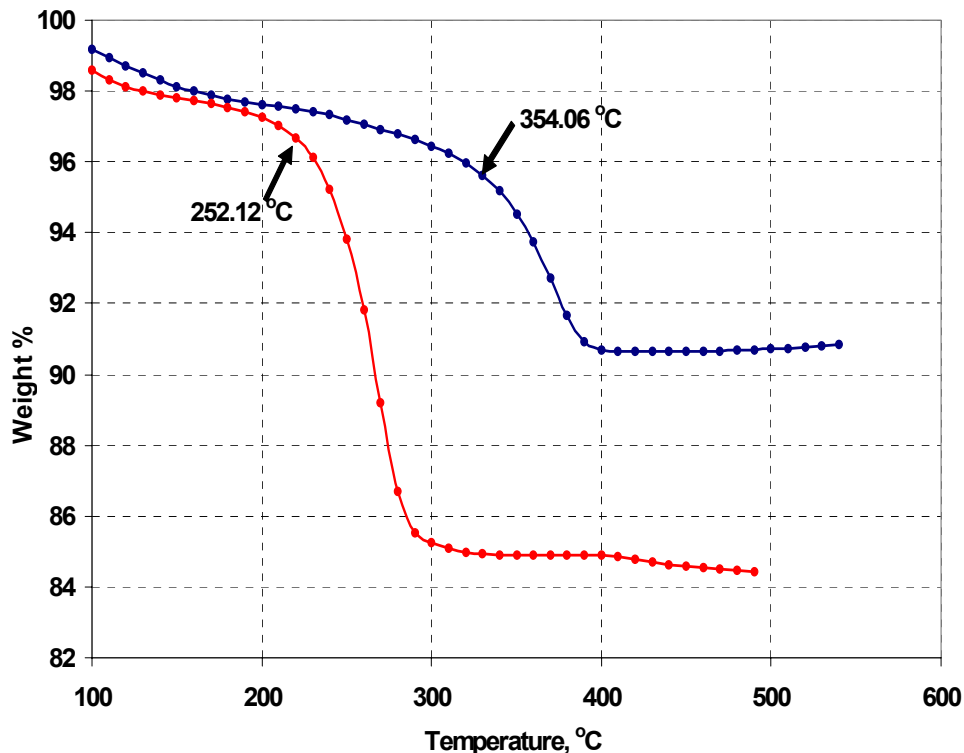
# Accomplishments/Progress (cont'd)

## (Approach 2) Nanoscale hydride materials



### DSC and TGA Analysis of Unmodified and Li-modified n-Mg<sub>2</sub>FeH<sub>6</sub>

● - Mg<sub>2</sub>FeH<sub>6</sub>    ● - Li Modified Mg<sub>2</sub>FeH<sub>6</sub>



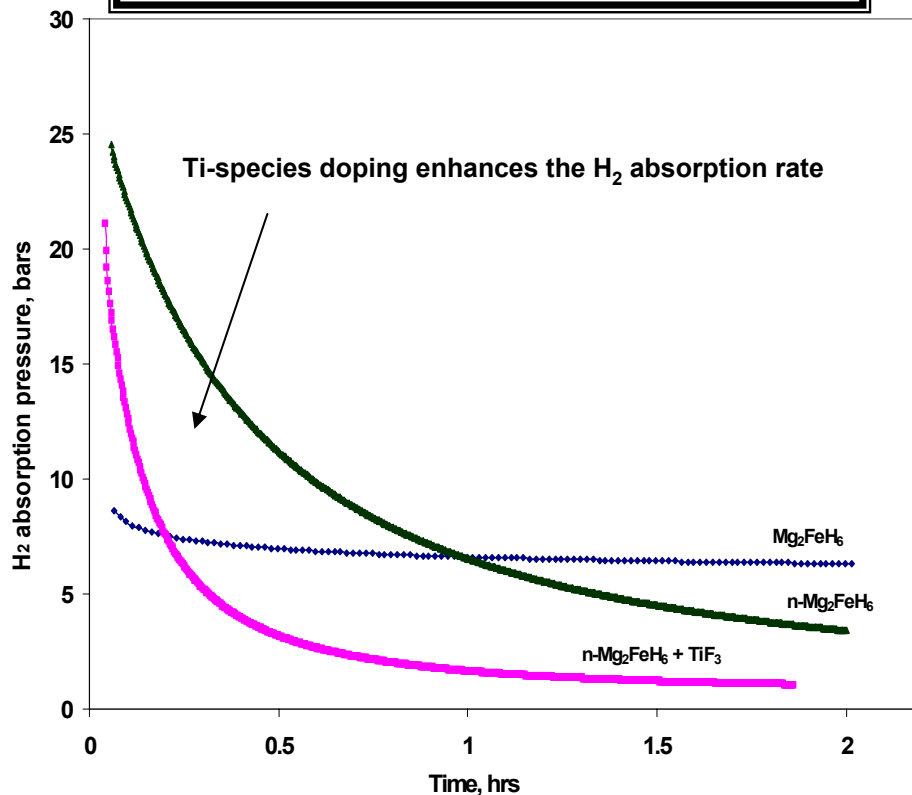
- Li- modification reduces the temperature of sorption by 100 °C
- Hydrogen weight percent stored is doubled at lower temperature
  - This is probably due to the lattice modification of n-Mg<sub>2</sub>FeH<sub>6</sub>

