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# ***2006 DOE Hydrogen Program Review***

Hydrogen Storage Research

University of South Florida

Presenters: Yogi Goswami and Elias  
Stefanakos

May 18, 2006

Project ID # STP43

# Participants and Projects

## Participants

### University of South Florida

- **CO-PI's: Yogi Goswami, Elias Stefanakos**
- V. Bhethanabotla (ChE), M. Calves (COT), C. Ferekides (EE), Y. Goswami (ChE), N. Kislov (CERC), B. Krakow (CERC), Ashok Kumar (ME), L. Langebrake (COT), D. Morel (EE), G. Moore (CERC), S. Onishi (COT), M. Ross (Civil E), M. Smith (CERC), S. Srinivasan (CERC), E. Stefanakos (EE), P. Wiley (EE), J. Wolan (ChE), 8 graduate students, 2 undergraduate.

### University of Florida

- L. McElwee-White (Chemistry), B. Lear (ME), M. Su Lee (ME), S. Ingley (ME), Nikhil Kothurkar (ME), 6 graduate students

### University of Central Florida

- Clovis Linkous (FSEC)

## Projects

### Hydrogen Production (STP37)

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

### Hydrogen Storage (STP43)

- Advanced material-based technologies for on-board vehicular storage (USF and UF)
- Nano-structured Materials (USF)
- Nano-structured Films (USF)

### Fuel Cells (STP37)

- PEM Fuel Cell Research (UCF)
- PEM Fuel Cell Research (UF)
- PEM Fuel Cell Research (USF)

### Delivery (STP37)

- Geologic Storage (USF)
- Thermal Hydrogen Compressor (USF)

# Overview

## Timeline

- Oct 2004 to Sept 2008
- 40% Complete

## Budget

- Total project funding
  - DOE \$4.8M (\$1.2M/year)
  - Contractor \$1.25M
  - FY05 \$2.9M

## Barriers

### **Task 1: Hydrogen Production**

- 1.1: Photoelectrochemical/Photocatalytic
  - 3.1.4.2.6 AP, AQ (Materials efficiency, Materials durability)
- 1.2: Thermochemical Cycle
  - 3.1.4.2.7 AU (High temperature thermochemical technology development)
- 1.3: Biomass Gassification
  - 3.1.4.2.4 W, 3.1.4.2.4 V (Feedstock cost and availability, Capital cost and efficiency of biomass gasification/pyrolysis technology)
- 1.4: Solid State Ionic Conductors
  - 3.1.4.2.2 H, I, K (Fuel processor capital costs, System efficiency, Grid electricity emissions, Electricity costs)

## **Barriers (continued)**

### **Task 2: Hydrogen Storage**

- 2.1: Advanced material-based technologies for on-board vehicular storage
  - 3.3.4.2 A-D, J, P, Q (System weight and volume, System cost, Efficiency, Durability/Operability, Thermal management, Lack of understanding of H<sub>2</sub> physisorption and chemisorption, Reproducibility of performance)
- 2.2: Nano-structured Materials
  - 3.3.4.2 A-C, J, P, Q (System weight and volume, Efficiency, Durability/Operability, Thermal management, Lack of understanding of H<sub>2</sub> physisorption and chemisorption, Reproducibility of performance)
- 2.3: Nano-structured Films
  - 3.3.4.2.1 B, D (System cost, Durability/Operability)

### **Task 3: Fuel Cells**

- 3.1.1: PEM Fuel Cell Research (UCF)
  - 3.4.4.2 A-D (Durability, Cost, Electrode performance; Thermal, Air, and water management)
- 3.2.2: PEM Fuel Cell Research (UF)
  - 3.4.4.2 A-D, J (Durability, Cost, Electrode performance ; Thermal, Air, and water management; Start-up time/Transient operation)
- 3.3.2: PEM Fuel Cell Research (USF)
  - 3.4.4.2 B, C, D, I (Cost, Electrode performance ; Thermal, Air, and water management; H<sub>2</sub> purity/CO Clean-up)

### **Task 4: Delivery**

- 4.1: Geologic Storage
  - 3.2.4.2 G (Feasibility of geologic storage)
- 4.2: Thermal Hydrogen Compressor
  - 3.2.4.2 B (Reliability and costs of H<sub>2</sub> compression)

# Task 2.1 (storage): Advanced material-based technologies for on-board vehicular storage

S, Srinivasan, L. McElwee-White, J. Wolan, V. Bethanabotla, M. Smith, Y. Goswami, E. Stefanakos, L. Rivera, S. Dumbri, P. Choudhury

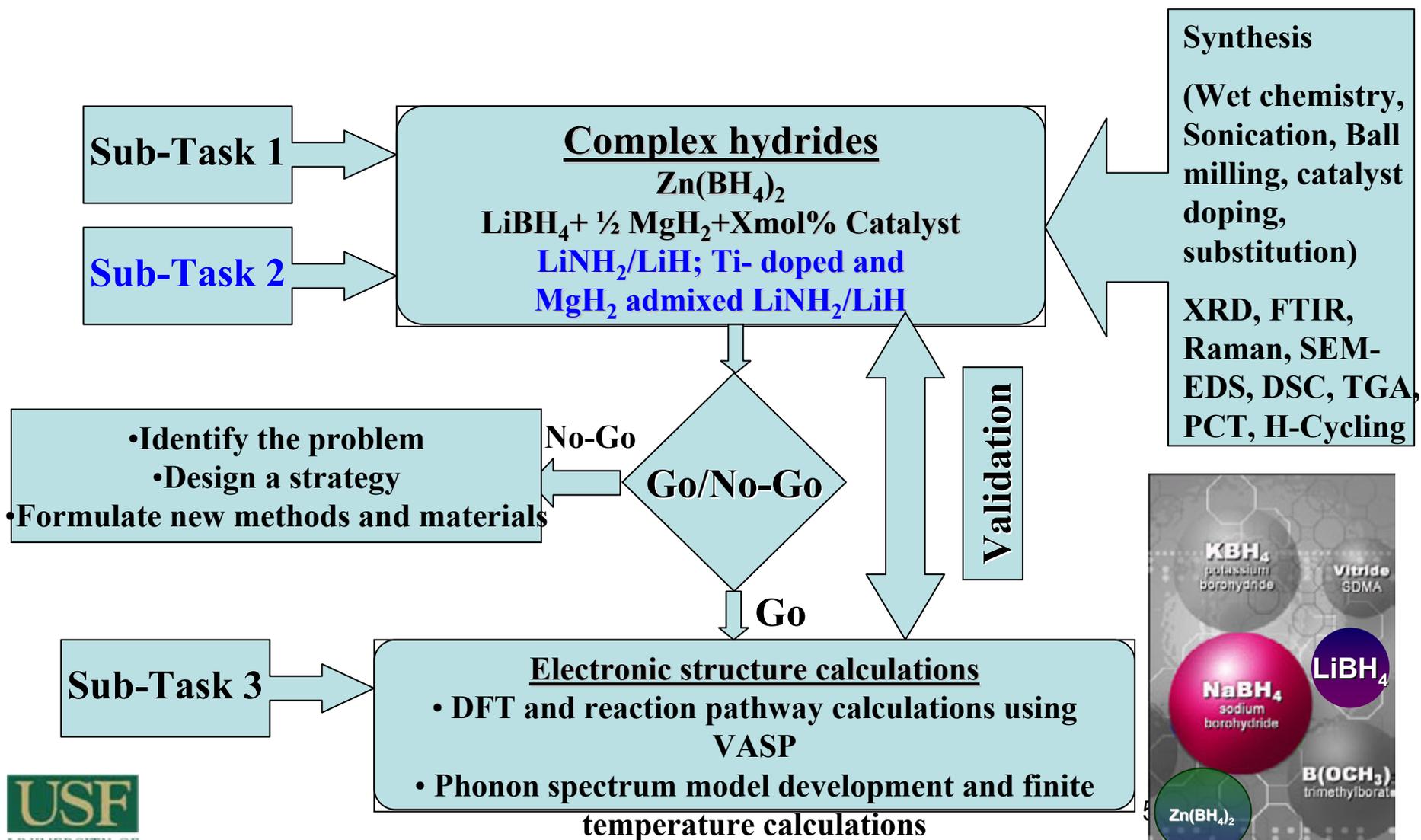
## Objectives

- Synthesis and characterization of materials with high reversible storage capacity that can operate at  $T < 100^\circ \text{C}$ .
- New complex borohydrides and Alkali amides/hydrides. Catalytic doping and substitution mechanisms to tailor the kinetic and thermodynamic properties
- Electronic structure calculations of thermodynamically stable phases of complex borohydrides
- Address barriers 3.3.4.2 A-D, J, P, Q (System weight and volume, System cost, Efficiency, Durability/Operability, Thermal management, Lack of understanding of  $\text{H}_2$  physisorption and chemisorption, Reproducibility of performance)

Year	Materials
Oct.'04- May'05	Nanostructured $\text{Mg}_2\text{FeH}_6$ ; Ti-catalyzed and $\text{Li}^+$ substituted $\text{Mg}_2\text{FeH}_6$ - <b>[Discontinued]</b>
June'05- May'07	$\text{Zn}(\text{BH}_4)_2$ ; $\text{LiBH}_4 + \frac{1}{2} \text{MgH}_2 + \text{Xmol}\%$ catalyst Mixed borohydrides; $\text{NaBH}_4 + \text{LiBH}_4 + \text{Xmol}\%$ catalyst $\text{LiNH}_2/\text{LiH}$ Ti-doped $\text{LiNH}_2/\text{LiH}$ $\text{MgH}_2$ ad-mixed $\text{LiNH}_2/\text{LiH}$ (Sonicated and ball milling)
Jan'06 – May'07	Electronic structure (DFT) calculations to identify the thermodynamic stable phases of complex borohydrides