# Accomplishments/Progress (cont'd)

## (Approach 2) Nanoscale hydride materials

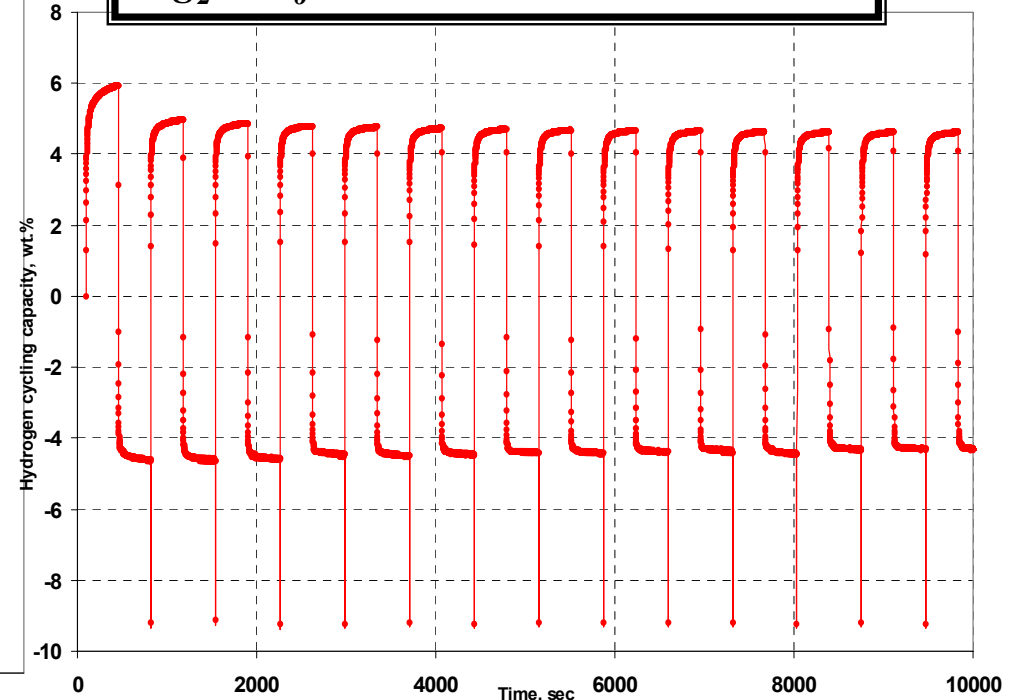


*Absorption Kinetics of Mg/Fe at 300 °C*



Rate of absorption increases by nanoscaling and catalytic doping