## Task 2.1 (storage): Advanced material-based technologies for on-board vehicular storage

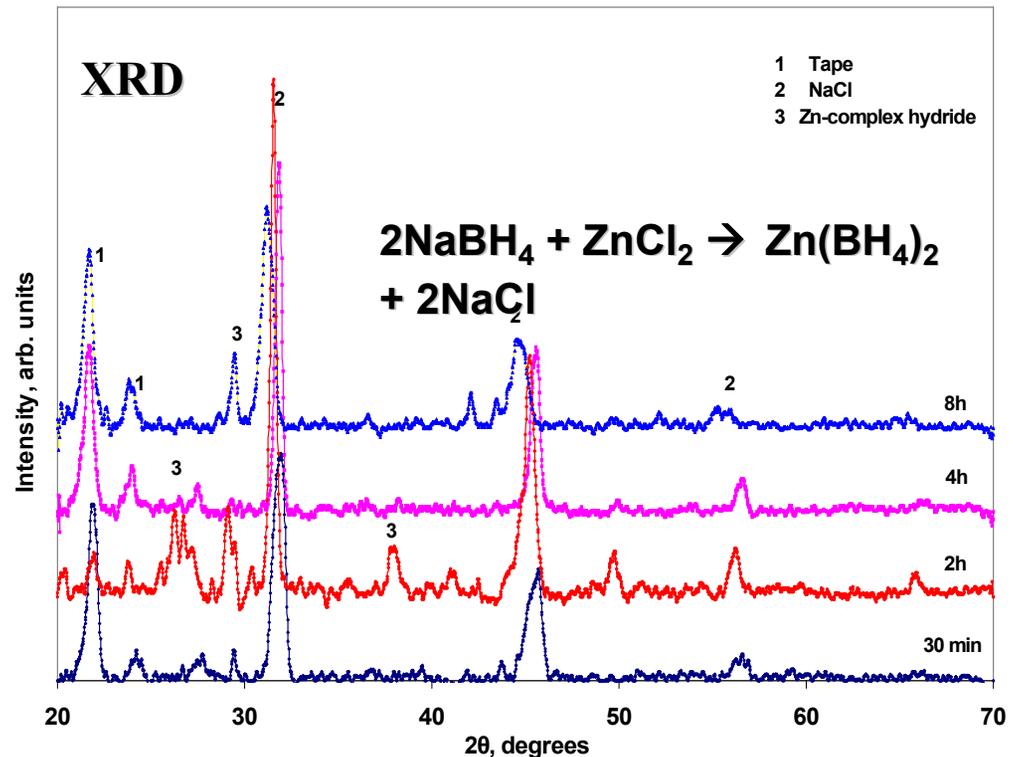
# Approach



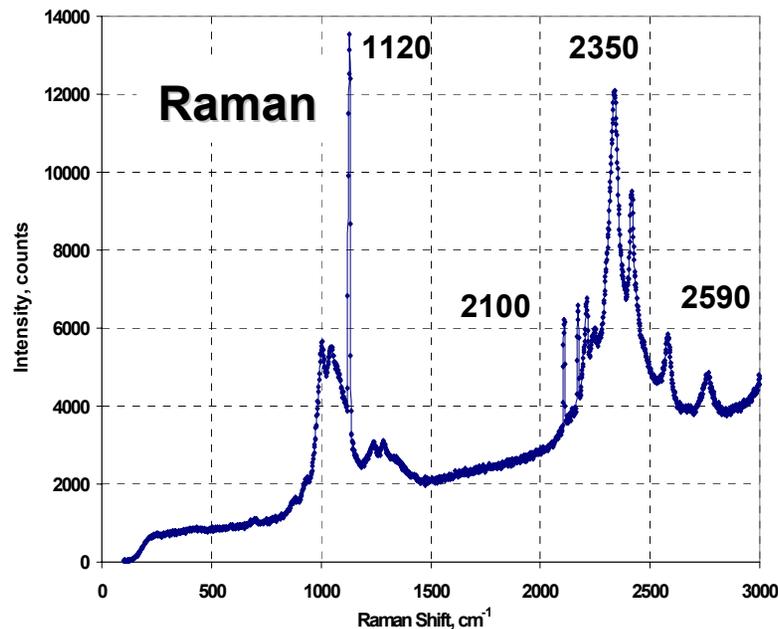
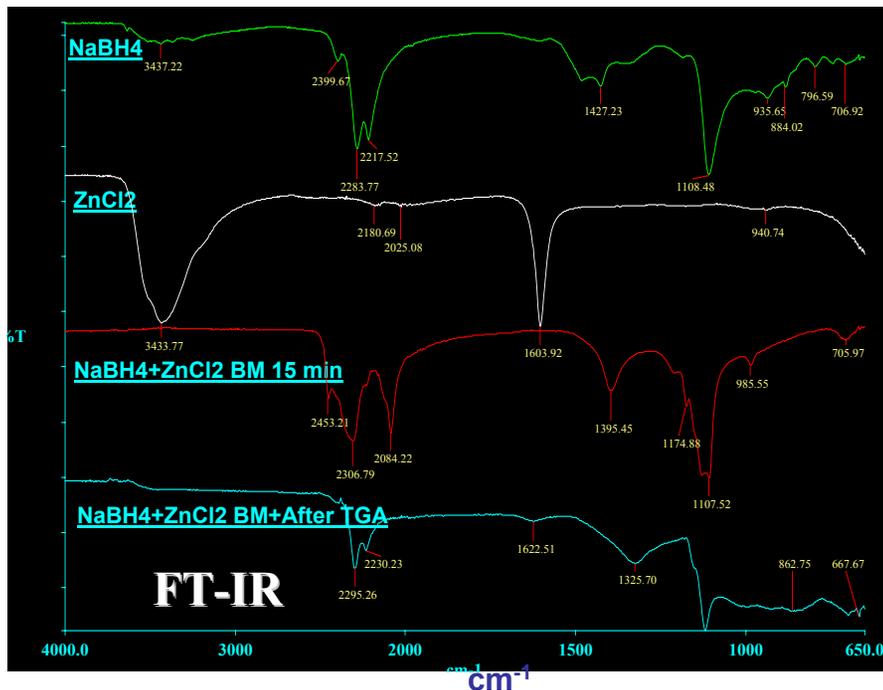
## Task 2.1 (storage): Advanced material-based technologies for on-board vehicular storage

# Results - $\text{Zn}(\text{BH}_4)_2$

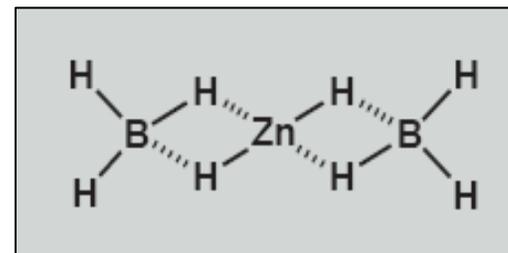
- Successful synthesis of  $\text{Zn}(\text{BH}_4)_2$  by an inexpensive mechanochemical process
- Confirmation of phase formation and completion of reaction by XRD
- No initial elemental peaks for  $\text{NaBH}_4$  and  $\text{ZnCl}_2$  observed after milling
- Full width half maximum (FWHM) increases with an increase of milling time (30 min-8h)



# Results - $Zn(BH_4)_2$ [contd.]

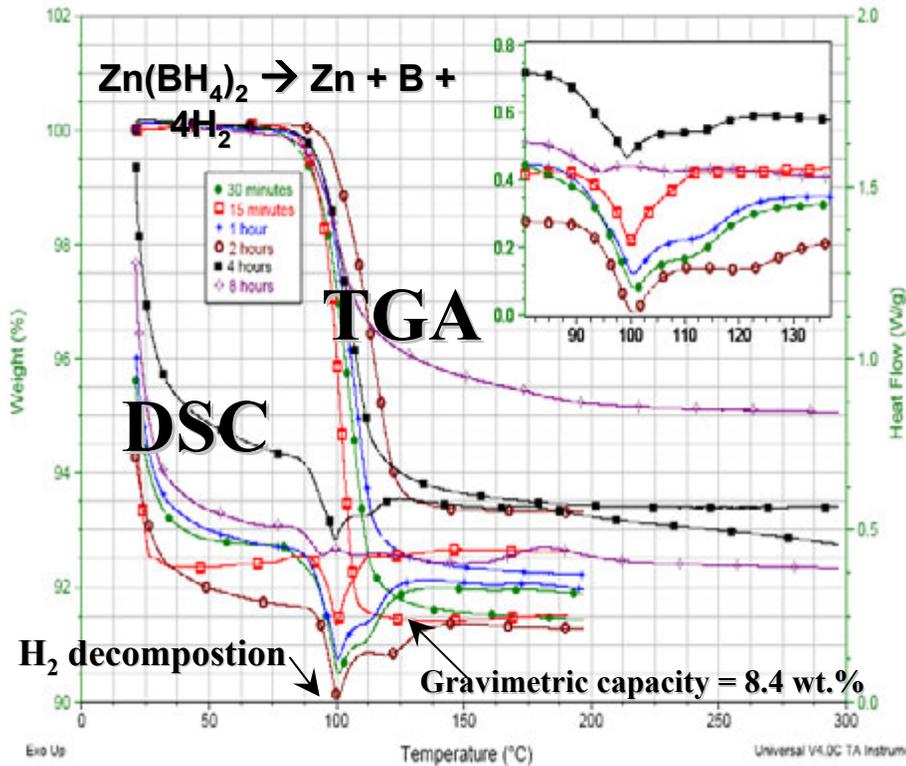


- FT-IR and Raman spectra demonstrate the presence of B-H (bridging) and B-H (terminal) bonds for  $Zn(BH_4)_2$
- B-H stretch for  $NaBH_4$  occurs at 2283 and 2217  $cm^{-1}$  for  $Zn(BH_4)_2$  at 2084 (bridging) and 2453 (terminal) B-H bonds
- FT-IR of  $Zn(BH_4)_2$  after thermal decomposition shows different bonding band positions



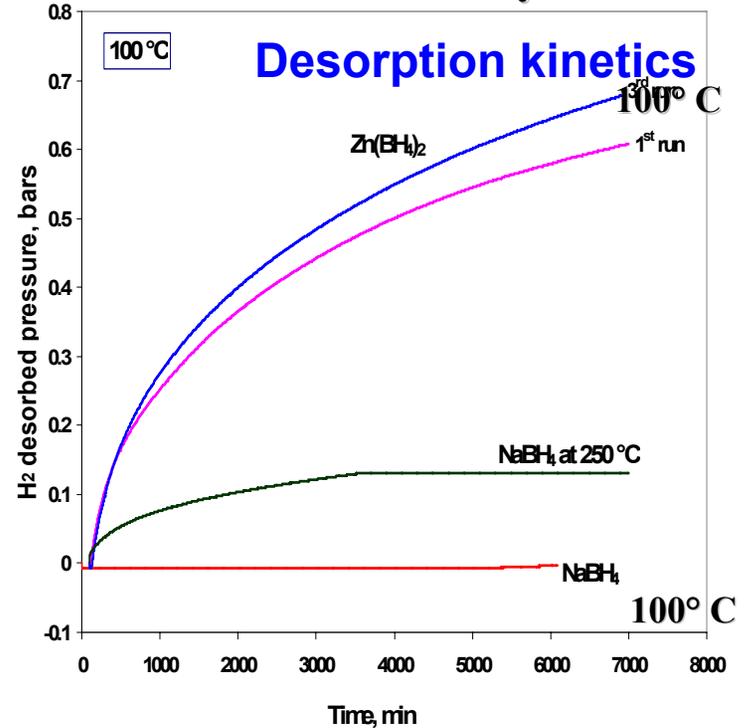
# Results - $Zn(BH_4)_2$ [contd.]

## Gravimetric Analysis



- Theoretical capacity of 8.4 wt.% has been achieved with milling of 15-30 minutes
- However, the gravimetric capacity decreases with increase of milling duration.

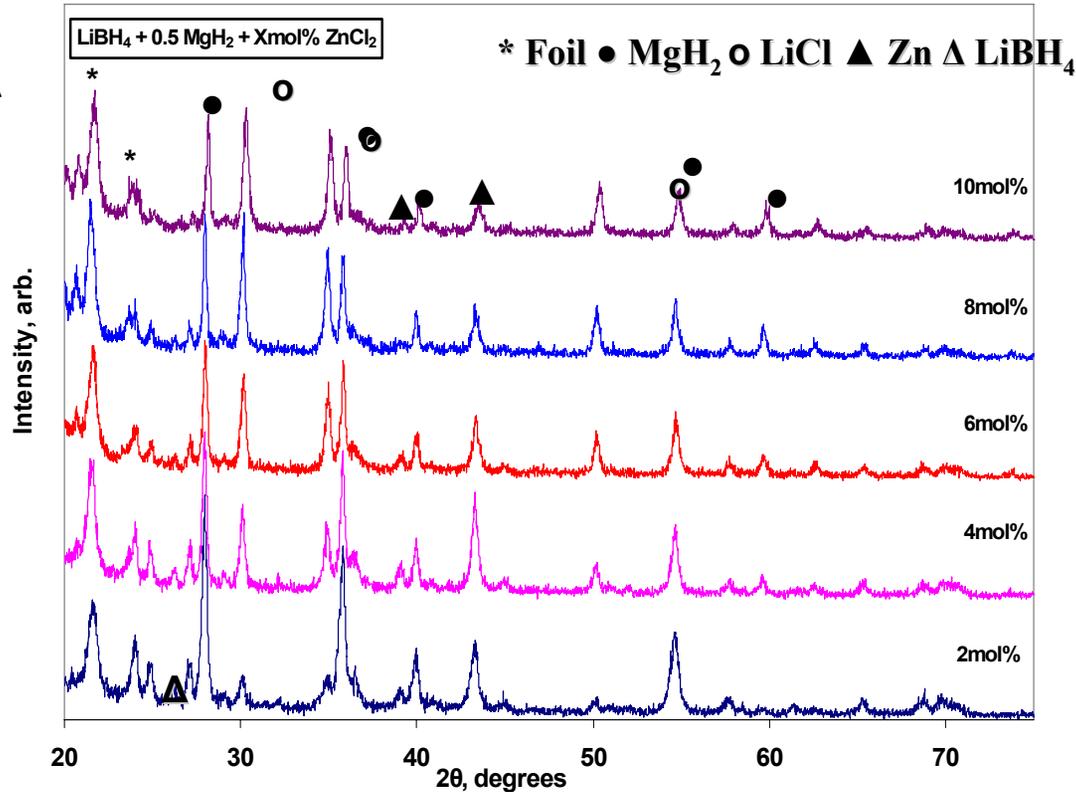
## Volumetric Analysis



- $Zn(BH_4)_2$  exhibits reversibility at 100° C
- $NaBH_4$  shows no reversibility even at 250° C
- Possibility of  $B_2H_6$  decomposition will be determined by GC/Mass-spec
- $MgH_2$  incorporation for improving the cyclic reversibility

# Results - $\text{LiBH}_4 + \frac{1}{2} \text{MgH}_2 + X\text{mol}\% \text{ catalyst}$

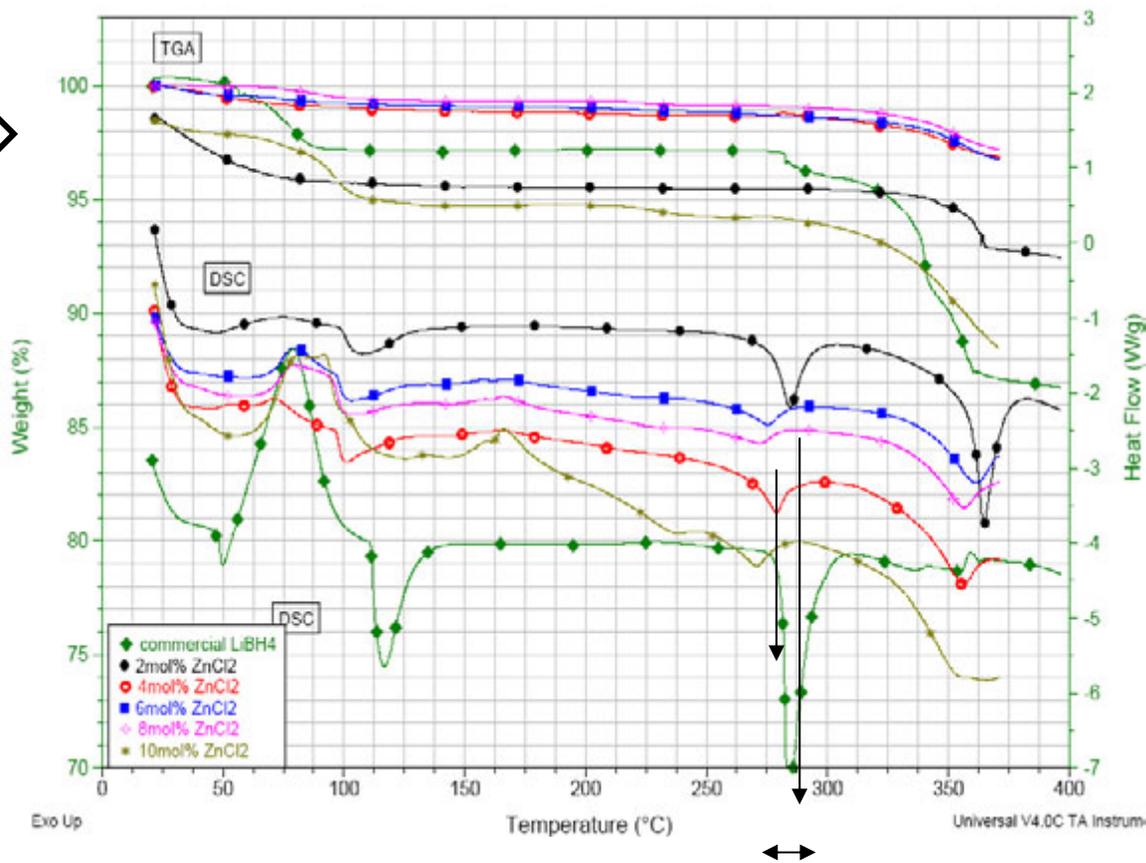
XRD



- No apparent formation of  $\text{MgB}_2$  phase observed for the ball milled samples
- The  $\text{LiCl}$  peak intensity increases with increased amount of catalyst concentration ( $\text{ZnCl}_2$ )
- The optimum concentration of 4mol% of catalyst seems to have correct phase proportions

# Results - $\text{LiBH}_4 + \frac{1}{2} \text{MgH}_2 + X\text{mol}\%$ catalyst [contd.]

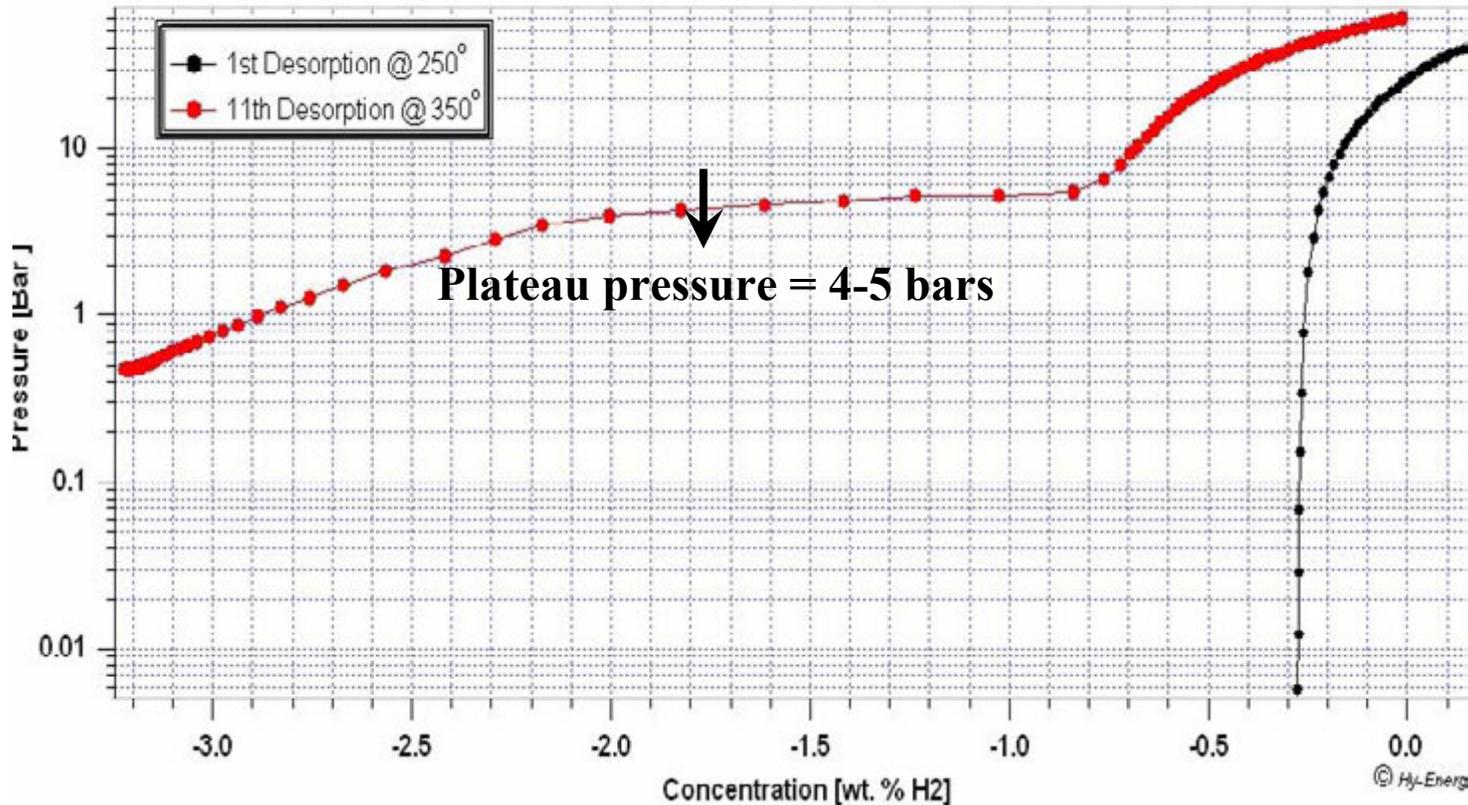
DSC & TGA



- Endothermic peaks due to  $\text{H}_2$  decomposition of  $\text{LiBH}_4$  occurs at lower temperature by  $\text{ZnCl}_2$  catalyst doping (DSC examination)
- The reduction in the thermodynamic barrier of  $\text{LiBH}_4$  will be studied by ad-mixing various concentrations of  $\text{MgH}_2$