*Absorption/desorption cycling of n-Mg<sub>2</sub>FeH<sub>6</sub> at 300 °C*



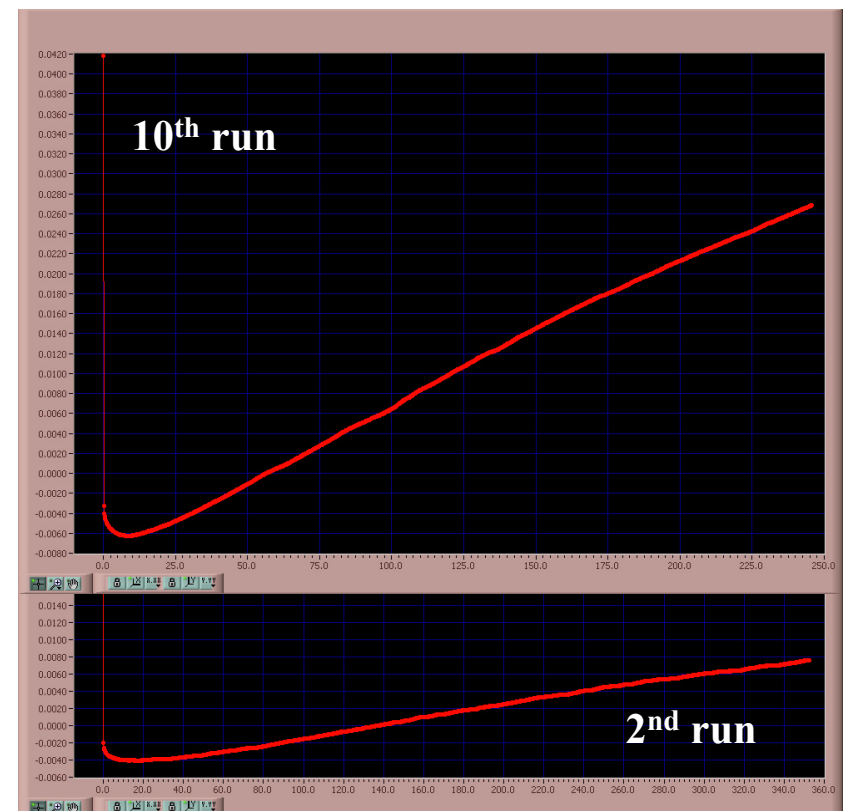
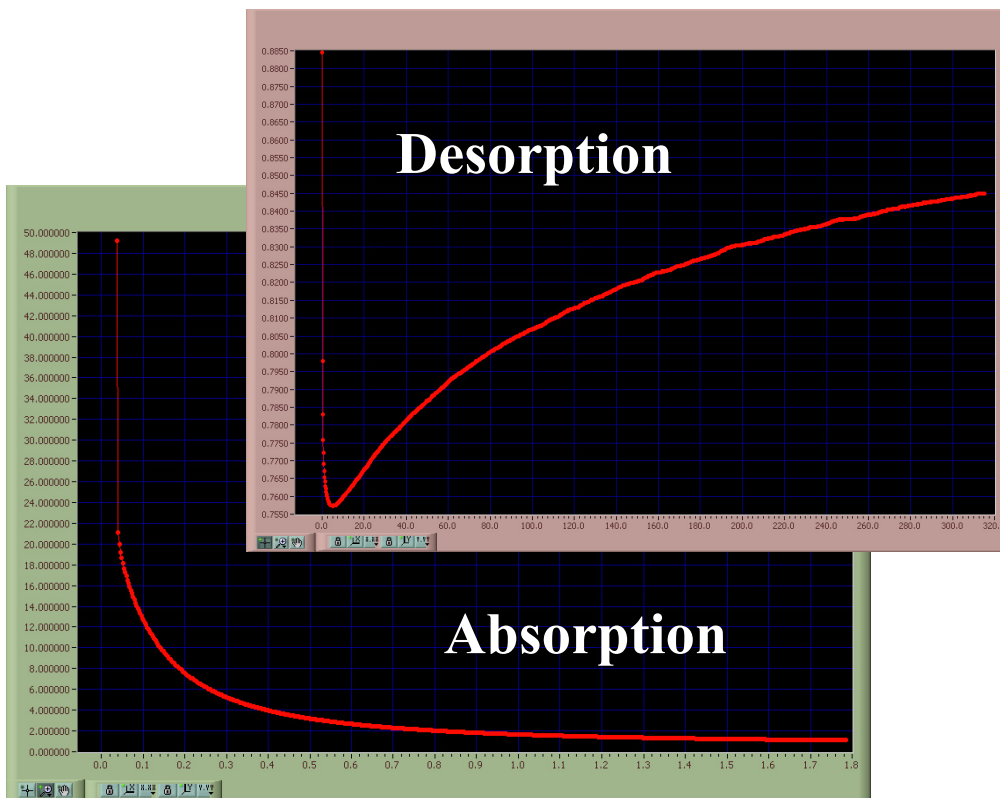
Highly reversible H-capacity of 5.0 wt.% achieved in the initial 10 cycles

# Accomplishments/Progress (cont'd)

## (Approach 2) Nanoscale hydride materials



### Kinetics of $\text{TiF}_3$ doped $\text{Mg}_2\text{FeH}_6$



With the doping of Ti-species, we see enhancement in the hydrogen absorption and desorption rate

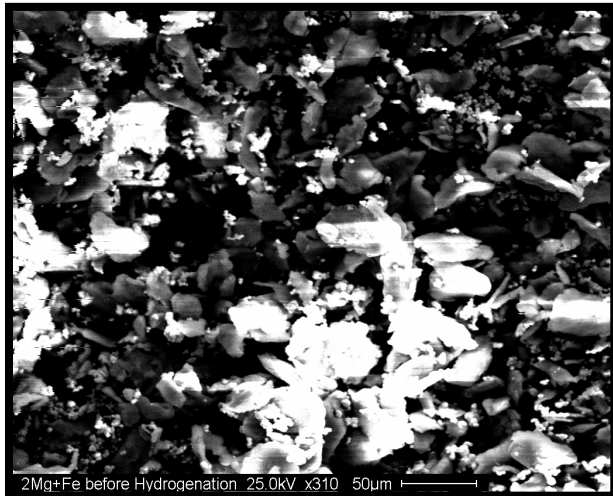
Increase of H-capacity with cycling



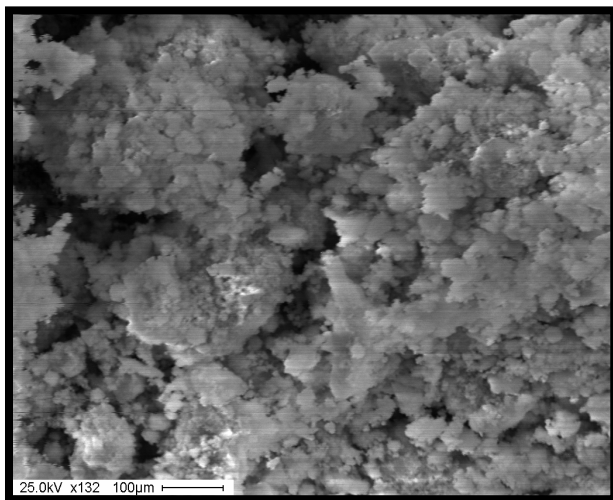
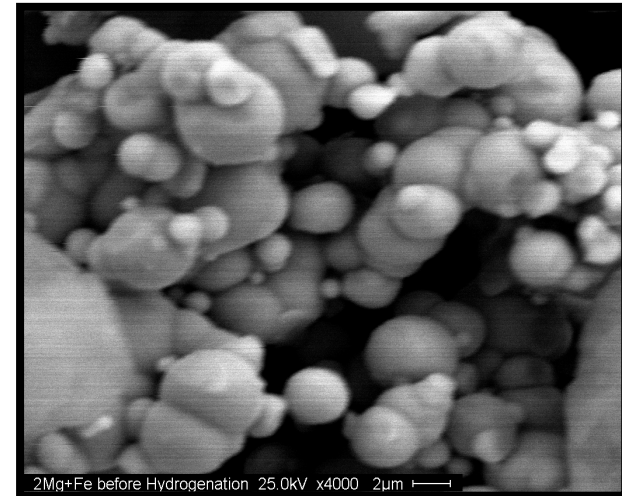
# Accomplishments/Progress (cont'd)