# Task 2.1 (storage): Advanced material-based technologies for on-board vehicular storage

## Results - $\text{LiBH}_4 + \frac{1}{2} \text{MgH}_2 + X \text{ mol\% catalyst [contd.]}$

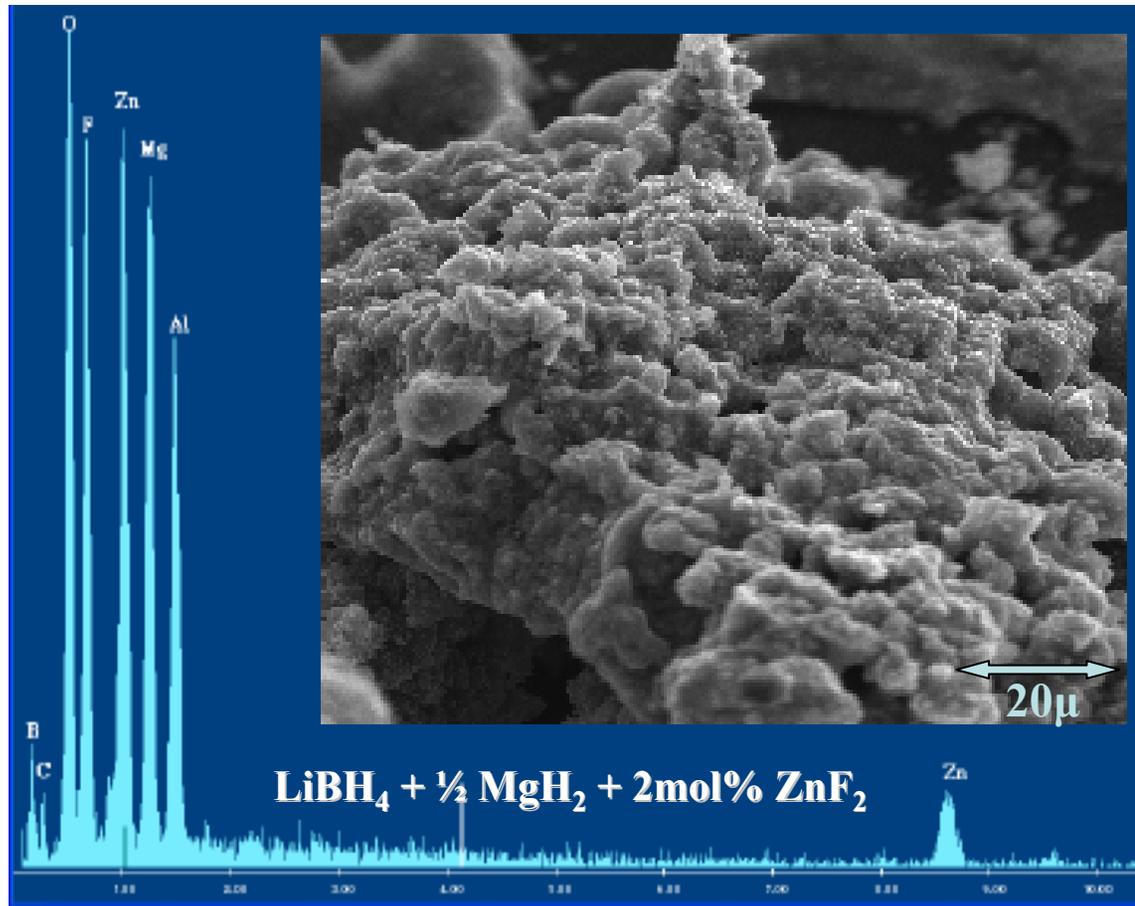


- Capacity ~3.0 wt.% in 11 cycles
- Capacity increases with temperature. Indicates that it is thermodynamically stable

## Task 2.1 (storage): Advanced material-based technologies for on-board vehicular storage

### Results - $\text{LiBH}_4 + \frac{1}{2} \text{MgH}_2 + X \text{ mol\% catalyst}$ [contd.]

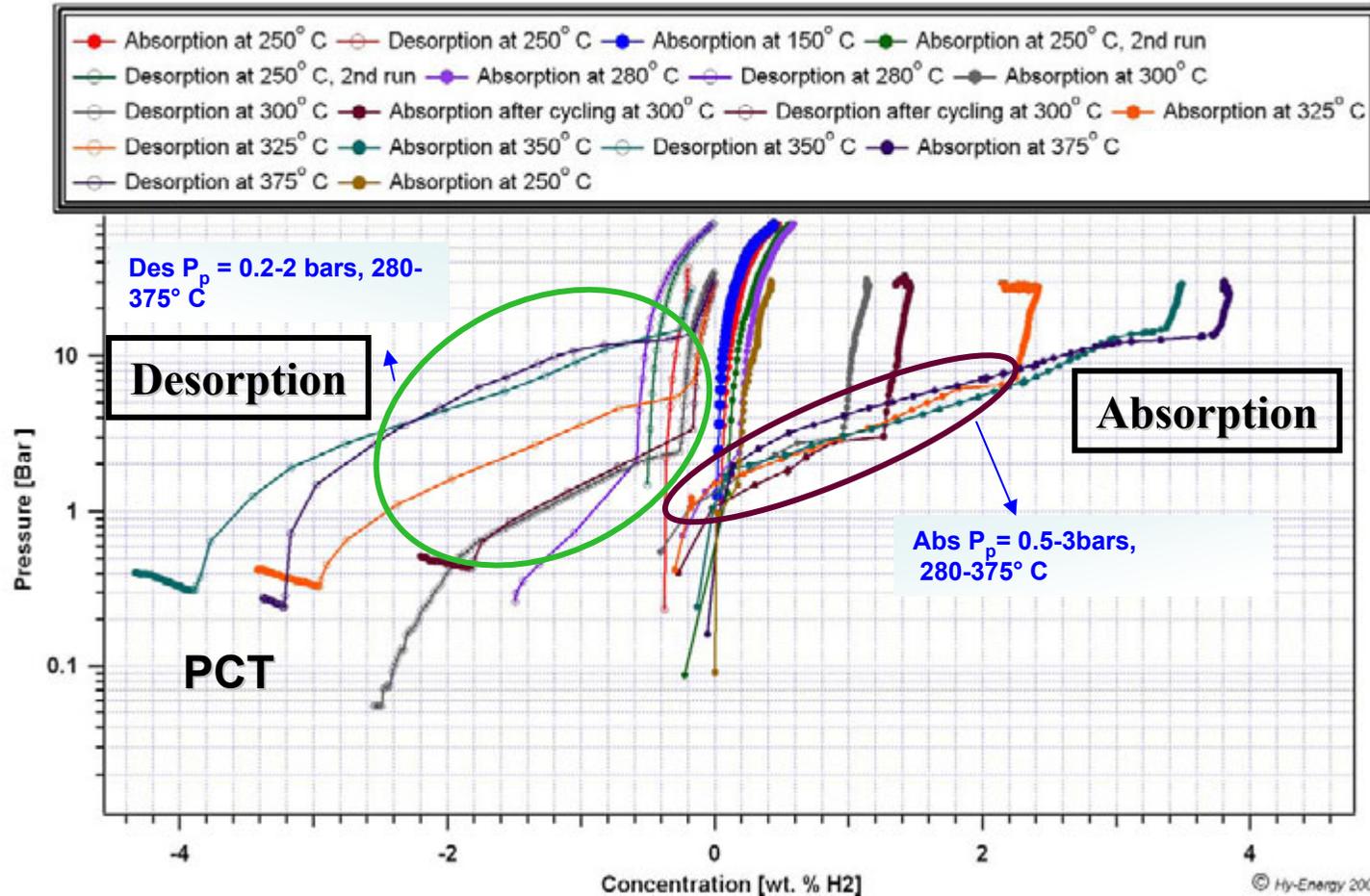
SEM-EDS



- EDS mapping of the complex hydride mixture shows correct stoichiometry
- Elemental boron has been found from the EDS spectrum

## Task 2.1 (storage): Advanced material-based technologies for on-board vehicular storage

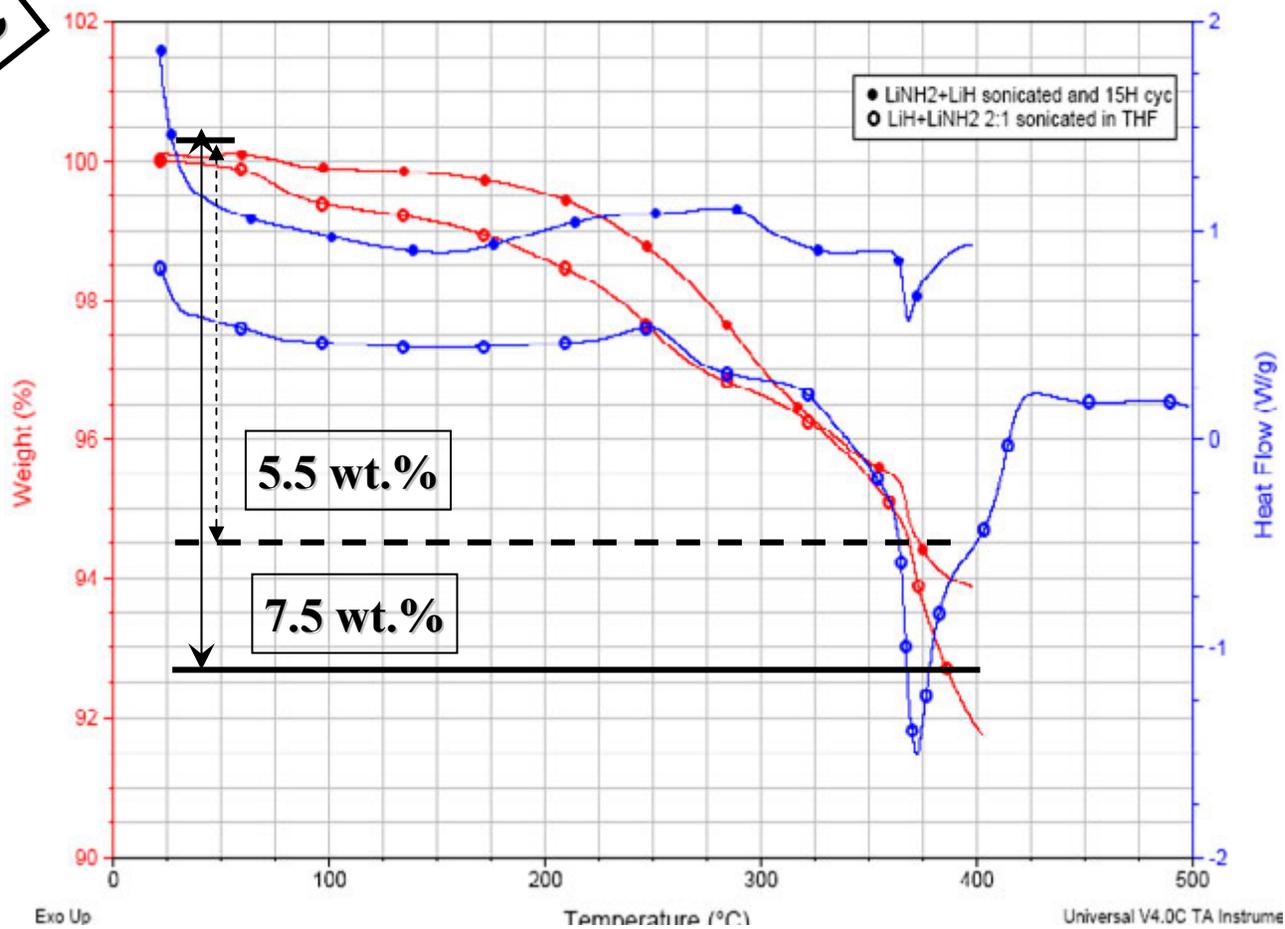
# Results - Sonicated $\text{LiNH}_2/\text{LiH}$