## (Approach 2) Nanoscale hydride materials

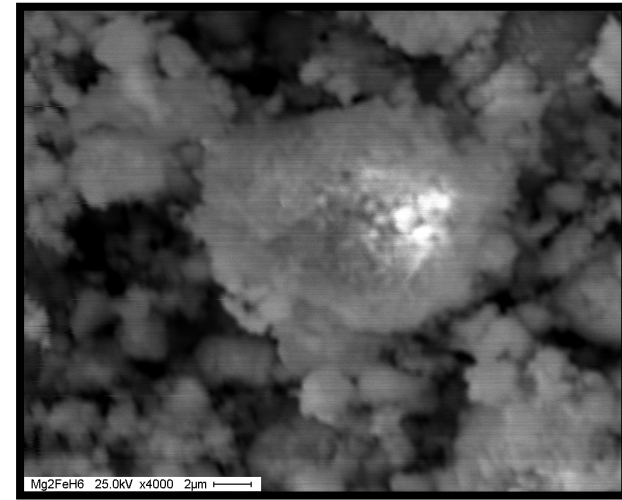
### SEM-Image of n-Mg<sub>2</sub>FeH<sub>6</sub> prepared from Ball milling and Hydrogen Cycling



Before  
Hydrogenation



After  
Hydrogeantion



- Hydrogen charging/discharging makes the surface more porous, uniform and spongy

# Future Plans



## (Approach 2) Nanoscale transition hydride materials

- Develop new complex hydrides to achieve reversible capacity above 6 wt.% at  $T < 100\text{ }^{\circ}\text{C}$
- Identify, synthesize, and evaluate new complex hydrides, such as  $\text{Zn}(\text{BH}_4)_2$ , as a potential system.
- Develop chemical synthesis for an amide system through solvation and reprecipitation of  $\text{LiH}/\text{LiNH}_2$ .



# Responses to Previous year Reviewer's Comments (Approach 2) Nanoscale hydride materials



## 1. **Traditional hydrides unlikely to meet anything but the 2005 goals**

Destabilized hydrides may lead to better performance than the conventional hydrides for achieving DOE's 2010 technical targets. We have proposed to investigate new complex chemical hydride systems for high reversible hydrogen storage capacity exceeding 6.0 wt.% at  $T < 100\text{ }^{\circ}\text{C}$ . This will be our future plan.

## 2. **$\text{Mg}_2\text{FeH}_6$ is "well-plowed" ground. What's new?**

Nanoscale  $\text{Mg}_2\text{FeH}_6$  is not yet reported. The new aspect in the present study is catalytic doping and lattice modification, which enhances the kinetics and reduces the operating temperature of  $\text{Mg}_2\text{FeH}_6$ .

Investigators are aware and up to date in the literature survey on the proposed hydrogen storage system. Go/No-Go decision is critically reviewed by the investigators based on the results from this proposed work.

## 3. **Methods to improve performance by catalyst doping is not well understood by the presenter and catalysts seem to be essentially based on weight or benefits in the alanate system, which is functionally quite different.**

Catalyst doping with the n- $\text{Mg}_2\text{FeH}_6$  certainly enhances the kinetics of absorption/desorption at lower temperatures as evidenced from the accomplishments in this work

# Responses to USCAR Tech Team

## (Approach 2) Nanoscale hydride materials



1. **Capacity of the materials is less than 6 wt% and cannot meet 6 wt% system target.**

No-Go decision is being considered for the present system. A new complex hydrogen storage system,  $\text{Zn}(\text{BH}_4)_2$  has been identified. The amide system ( $\text{LiH-LiNH}_2$ , 10 wt. %) will also be investigated. Efforts will be made to evaluate the new systems for effective reversible H-capacity.

2. **Some concern was expressed over slow kinetics. Too much heat is required for desorption which reduces the system efficiency.**

Efforts have been made to reduce the decomposition temperature and improve the kinetics by Li modification on the host lattice structure of  $\text{Mg}_2\text{FeH}_6$  and catalytic (Ti-species) doping

3. **USF should communicate with SwRI for testing requirements and procedures.**

Yes, USF is communicating with SWRI for testing requirements and procedures

# Approach 3

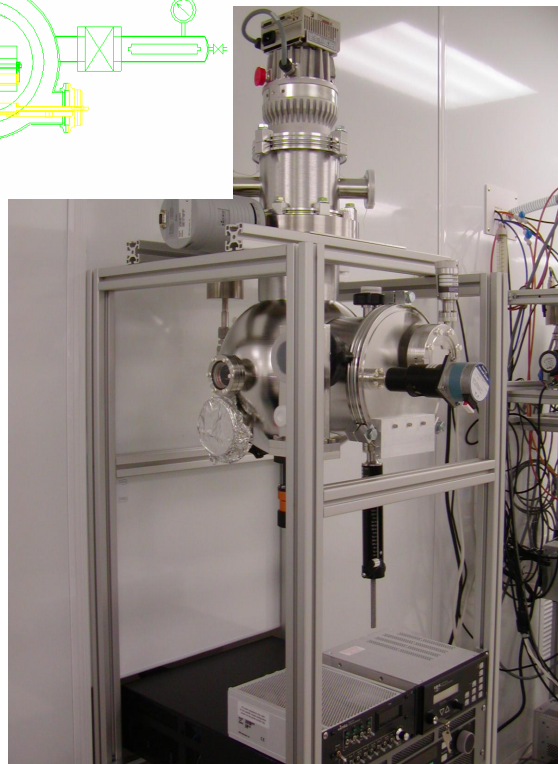
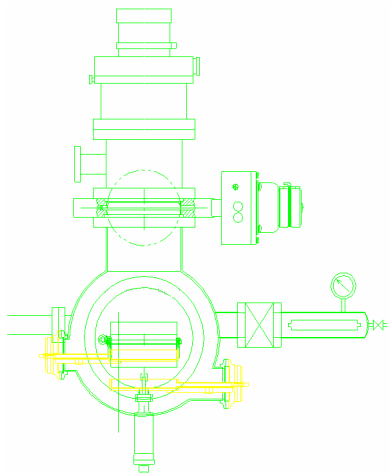
## Nanostructured film



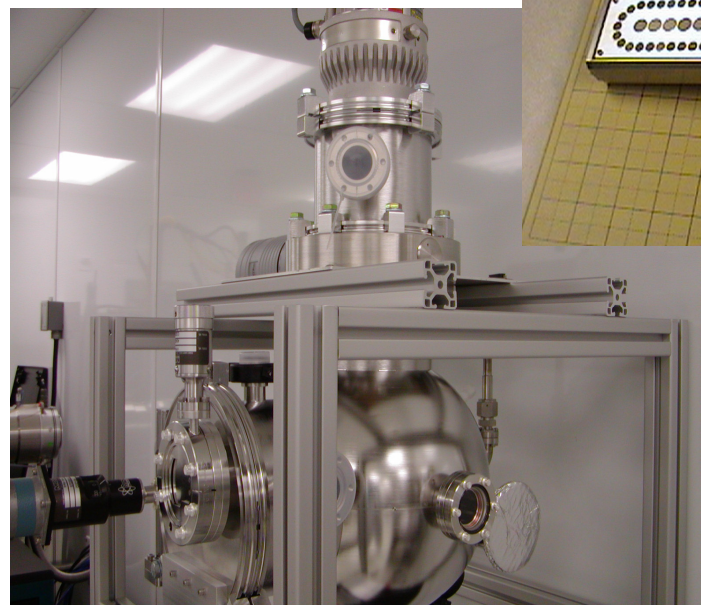
- Manufacturing process to produce films for the efficient containment of H<sub>2</sub> storage materials
  - by producing nanocrystalline metals or other new storage materials
    - in free-standing films
    - coiled inside a sealed vessel
    - without exposure to ambient oxygen and moisture
  - utilizing physical vapor deposition in a plasma thin film deposition tool
    - novel mechanism to separate the storage material from the deposition substrate
    - in situ storage of material into a canister and in situ sealing under high vacuum