- Wet chemical synthesis of stoichiometric  $\text{LiNH}_2$  and  $\text{LiH}$  treated in solvents under  $\text{N}_2/\text{Ar}/\text{Vac}$ .
- Absorption and desorption plateau pressures,  $P_p$  matches with the earlier SNL literature
- Good cyclic capacity (performed at 25 cycles)

# Results - Sonicated $\text{LiNH}_2/\text{LiH}$ [contd.]

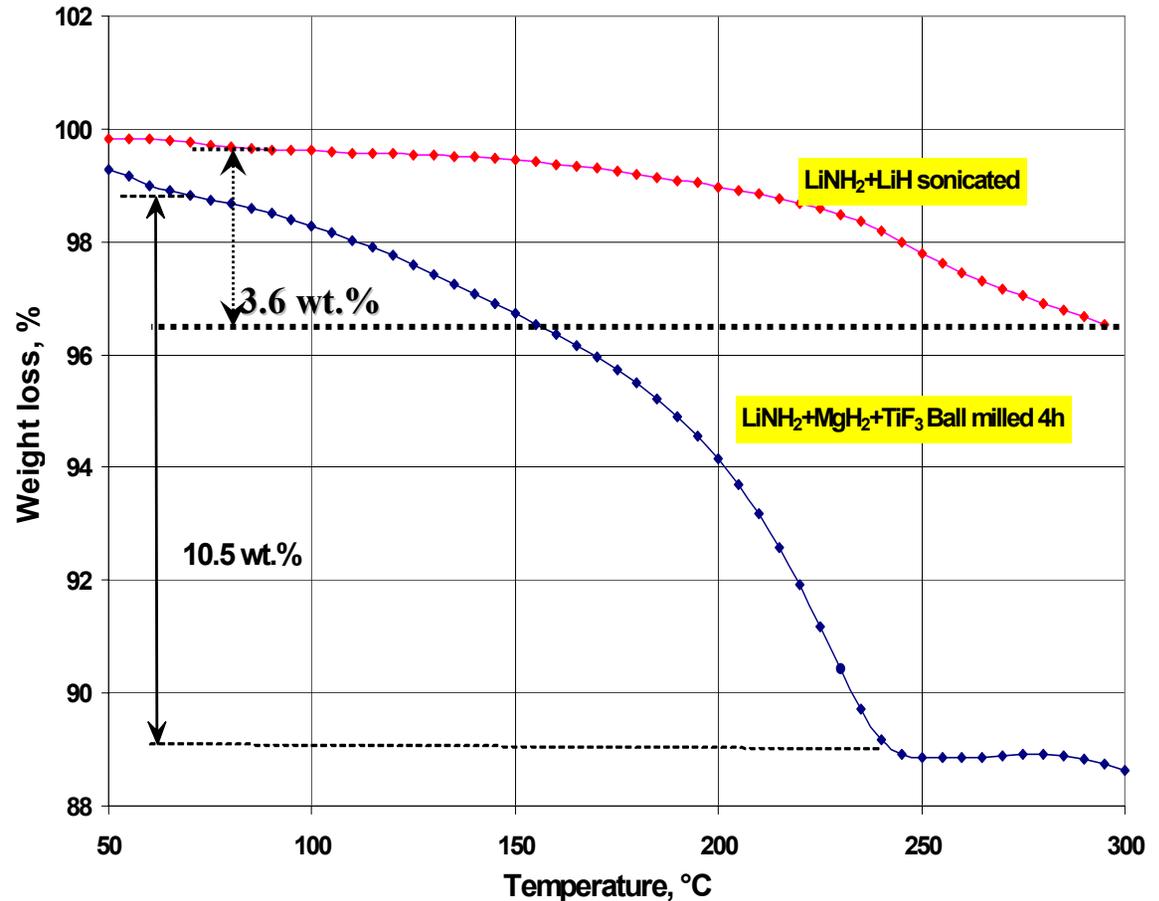
TGA & DSC



- TGA curves before and after 15 DH-RH cycling shows complete reversibility at around 250° C; H-capacity in 1<sup>st</sup> run = 5.5 wt.% and 15<sup>th</sup> run = 7.5 wt.%
- Long term cycling experiment will be carried out to identify the stability of the complex.

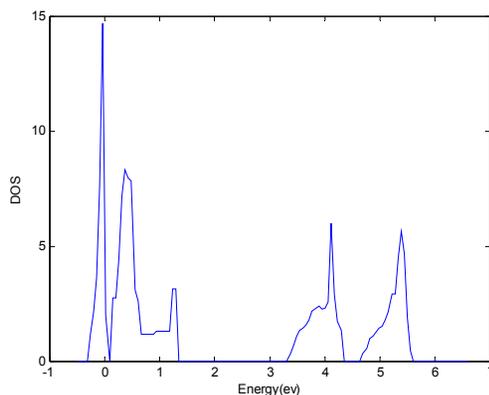
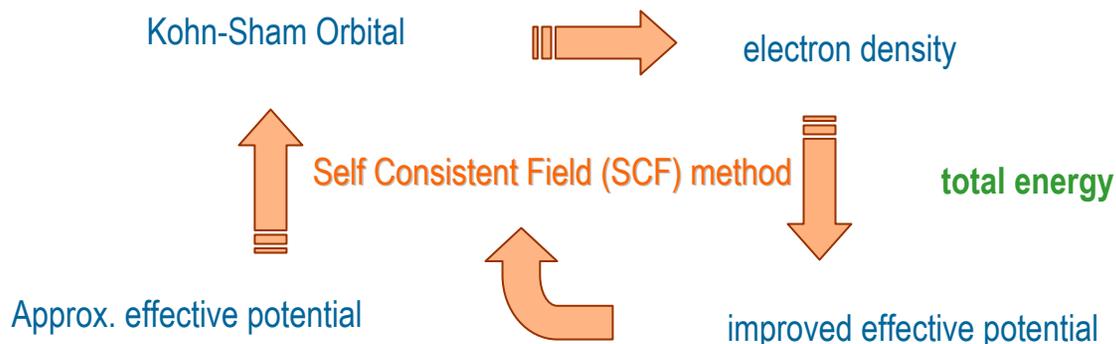
# Results - $\text{LiNH}_2/\text{MgH}_2$ (Ti- doped) [contd.]

- Ti- doping and  $\text{MgH}_2$  admixing enhances the kinetics and thermodynamic properties of  $\text{LiNH}_2/\text{LiH}$
- Reduction in the temperature of desorption with weight loss (> 6%) indicates  $\text{H}_2$  decomposition for the complex hydride mixture  $\text{LiNH}_2 + \text{MgH}_2 + 2 \text{ mol\% TiF}_3$  ball milled for 4h



## Task 2.1 (storage): Advanced material-based technologies for on-board vehicular storage **Just Started New Effort** – Electronic structure calculations of complex borohydrides

- Density functional theory and reaction pathway calculations using VASP software
- Phonon spectrum model development and finite temperature calculations
- Comparison with experimental results in the group and elsewhere



The DFT/GGA electronic density of states (DOS) of LiBH<sub>4</sub>

## **Future Work**

- Systematic investigation of the  $\text{H}_2$  storage properties of new complex borohydrides and alkali amides/hydrides
- Analysis of the residual gas after thermal decomposition of  $\text{Zn}(\text{BH}_4)_2$  by GC/Mass-spec
- Synergistic behavior of catalytic doping and  $\text{MgH}_2$  ad-mixing on the kinetics and thermodynamics of  $\text{Zn}(\text{BH}_4)_2$  and related systems
- Preparation of complex/composite hydrides with mixed hydrogenation properties
- Li-amides structural modification and catalyst doping to enhance the kinetics and reduce the dehydrogenation temperature
- Long term cycling and hydrogenation behavior of Li- amides and borohydrides
- Electronic structure calculations of thermodynamically stable phases of complex borohydrides (DFT)
- Different additives will be executed for the optimization

## Task 2.1 (storage): Advanced material-based technologies for on-board vehicular storage

# Summary

### Sub-Task 1:

- Literature survey identified the advanced material-based technologies for on-board vehicular storage
- Synthesis of new complex borohydride  $\text{Zn}(\text{BH}_4)_2$  by an inexpensive mechanochemical process
- Structural, microstructural, thermal and volumetric characterization of  $\text{Zn}(\text{BH}_4)_2$  systems
- An optimum milling duration of 15-30 minutes was sufficient to complete the reaction  $2\text{NaBH}_4 + \text{ZnCl}_2 \rightarrow \text{Zn}(\text{BH}_4)_2 + 2\text{NaCl}$
- Synthesis of  $\text{LiBH}_4 + \frac{1}{2} \text{MgH}_2 + 2\text{mol}\% \text{ZnCl}_2$  and performed the desorption kinetics and hydrogenation characteristics
- Volumetric capacity of 3.0 wt.% was achieved in 11 cycles at 350° C and it increases with increased no of cycling. The plateau pressure of desorption was found as 4- 5 bars.

### Sub-Task 2:

- $\text{LiNH}_2/\text{LiH}$  has been prepared by a sonication procedure and crystallized in THF solvent
- PCT characteristics of  $\text{LiNH}_2/\text{LiH}$  exhibit reversible cycling capacity above 300° C
- Ti- doped and  $\text{MgH}_2$  ad-mixed  $\text{LiNH}_2$  shows excellent gravimetric capacity of 10.5 wt.% below 200° C; the capacity remains the same even after 15 DH-RH cycles
- The plateau pressure of Li-amide/LiH has been tailor-made to 30-40 bars  $\text{H}_2$  by ad-mixing  $\text{MgH}_2$  in the ball milling process. The results have been quite promising and encouraging.

### Sub-Task 3:

- Initial efforts have started to apply electronic structure calculations (DFT) to identify thermodynamically stable phases of complex borohydrides.