# Accomplishments/Progress

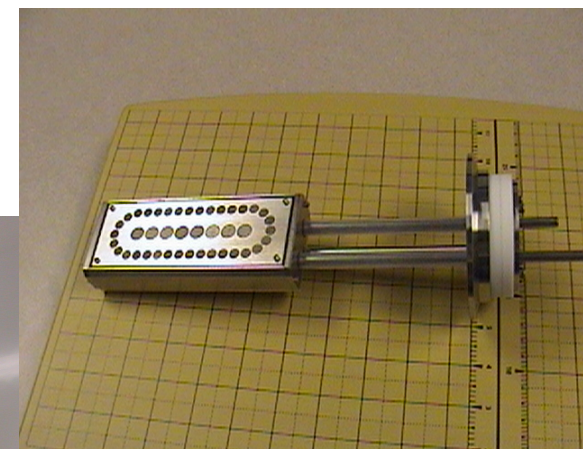
## (Approach 3) Nanostructured film



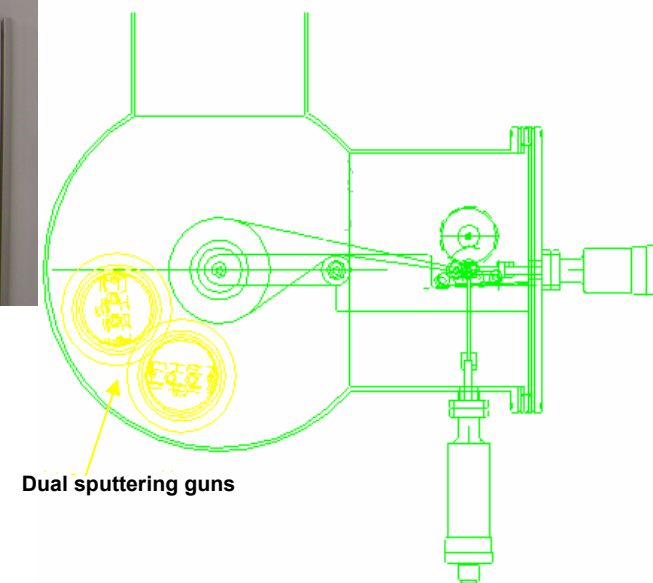
PVD system



Sputtering chamber



Sputtering gun



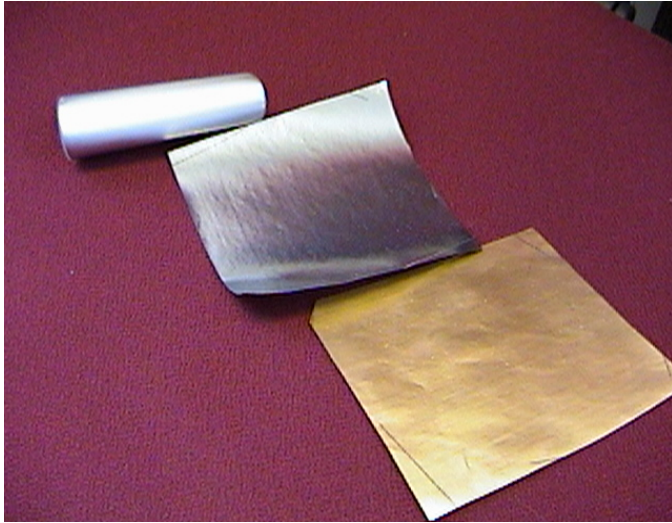
Dual sputtering guns

Development of physical vapor deposition system



# Accomplishments/Progress

## (Approach 3) Nanostructured film



**Resolute metal foils deposited on Teflon, Teflon/glass, and Au substrates**



**Delaminated metal foils deposited on Stainless steel substrates**

- Performed initial foil/substrate separation tests on Teflon, Teflon/glass, Au, and stainless steel. Metal film delaminated from stainless steel substrate.
- Designed and initiated machining of the spool canister.
- Designed foil substrate handling and separation subsystem.