# ***Publications and Presentations***

- Synthesis and characterization of nanoscale transition metal complex for hydrogen storage, S. S. Srinivasan, M. T. Smith, D. Deshpande, E.K. Stefanakos, Y. Goswami, M. Jurczyk, A. Kumar, A. Kumar, Materials Research Society Symposium Proceedings, Vol. 884E, Warandale, PA, 2005, GG 3.7
- Thermal and volumetric studies of complex chemical hydrides: Li-modified/Ti- doped  $Mg_2FeH_6$ , Sonicated  $LiNH_2/LiH$  and Zn- doped  $NaBH_4$ , S. S. Srinivasan, S. Dumbris, L. McElwee-White, E. Stefanakos, Y. Goswami, Materials Research Society Symposium Proceedings. Vol. 885E, Warandale, PA, 2005, A07-03.1
- Synthesis and characterization of new complex borohydrides for hydrogen storage, S.S. Srinivasan, E. K Stefanakos, Proceedings of the TMS Annual Meeting and Exhibition, Advanced Materials for Energy Conversion III, March 12-16, 2006, San Antonio, Texas
- Novel light weight complex hydrides for hydrogen storage, S. Srinivasan, E. Stefanakos, Proceedings of the AIChE spring national meeting, Hydrogen storage scenarios for transport applications, April 23-27, 2006, Orlando, FL
- Mechanochemical synthesis and characterization of new complex hydrides for hydrogen storage, S. Srinivasan, E. Stefanakos, To be presented, MRS Spring Meeting, April 17-20, 2006
- Transition metal assisted new complex hydrides for hydrogen storage, S. S. Srinivasan, E.K. Stefanakos, Y. Goswami, To be presented, 16th World Hydrogen Energy Conference, Lyon, France, June 14, 2006
- New complex borohydrides and their hydrogenation characteristics for on-board storage applications, S. S. Srinivasan, E.K. Stefanakos, Y. Goswami, Journal of Alloys and Compounds (Accepted) 2006

## **Task 2.1 (storage): Advanced material-based technologies for on-board vehicular storage**

# **Responses to Previous Year Reviewers' Comments**

**Question 1: Materials under study not relevant to the program; MgFe is well understood and will not meet goals; PI should terminate work on Mg<sub>2</sub>FeH<sub>6</sub>**

**Answer:** The work on nanostructured Mg<sub>2</sub>FeH<sub>6</sub> has been discontinued after the last annual review meeting in May 2005 (see slide 3).

**Question 2: PI has not identified any metal hydride type material that has potential to reach 2007 or 2010 target**

**Answer:** After the last annual review meeting, PI and the researchers involved in the project did an extensive literature survey on new and novel hydrides to meet the 2007 or 2010 DOE technical targets. In the new project, PI and his group proposed an advanced material-based technology involving new complex borohydrides [Zn(BH<sub>4</sub>)<sub>2</sub>] for on-board hydrogen storage. We successfully synthesized this hydride by an inexpensive mechanochemical process.

**Question 3: New Materials discovery not discussed in any detail**

**Answer:** The present sub-tasks mentioned in the earlier slides will give an idea about the new materials discovery and it is well aligned with the DOE scope of activities

**Question 4: TGA data for Li-modified Mg<sub>2</sub>FeH<sub>6</sub> indicates about 15% wt.% hydrogen released from the material at a temperature of about 300° C. Data needs to be confirmed**

**Answer:** New TGA experiments have been carried out with great care for the same material. PI and group found a way to seal the TGA pan with an alumina lid for better accuracy.

## **Task 2.1 (storage): Advanced material-based technologies for on-board vehicular storage**

### **Responses to Previous Year Reviewers' Comments [contd.]**

**Question 4: Collaboration among several Florida Universities, but no industrial and/or commercial participation noted**

**Answer:** PI and the researchers involved in the project have started establishing collaborations outside the Florida schools. An international collaboration was sought with IFE, Norway scientists for utilizing the synchrotron facilities for new materials developed at the PI's research facility. **Sigma-Aldrich Fine chemicals (Contact: Dr. V. Balema)** has shown an interest to prepare  $\text{Zn}(\text{BH}_4)_2$  in commercial scale once this new material demonstrates theoretical reversible capacity at operating temperature  $<100^\circ \text{C}$ . PI and the group initiated a formal collaboration with **GE Global Research (contact: Dr. Zhao)** for developing the complex borohydrides.

**Question 5: Encourage PI to continue in amides where potential for higher storage exists. PI also is encouraged to collaborate with many other PIs on this subject**

**Answer:** Li-amide/LiH system is being presently investigated with a new sonication procedure developed by our partner from University of Florida, as well as prepared at USF by the high energy mechanochemical approach. Initially the undoped  $\text{LiNH}_2/\text{LiH}$  developed by USF-UF matches literature results of **SNL and Univ. Singapore**. The Ti-doped  $\text{LiNH}_2/\text{LiH}$  shows an enhancement in the kinetics at lower temperatures. The PI and the group invited **Dr. Jim Wang (Ex-director of MHCoe, SNL)** for discussion of materials development and critical issues involving the synthesis of Li-amide/LiH systems.

**Question 6: Conduct go/no-go assessment**

**Answer:** Yes, PI and the group have mentioned the go/no-go decision in the flow chart (See slide 4)

# Task 2.2 (storage): Nanostructured Materials

*M. Jurczyk, A. Kumar, S. Srinivasan, E. Stefanakos*

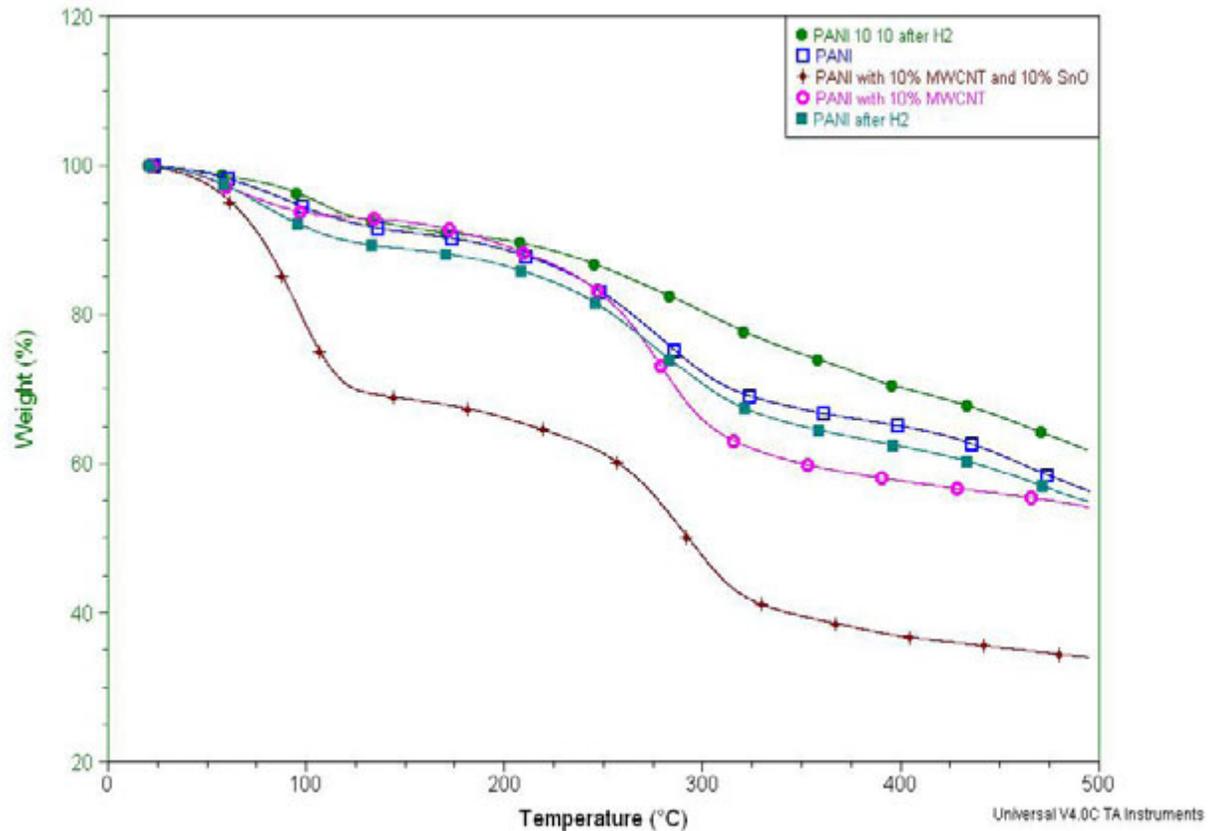
## Objectives

- Overall
  - Develop a novel nanocomposite material to meet targets for H<sub>2</sub> storage
- 2005
  - Investigate temperature and pressure effect on hydrogen sorption capabilities
  - Investigate addition of various concentrations of aluminum as well as other materials to the nanocomposite material to improve sorption capabilities
  - Investigate voltage/current effect on nanocomposite material during H<sub>2</sub> sorption

## Approach

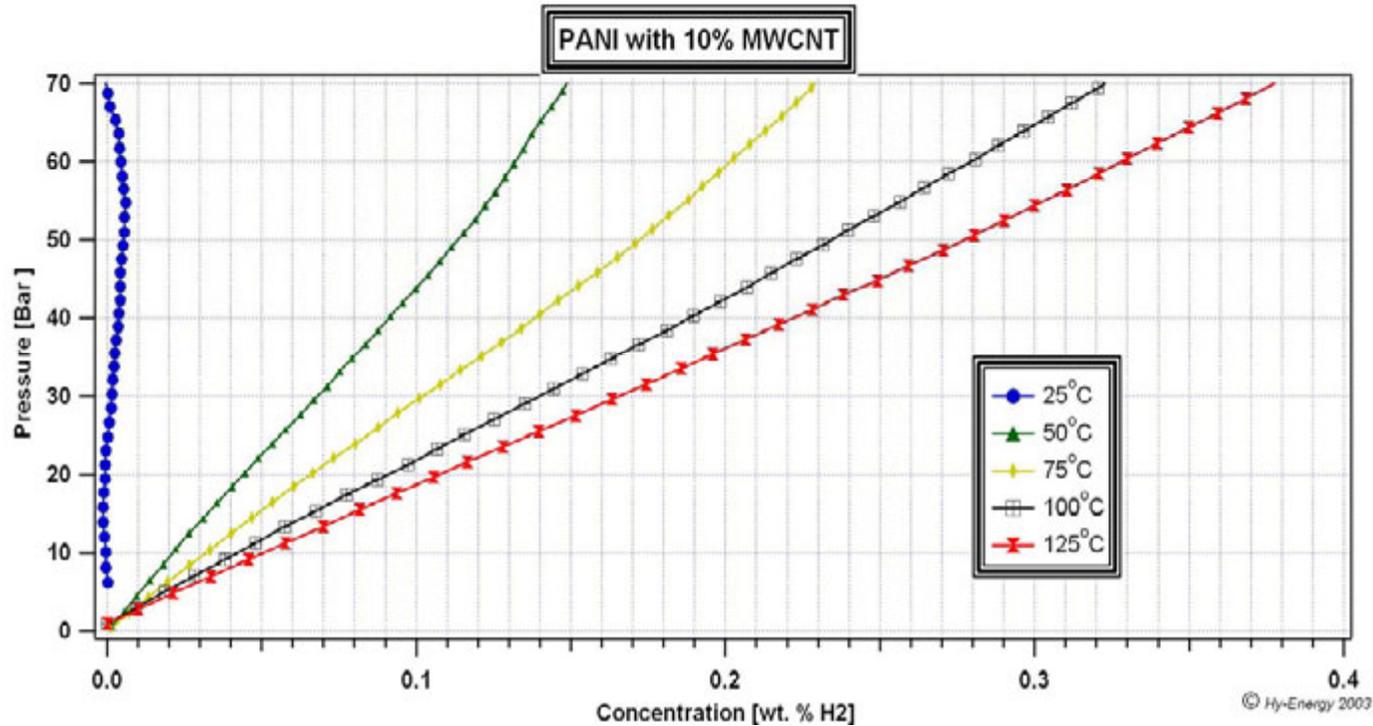
- Synthesize polyaniline (conducting polymer) as matrix material for nanocomposite
- Add additives to polyaniline nanocomposite material during polymerization to affect conductivity and hydrogen sorption capabilities
- Study hydrogen sorption characteristics at different pressures and temperatures
- Apply voltage to nanocomposite material and study its effect on hydrogen sorption
- Investigate different additives to nanocomposite material

# Results



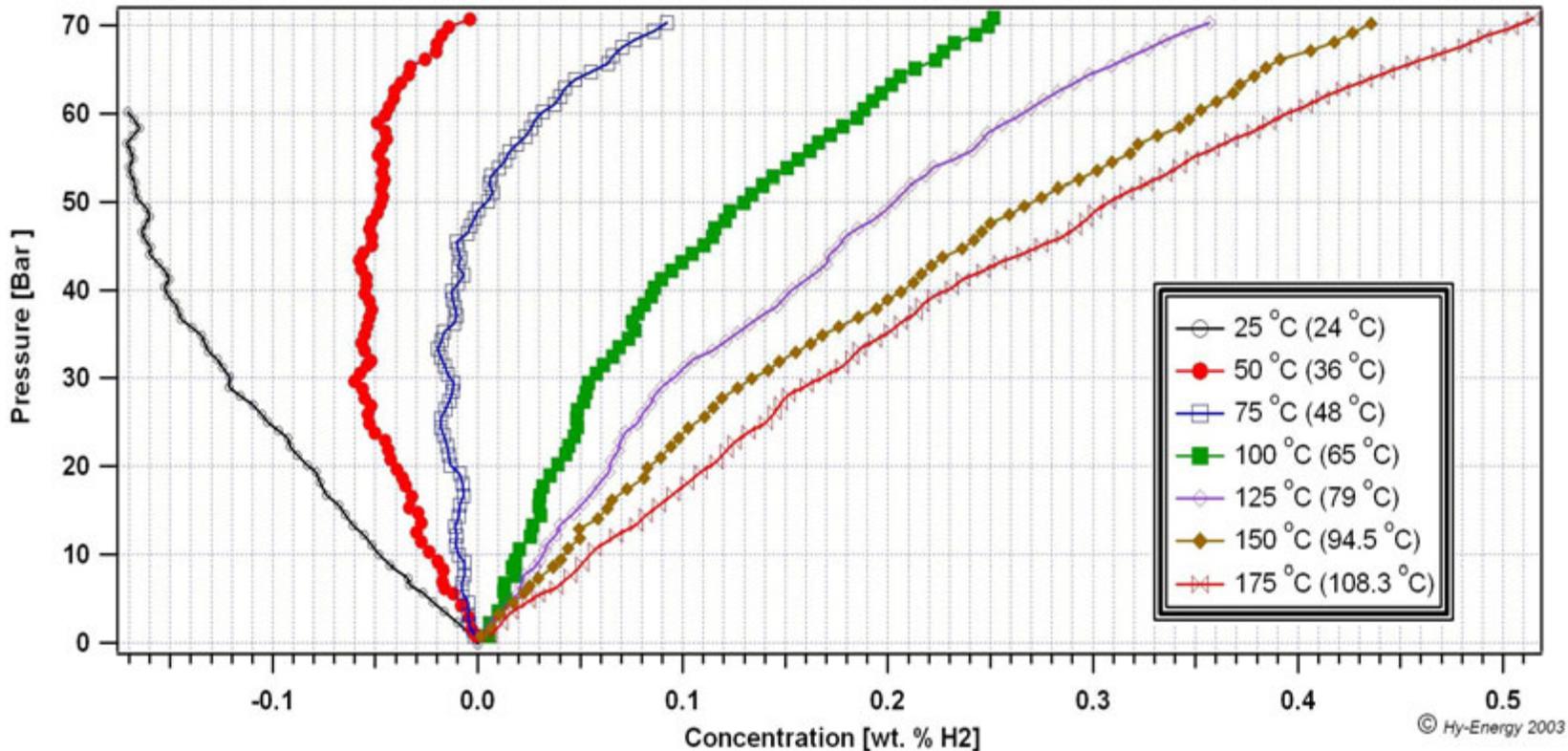
- TGA data: Nanocomposite material stable up to ~180 °C → meets DOE requirements
- Additives physically mixed, not chemically → hence similar decomposition

# Results (continued)



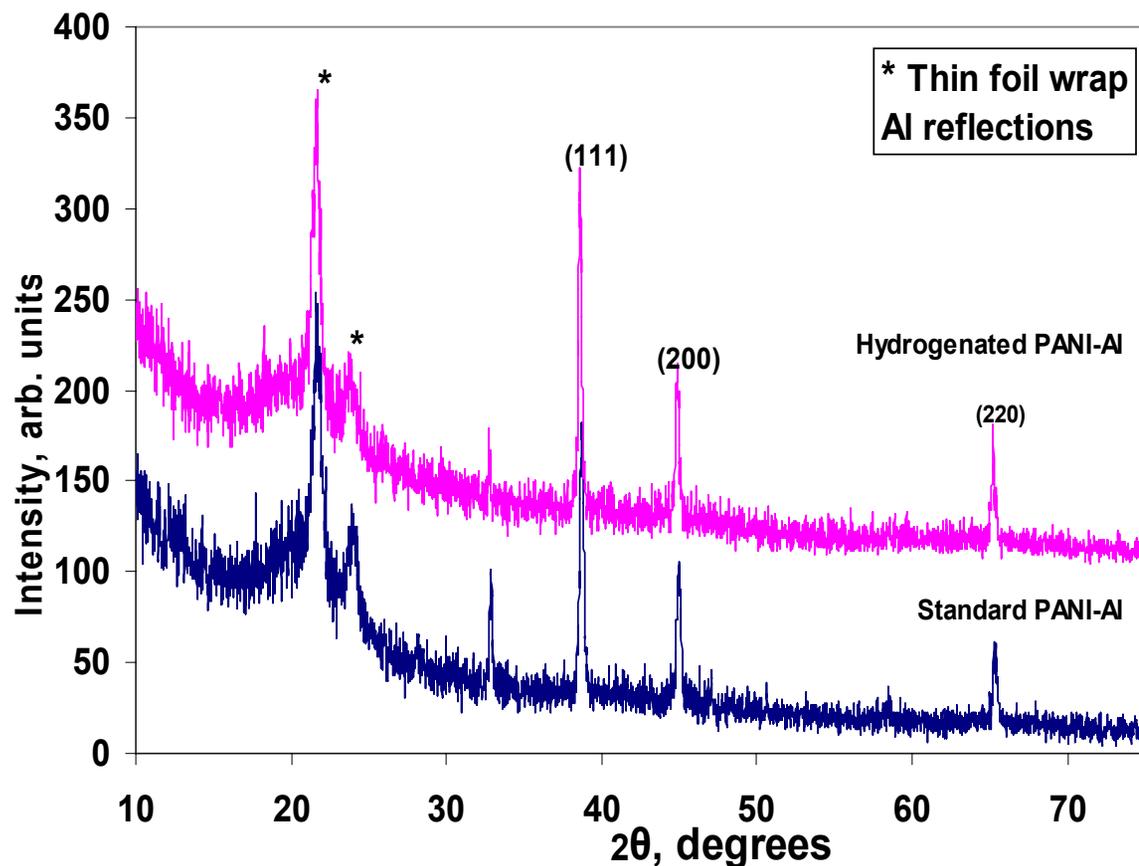
- Nanocomposite material absorbs more hydrogen with higher pressure and higher temperature
- Minimum temperature of ~35 °C required for hydrogen sorption
- Hydrogen sorption capabilities too low to meet DOE targets

# Results (continued)



- Nanocomposite with aluminum shows higher sorption capabilities, but still too low to meet DOE goals
- Temperature of ~ 50 °C required to store hydrogen
- Voltage application shows no effect on powdered form

# Results (continued)



- Aluminum in nanocomposite shows no chemical reaction with hydrogen
- Aluminum present, not alanate, and not aluminum oxide
- Aluminum shows no chemical reaction with matrix material

# ***Future Work and Summary***

## **Future Work**

- Investigate effect of voltage applied to solid sample vs. powdered sample
- Explore new materials for nanocomposite materials – to replace polyaniline
- Investigate role of aluminum in increasing hydrogen sorption
- Make final go / no-go decision on polyaniline based nanocomposite material

## **Summary**

- Polyaniline nanocomposite shows increasing hydrogen sorption capabilities above 30 °C, but too low to meet DOE targets
- Additives are being investigated, though with limited success
- An alternative to polyaniline is being investigated
- The addition of aluminum has improved hydrogen sorption and is being investigated in more detail

## Task 2.2 (storage): Nanostructured Materials

# Responses to Previous Year Reviewers' Comments

**Question 1: The use of voltage to maintain capacity seems certain to have excess parasitic loss.**

**Answer:**

The voltage would only be applied during the hydrogen sorption cycles, i.e. whenever hydrogen needs to be “refueled” or when hydrogen is needed to run the fuel cell or ICE. Of course, there will be a loss in energy overall, but the amount of energy required during the hydrogen sorption will overall be minimal as compared to, for example, the energy required to compress hydrogen.

**Question 2: Why would alignment increase absorption? Low fields wouldn't ionize or align polymer**

**Answer:**

It is not expected that alignment will increase absorption. This experimental work has been discontinued.

**Question 3: The results from the carbon-doped nanocomposite work showed that the H<sub>2</sub> capacity is only about 3%.**

**Answer:**

The carbon-doped nanocomposite actually only can store ~ 0.5 wt% hydrogen, but we have been able to increase its capacity with the addition of additives. Hence, while there is still the possibility of increasing the storage capacity significantly, there will have to be a go/no-go decision on the fate of the material.

**Question 4: Effect of potential is interesting but ignores the effect maintaining a field will have on net storage**

**Answer:**

See answer to question 1.