# Future Plans



## (Approach 3) Fabricate nanostructured film

- Complete system construction – Q2 2005
- Demonstrate baseline operation with standard metal and advanced operation with multi-component materials ( $\text{NaAlH}_4$ ,  $\text{LiAlH}_4$ , Mg, K, Ti catalyst, nanostructured materials)– Q4 2005 – Q3 2006
- Test  $\text{H}_2$  loading of a complete system (material and canister) via NREL contact next year - Q2 2006
  - Per initial discussion with NREL during proposal preparation.

# Responses to Previous Year Reviewers' Comments

## (Approach 3) Fabricate nanostructured film



- **Capacity of the materials is about 6 wt% and cannot meet system target.**  
Distinguish an initial system baseline operation with Ti and Al: We will demonstrate PVD system's ability to produce free-standing films with PVD industry standard metals, Ti and Al. We will then evaluate new materials, including reactive sputtering of complex metal hydrides, that show promise of reaching the target.
- **Some concern was expressed over technical details that were absent e.g. high volume production requirement (and cost), slow kinetics, volumetric density, heat requirements for desorption.**  
High V production and cost can be achieved using amplified power sputtering guns with only an initial high cost. Thermochemistry of the materials improved via nanostructured architecture of materials.

# Additional Projects that will be Initiated in FY05



## 1. **Geologic hydrogen storage**

- Identify potential sites for underground hydrogen storage and to assess the viability of the concept through modeling and experimentation in the lab and at a sub-scale pilot site. A techno-economic simulation will be performed.

## 2. **Advanced materials-based technologies for on-board vehicular storage**

- Develop, synthesize, characterize, and advanced materials-based technologies that can operate with a high reversible hydrogen capacity at temperatures less than 100°C, with a focus on new complex hydrides. A candidate hydride exhibits a thermal decomposition temperature of 85°C and a theoretical 8.4 wt.% storage capacity which meets the DOE target. Other materials may be evaluated.

## 3. **Advanced thermal H<sub>2</sub> compressor**

- Design, build, and test a hydrogen compressor based on sequential metal hydride charge/discharge cycles using electrical discharge within the hydride bed to provide the heat for H<sub>2</sub> release. The thermal H<sub>2</sub> compressors are expected to be smaller, cheaper, faster, lighter and more efficient than conventional hydrogen compressors.



# Publications/Presentations/Patents



- Synthesis and characterization of nanoscale transition metal complex for hydrogen storage  
Sesha S. Srinivasan, Deepak Deshpande, Matthew T. Smith, Elias K. Stefanakos, Yogi Goswami, Michael Jurczyk, Arun Kumar, Ashok Kumar  
Oral Presentation at the MRS Spring Meeting, San Francisco, CA, March 30, 2005
- Transition Metal Hydrides for Hydrogen Storage  
Sesha S. Srinivasan, Elias (Lee) Stefanakos, Deepak Deshpande, Matthew T. Smith Yogi Goswami, Lisa McElwee-White  
Presentation at the DOE Safety Review Meeting, University of South Florida, Tampa, FL, March 11, 2005
- Presentation at MRS Fall 2004: Arun Kumar, Michael U. Jurczyk, Ashok Kumar, Sesha Srinivasan, Elias Stefanakos: Polymeric Carbon Nanocomposites for Hydrogen Storage
- Presentation at MRS Spring 2005:
  - Michael U Jurczyk, Arun Kumar, Ashok Kumar, Lee Stefanakos, Sesha S. Srinivasan, Effect of Physical State of Carbon Nanocomposite on Hydrogen Adsorption and Desorption
  - Arun Kumar, Michael U Jurczyk, Ashok Kumar, Lee Stefanakos, Sesha S. Srinivasan, Nanocomposite with Carbon Nanotubes Aligned in High Magnetic field for Hydrogen Storage Applications
- Patents
  - Arun Kumar, Michael U. Jurczyk, Ashok Kumar, Elias Stefanakos: Carbon Based Nanocomposite Material for Hydrogen Storage (patent filed to USF)
  - Non-Provisional Patent application # 10/711,552 'Hydrogen Storage Nano-foil and Method of Manufacture' filed September 24, 2004
  - Patent application to be submitted Q2-2005 'Reactive Sputtering of Nanostructured Multi-component Hydrides'