# ***Future Work***

- Due to comments from last review and current results, effort will cease at end of current quarter.
- NO Future Work

# Task 2.3 (storage): Nanostructured Films

*M. Calves, S. Onishi, J. Bumgarner, L. Langebrake*



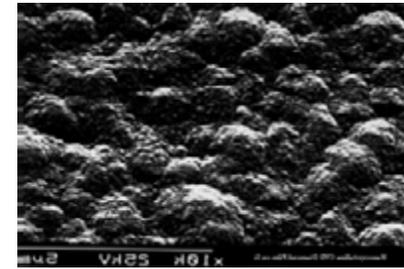
All-Foils Inc.

## Objectives

- Overall goal: To develop a coiled high purity, nanostructured film for storing hydrogen which will meet or exceed 2 kWh/kg or 6 wt% and \$4/kWh with a high charge/discharge rate.
- FY05 - Design, construct and operate a research physical vapor deposition system to produce freestanding (substrate removed) nano-crystalline alloys for the cyclic storage of hydrogen.
- FY06 – Following the reviewers' suggestion this project was discontinued during Q1 2006.

## Task 2.3 (storage): Nanostructured Films

# Approach



- Manufacturing process to produce hydrogen storage materials close to theoretical efficiency
  - by producing nanocrystalline materials and incorporating complex hydrides and/or carbon based nanostructures into robust alloy or composite films
    - coiled inside a sealed vessel
    - without exposure to ambient oxygen and moisture
    - novel approach to tailoring architecture of films to yield desired kinetic and thermodynamic properties (G. Sandi, The Electrochemical Society *Interface*, Fall 2004)
  - 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

## Task 2.3 (storage): Nanostructured Films

# Accomplishments

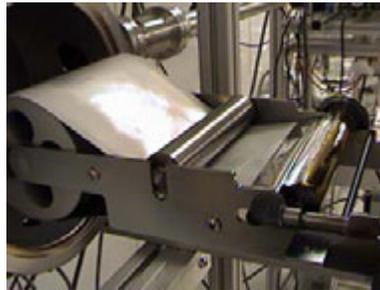
- Completion of the design and drawing documentation for the physical vapor deposition system and the nanofoil handling system.
- Assembly of the research reactor for the deposition of innovative films with the capability of sealing those films in situ in a canister, eliminating any influence of ambient atmosphere to the performance of the material. The completion of the tool emerged with the capability of placing it under load lock and vacuum.
- Assembly of the spooling device in the PVD chamber.
- Demonstration of the system characteristics using standard metal hydride materials Ti and Al. Freestanding nanofoils were produced and characterized.

## Task 2.3 (storage): Nanostructured Films

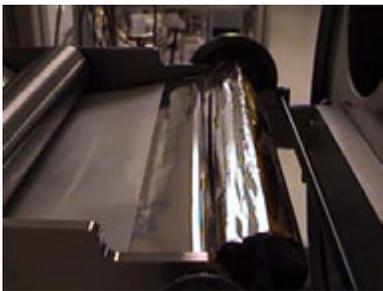
# Accomplishments/Progress



Surface of ss shim front of polished ss



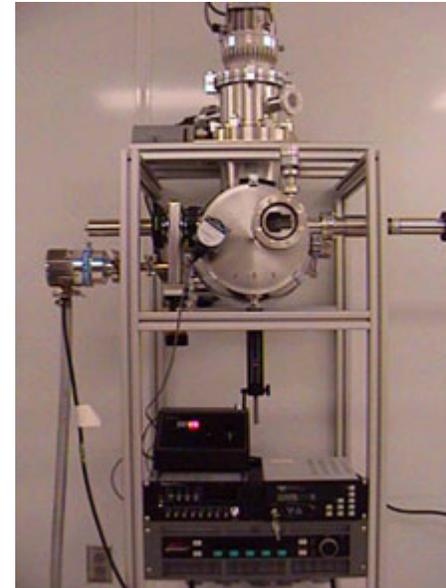
Al film is separating from ss belt.



Heat sink, ss belt & spool



Spooled film inside canister.



PVD system

## *Task 2.3 (storage): Nanostructured Films*

# ***Future Work***

- Due to comments from last review, effort for packaging deliverable has ceased.
- NO Future Work

# Task 1.1 (production): Photoelectrochemical/catalytic

D. L. Morel, C. S. Ferekides, S. Vakkalanka, S. Bates, Nikolai Kislov, M. Schmidt, S. Srinivasan, E. Stefanakos, M. Smith

## Significant Results

### Development of Solar Cells

- Primary near-term technical objectives have been met
  - Voc > 500 mV in Si devices
  - Operable tandem devices
- Key technical issue for current effort
  - Improved doping in CdSe p-contacts
  - Higher Voc's in CdSe devices

### Development of Catalyst

- TiO<sub>2</sub>-ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites were optimized based on control parameters
  - ball to powder weight ratio, milling duration, milling speed, and calcination temperature.
  - Compound is more than twice efficient in comparison with pure TiO<sub>2</sub> photocatalyst.
- A detailed investigation of quantum-sized effects in ball-milled ZnFe<sub>2</sub>O<sub>4</sub> has been performed in order to understand the photophysical properties of ZnFe<sub>2</sub>O<sub>4</sub>/TiO<sub>2</sub> nanoclusters
- Developed TiO<sub>2</sub> carbon doped photocatalyst having improved photocatalytic properties
  - Two times more efficient than pure TiO<sub>2</sub> photocatalyst

# ***Task 1.2 (production): Thermochemical***

***M. Su Lee, S. Dolan, H. Ingley – University of Florida***

***Y. Goswami, E. Stefanakos – Univ. of South Florida***

## ***Significant Results***

- Completed installation of laboratory scale facility
- The bromination and hydrolysis of Ca-pellet has been conducted using laboratory experimental set-up.
- Degradation and low hydrolysis rate was observed.
- The pore size distribution data showed that the reduction of pore volume is a cause of degradation and low hydrolysis rate

# **Task 1.3 (production): Biomass Gasification**

*M. Mahishi, M. Nath, N. Rajvanshi, W. Lear – Univ. of Florida*

*Y. Goswami, E. Stefanakos – Univ. of South Florida*

## **Significant Results**

- H<sub>2</sub> yield increased by 20%; CO and CO<sub>2</sub> in product gas reduced by 44% and 60.6% respectively from base (no sorbent) case
- higher gas yield (about 30%) observed in presence of sorbent
- product gas has less tars and particulates while using sorbent
- higher H<sub>2</sub> yield obtained at lower temperature offers potential to reduce gasification temperature (by about 100-150°C)<sup>1</sup>

# ***Task 1.4 (production): Solid State Ionic Conductor Development***

*B. Krakow, P. Wiley, L. Ecklund-Mitchell, D. Payne, E. Weaver, E. Stefanakos*

## ***Significant Results***

- Impermeability of pellets after high temperature treatment with methanol while maintaining other crucial characteristics (conductivity, strength) supports viability of CsHSO<sub>4</sub> as material in combined hydrogen production/separation processes.
- CsHSO<sub>4</sub> produced in current synthesis is high-purity, with sharp crystalline structure, and reproducible thermal properties.
- Groundwork has been laid to begin rigorous testing of performance of electrodes and catalysts to specific fuel gases

# ***Task 3.1.1 (Fuel Cells): PEM Fuel Cell Research***

## ***C. Linkous – Univ. of Central Florida***

### ***Significant Results***

- Demonstrated protection of amine substituents on benzyltrifluoride monomer by making the acetamide, a necessary step in the synthesis of fluorosulfonic PEEK polymer
- Developed mechanical, permeation, and conductivity methods for accelerated testing of PEM electrolytes under oxidizing conditions
- Synthesized highly conductive SPEEK (260 EW) to incorporate into cross-linked PEM electrolytes

## ***Task 3.1.2 (Fuel Cells): PEM Fuel Cell Research (UF)***

***N. Kothurkar, Y. Goswami, E. Stefanakos***

### ***Significant Results***

- Setup fuel cell test stand
  - Constructed test stand with temperature, humidity, etc. control including low temperature operation
- PEM Material Development
  - Synthesized and Characterized ABPBI—poly(2, 5-benzimidazole)
  - Fabricated membrane electrode assemblies (MEA)

## ***Task 3.1.3 (Fuel Cells): PEM Fuel Cell Research (USF)*** ***J. Wolan, B. Grayson, E. Stefanakos, V. Gupta***

### ***Significant Results***

- Pt/Ru/Au/TiO<sub>2</sub> nano-catalyst shows approx. 3% improvement over conventional catalyst in selective oxidation of CO in operation temperature ranges of 80-120°C.
- $\beta$ -zeolite nanocomposite acid functionalized membranes have been successfully developed for incorporation into a high temperature proton exchange fuel cell MEA.

# **Task 4.1 (delivery) Geologic H<sub>2</sub> Storage**

**Kim Clayback, Mark Ross, G. Moore, E. Stefanakos**

## **Significant Results – Established formation Benefits and Drawbacks**

### **Benefits**

- Depleted Reservoirs
  - Geologic characteristics generally well known
  - Transportation infrastructure in place
- Aquifers
  - Geographically well dispersed
  - Large volumetric storage possibilities
- Salt Caverns
  - Easiest, quickest recovery of gas
  - Lowest cushion gas requirement

### **Drawbacks**

- Depleted Reservoirs
  - Possible chemical reactions with petroleum products
  - Not located near population (end user) centers
- Aquifers
  - Expensive exploration of geologic properties
  - Greatest cushion gas requirement
  - Additional cost of dehydration of gas during recovery process
  - Additional installation expense for wells at the perimeter for recovery
- Salt Caverns
  - Generally the smallest formation for storage use
  - Limited geographic distribution

# ***Task 4.2 (delivery): Advanced Thermal H<sub>2</sub> Compressor***

***B. Krakow, S. Srinivasan, P. Wiley, D. Escobar, E. Stefanakos,***

## ***Significant Results***

In the 6 months since this project began we have:

- Prepared a sample of ZrMn<sub>2</sub> alloy by ball milling and sintering the metal powders.
- Identified the ZrMn<sub>2</sub> by XRD.
- Acquired ZrMn<sub>2</sub> DSC data with a view to determining its heat capacity
- Reactivated a high voltage power supply that was once used for lightning research and has properties needed for producing the electric discharge needed for this project.

# ***Acknowledgements and Interactions***

- **Hydrogen Workshop(s) at USF**
  - Dr. Jim Wang, SNL; Dr. Bill Tumas, LANL; Dr. Lin Simpson, NREL; Dr. Craig Jensen, Univ. Hawaii; Dr. Jim Fenton, FSEC; Dr. John Petrovic, DOE (agreed to visit in June'06)
- **US Department of Energy (DE-FG36-04G014224)**
  - IFE, Norway; AIST, Japan
  - University of Hawaii
  - HY-Energy Inc; SWRI
  - NREL; NNRC, USF
  - University of Florida
  - University of Central Florida (FSEC)
  - Sigma-Aldrich Fine Chemicals